SYNTHESIS AND PROPERTIES OF SOME
NOVEL ELECTRICALLY ACTIVE IONOPHORES

by

MARK RICHARD GOLDSPIKE

A Thesis
presented for the Degree of
Doctor of Philosophy
in the Faculty of Science of the
UNIVERSITY OF LONDON

ROYAL HOLLOWAY AND BEDFORD
NEW COLLEGE

JUNE 1988
ACKNOWLEDGMENTS

I would like to take this opportunity to thank Dr. Martin Pearson for his help, guidance and constant friendship during the course of this project. The Chemistry Department of Royal Holloway and Bedford New College and the London University as a whole have been of great support to me during this research programme. I am also grateful to all the technical staff who have assisted me during the task of putting this thesis together. I am also indebted to those people who have always been so willing to help me do this work, especially Mr. T. Collinge, Dr. P. Rollin, Dr. J. Mitchell, Mr. A. Beecro and Professor E. HILL.

In particular I would like to acknowledge the help of Dr. J. Crick who refined the crystallography data and of Dr. A. Greenham for allowing me to use the facilities in the Department of Crystallography, Oxford University. Thanks are also extended to Mr. F. Ryan for his constant patience and help with all the conductivity measurements taken in the course of this project.

The financial support for this research came from many different directions and I would like to thank all the people who have employed me during the past four years. Financial worries have been reduced...
ACKNOWLEDGEMENTS

I would like to take this opportunity to thank Dr. Martin Grossel for his help, guidance and constant friendship during the course of this project. The Chemistry Department of Royal Holloway and Bedford New College and the London University as a whole have been of great support to me during this research programme. I am also grateful to all the technical staff who have tolerated me during the task of putting this thesis together. In addition I must thank those people who have always been so willing to help me develop a greater scientific knowledge, especially, Mr. C. McCullough, Dr. R. Bolton, Dr. J. Mitchell, Dr. A. Beezer and Professor R. Hill.

In particular I would like to acknowledge the help of Dr. J. Hriljac who refined the crystallography data and to Dr. A. Cheetham for allowing the use of the facilities in the Department of Crystallography, Oxford University. Thanks are also extended to Mr. F. Evans for his constant patience and help with all the conductivity measurements taken in the course of this project.

The financial support for this Ph.D. has come from many different directions and I would like to thank all the people who have employed me during the past four years. Financial worries have been reduced
considerably by our kind and extremely helpful landlady Dr. M. Bradburn. I am extremely grateful for the help of Jackie Evans whose professional approach has been invaluable during the typing of this thesis.

Finally I must thank my parents who through great sacrifice have constantly supported me and helped me during my education. They, along with my brothers and friends, have given me the strength to continue when things have been tough. Thank you all.
ABSTRACT

This thesis reports an investigation of the synthesis and properties of a series of electrically active crown ethers and cryptand complexes. The work has fallen into a number of distinct categories:

(i) The synthesis of and structural studies on an ion-binding ferrocene-bridged cryptand in which the ferrocene unit as a potential redox centre has been investigated. The ion-binding abilities of and selectivities shown by these materials have been established by a variety of chemical and spectroscopic techniques. The results obtained have been compared with their receptor cavity sizes as established by X-ray structural studies. There is no spectroscopic evidence for any direct interaction between the iron atom and a metal ion residing in the cryptand cavity.

(ii) The effect of crown ether or cryptand encapsulation of a metal ion on the properties of some electrically active salts have been investigated. Two different types of material have been studies; (a) TCNQ salts which show metallic/semiconducting behaviour and (b) oxonol dye salts which are semi-insulators. It has been shown that the presence of crown ethers significantly modifies the electronic behaviour of these materials.
and can cause a complete change in the dominant conduction mechanism.

(iii) A series of substituted and polymeric crown ethers have been prepared and synthetic routes to a polymerisable cryptand have been explored. Polymeric crown ether/TCNQ salts are found to show similar electrical behaviour to that seen for the monomeric anaolgues.
CONTENTS

ABSTRACT .......................... 5

0.1 ABBREVIATIONS .................. 18

0.2 TABLE OF IONIC RADII .......... 19

1. INTRODUCTION .................... 20

1.1 CROWN ETHERS ................... 21

1.1.1 Nomenclature .................. 23

1.2 SYNTHESIS OF CROWN ETHERS ... 24

1.2.1 Operation of the Template Effect 25

1.3 AZA-CROWN ETHERS .............. 27

1.4 CRYPTANDS ...................... 28

1.4.1 Nomenclature .................. 30

1.5 SYNTHESIS OF DIAZA CROWNS AND CRYPTANDS 31

1.6 NOVEL CROWN ETHER/CRYPTAND STRUCTURES 32

1.6.1 Lariat Ethers ................. 32

1.6.2 Crown Ethers ................ 33

1.6.3 Polypodes and Octopus Molecules 34

1.6.4 Host Guest Chemistry ........ 34

1.7 STRUCTURE AND SELECTIVE ION-BINDING IN CROWN ETHERS .... 35

1.7.1 Structure and Selective Ion-Binding in Cryptands 42

1.7.2 The Effect of the Ligand on the Properties of the Cation 45

1.7.3 Anion Receptor Molecules .... 46

1.7.4 Electrides .................... 49
1.8 USES OF CROWN ETHER AND CRYPTANDS IN CHEMISTRY

1.8.1 Liquid-Liquid Extractions 51
1.8.2 Other Separation Processes 54
1.8.3 Separation of Optically Active Amino Acids 56
1.8.4 Membrane Separations 56
1.8.5 Ion Selective Electrodes 57
1.8.6 Catalysis by Macrocyclic Compounds. 61

1.9 NATURALLY OCCURRING MACROCYCLES BIOLOGICAL IONOPHORES

1.9.1 Macrocyclic Antibiotics and Their Alkali Metal Complexes 67
1.9.2 Binding Properties 72

2. AIMS AND OBJECTIVES

2.1 SYNTHESIS AND STRUCTURAL ANALYSIS OF A REDOXABLE CRYPTAND 80

2.2 ELECTRICALLY ACTIVE CROWN ETHER COMPLEXES 81

2.2.1 Conduction Mechanisms in Crown Ether/TCNQ Complexes 86

2.2.2 Novel Crown Ether/Photographic (Oxonol) Dye Complexes 87
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>SYNTHESIS OF SUBSTITUTED AND POLYMERIC MACROCYCLIC SYSTEMS</td>
<td>88</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Electrically Active Substituted Crown Ethers</td>
<td>88</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Electrically Active Polymeric Crown Ethers</td>
<td>91</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Development of a Polymeric Metallocene Cryptand</td>
<td>92</td>
</tr>
<tr>
<td>3.1</td>
<td>INTRODUCTION TO FERROCENE CHEMISTRY</td>
<td>94</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Application of Ferrocene Compounds</td>
<td>97</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Synthesis of Ferrocene and its Derivatives</td>
<td>100</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Reactions of Ferrocene and 1,1'-Disubstituted Derivatives</td>
<td>102</td>
</tr>
<tr>
<td>3.1.4</td>
<td>Condensation of Metallocene bis Acid Chlorides with Amines</td>
<td>107</td>
</tr>
<tr>
<td>3.1.5</td>
<td>Preparation of Ferrocene Amides</td>
<td>108</td>
</tr>
<tr>
<td>3.1.6</td>
<td>Preparation of Ferrocene Macrocyclic Amides</td>
<td>109</td>
</tr>
<tr>
<td>3.1.7</td>
<td>Preparation of Binding Ligands</td>
<td>109</td>
</tr>
<tr>
<td>3.2</td>
<td>SYNTHESIS OF FERROCENE CRYPTANDS</td>
<td>112</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Spectroscopic Analysis of the Ferrocene Amides</td>
<td>114</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Mass Spectrometry and Element Analysis</td>
<td>114</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Infra Red Analysis</td>
<td>114</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Mössbauer Spectroscopy (Structural Probe of Organometallic Compounds)</td>
<td>115</td>
</tr>
<tr>
<td>3.2.5</td>
<td>$^1$H N.M.R. Studies on Ferrocene Amides</td>
<td>120</td>
</tr>
<tr>
<td>3.2.6</td>
<td>$^{13}$C N.M.R. and Dynamic N.M.R. Studies on Ferrocene Amides</td>
<td>120</td>
</tr>
<tr>
<td>3.2.7</td>
<td>$^{13}$C N.M.R. and Dynamic N.M.R. Studies on Ferrocene Macrocyclic Amides</td>
<td>123</td>
</tr>
<tr>
<td>3.3</td>
<td>SOLID STATE STUDIES OF FERROCENE AMIDES</td>
<td>128</td>
</tr>
<tr>
<td>3.3.1</td>
<td>X-Ray Crystallography of a Simple Ferrocene Amide</td>
<td>128</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Packing Arrangements and Stereochemistry Adopted in 1,1'-Diacetylferrocene and 1,1'-Bis(N-Methylamido)ferrocene</td>
<td>137</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Solid State N.M.R. Studies on the Ferrocene Amides</td>
<td>141</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Solid State N.M.R. Studies on Other Ferrocene Derivatives</td>
<td>148</td>
</tr>
<tr>
<td>3.3.5</td>
<td>X-Ray Crystallography of Fc[2.2]M Dihydrate</td>
<td>154</td>
</tr>
</tbody>
</table>
3.3.6 Size of the Binding Site in Fc[2.2]M Dihydrate 161
3.3.7 Solid State $^{13}$C N.M.R. Studies on Fc[2.2]M Dihydrate 165
3.3.8 Discussion of the Solid State Features of Fc[2.2]M and the Comparison with other Ferrocene Cryptands 165

3.4 PHYSICAL PROPERTIES OF THE FERROCENE MACROCYCLE Fc[2.2]M 171
3.4.1 Cation Binding Properties 171
3.4.2 Extraction Experiments with Oxonol Dyes 173

3.5 SYNTHESIS OF FERROCENE CRYPTATE COMPLEXES 179
3.5.1 Spectroscopic Analysis of Fc[2.2]M Cryptate Complexes 179
3.5.2 Mass Spectrometry 180
3.5.3 Infra Red Spectroscopy 182
3.5.4 $^1$H N.M.R. 184
3.5.5 $^{13}$C N.M.R. 188
3.5.6 $^7$Li N.M.R. 192
3.5.7 Mössbauer Spectroscopy 200
3.5.8 X-Ray Crystallographic Study of an Fc[2.2]M Cryptate 202
3.5.9 Discussion of Fc[2.2]M Cryptates 203
3.6 FERROCENE [2.2]DIMER (Fc[2.2]D) 204
   3.6.1 Synthesis of Fc[2.2]D 205
   3.6.2 Spectroscopic Analysis of Fc[2.2]D 206
   3.6.3 Mass Spectrometry and Element Analysis 206
   3.6.4 Infra Red Spectroscopy 206
   3.6.5 Mössbauer Spectroscopic Study on Fc[2.2]D 206
   3.6.6 $^1$H N.M.R. 207
   3.6.7 $^{13}$C N.M.R. 208
   3.6.8 Dynamic N.M.R. Studies on Fc[2.2]D 208
3.7 SOLID STATE STUDIES OF Fc[2.2]D 209
   3.7.1 X-Ray Crystallographic Study of Fc[2.2]D 209
   3.7.2 Size of the Binding Site in Fc[2.2]D 215
   3.7.3 Solid State $^{13}$C N.M.R. Study on Fc[2.2]D 219
   3.7.4 Discussion of the Solid State Features of Fc[2.2]D 222
3.8 PHYSICAL PROPERTIES OF Fc[2.2]D 223
   3.8.1 Cation Binding Properties 223
3.9 SYNTHESIS OF Fc[2.2]D CRYPTATES 224
### 3.9.1 Spectroscopic Analysis of the Fc[2.2]D Cryptates
- Page 224

### 3.9.2 Mass Spectrometry
- Page 225

### 3.9.3 Infra Red Spectroscopy
- Page 225

### 3.9.4 $^1$H N.M.R.
- Page 227

### 3.9.5 $^{13}$C N.M.R.
- Page 228

### 3.9.6 Mössbauer Spectroscopy
- Page 229

### 3.9.7 X-Ray Crystallography of Fc[2.2]D Cryptates
- Page 230

### 3.9.8 Discussion of Fc[2.2]D Cryptates
- Page 232

### 4. RESULTS AND DISCUSSION II

#### 4.1 ELECTRICAL PROPERTIES OF SEMI-INSULATING AND SEMICONDUCTING MATERIALS
- Page 234
  - 4.1.1 Basic Classification
  - Page 234
  - 4.1.2 Band Theory
  - Page 236
  - 4.1.3 Metals
  - Page 238
  - 4.1.4 Insulators
  - Page 239
  - 4.1.5 Intrinsic Semiconductors
  - Page 240
  - 4.1.6 Extrinsic Semiconductors
  - Page 240

#### 4.2 ORGANIC CONDUCTING MATERIALS
- Page 244
  - 4.2.1 Superconductors
  - Page 252
  - 4.2.2 Organic Superconductors
  - Page 255
  - 4.2.3 Properties of Anion-Radical Derivatives and Complexes of $7,7,8,8$-Tetracyanoquinodimethane
  - Page 257
4.2.4 Simple Salts of the TCNQ\textsuperscript{−}, Anion-Radical Synthesis

4.3 NOVEL CROWN ETHER COMPLEXES

4.3.1 Crown Ether/TCNQ Salts

4.4 SYNTHESIS OF CROWN ETHER/TCNQ COMPLEXES

4.4.1 Crown Ether/Alkali Metal TCNQ Complexes

4.4.2 Crown Ether/Alkali Metal TCNQ/TCNQ Complexes

4.4.3 Crown Ether/Alkaline-Earth Metal TCNQ Complexes

4.4.4 Crown Ether/Alkaline-Earth Metal TCNQ/TCNQ Complexes

4.4.5 Spectroscopic Analysis of the Crown Ether/TCNQ Complexes

4.4.6 Mass Spectrometry

4.4.7 Infra-Red Spectroscopy

4.4.8 \textsuperscript{1}H N.M.R.

4.4.9 \textsuperscript{13}C N.M.R.

4.5 SOLID STATE STUDIES

4.5.1 Electrical Spectroscopy

4.5.1.1 D.C. Measurements

4.5.1.2 A.C. Measurements

4.5.2 Electron Spin Resonance

4.5.3 X-Ray Crystallographic Studies
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>4.6.1</td>
<td>Application of Dyes</td>
<td>306</td>
</tr>
<tr>
<td>4.6</td>
<td>4.6.2</td>
<td>Bleachable Dyes</td>
<td>308</td>
</tr>
<tr>
<td>4.6</td>
<td>4.6.3</td>
<td>Electrical Properties of the Dyes</td>
<td>311</td>
</tr>
<tr>
<td>4.6</td>
<td>4.6.4</td>
<td>Synthesis of Symmetrical Hydroxy-pyridone Methine Bridged Oxonol Dyes</td>
<td>313</td>
</tr>
<tr>
<td>4.6</td>
<td>4.6.4.1</td>
<td>Preparation of Cyano-acetamides</td>
<td>313</td>
</tr>
<tr>
<td>4.6</td>
<td>4.6.4.2</td>
<td>Conversion of Cyano-acetamides to Hydroxy-pyridones</td>
<td>313</td>
</tr>
<tr>
<td>4.6</td>
<td>4.6.4.3</td>
<td>Preparation of the Dye</td>
<td>314</td>
</tr>
<tr>
<td>4.7</td>
<td>4.7.1</td>
<td>Crown Ether/Alkali-Metal Oxonol Dye Complexes</td>
<td>315</td>
</tr>
<tr>
<td>4.7</td>
<td>4.7.2</td>
<td>Spectroscopic Analysis of Crown Ether/Oxonol Dyes</td>
<td>318</td>
</tr>
<tr>
<td>4.7</td>
<td>4.7.3</td>
<td>Mass Spectrometry</td>
<td>318</td>
</tr>
<tr>
<td>4.7</td>
<td>4.7.4</td>
<td>Infra Red Spectroscopy</td>
<td>319</td>
</tr>
<tr>
<td>4.7</td>
<td>4.7.5</td>
<td>$^1$H N.M.R.</td>
<td>321</td>
</tr>
<tr>
<td>4.7</td>
<td>4.7.6</td>
<td>$^{13}$C N.M.R.</td>
<td>322</td>
</tr>
<tr>
<td>4.8</td>
<td>4.8.1</td>
<td>Electrical Spectroscopy</td>
<td>325</td>
</tr>
<tr>
<td></td>
<td>4.8.1.1</td>
<td>D.C. Measurements</td>
<td>325</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.8.1.2 A.D. Measurements</td>
<td>328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.8.2 X-Ray Crystallography</td>
<td>331</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.8.3 Solid State N.M.R.</td>
<td>331</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. RESULTS AND DISCUSSION III</td>
<td>336</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1 CONDUCTING ORGANIC POLYMERANS</td>
<td>337</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1.1 Spinless Conductivity</td>
<td>339</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2 FUNCTIONALISED CROWN ETHERS</td>
<td>343</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2.1 Polymeric Crown Ethers</td>
<td>345</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.3 SYNTHESIS OF A POLYMERIC CROWN ETHER</td>
<td>346</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.3.1 Synthesis of Polymeric Dibenzo- [18]-crown-6</td>
<td>348</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4 SYNTHESIS OF FUNCTIONALISED AND POLYMERIC CROWN ETHER/TCNQ COMPLEXES</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4.1 Spectroscopic Analysis</td>
<td>351</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4.2 Mass Spectrometry</td>
<td>351</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4.3 Infra Red Spectroscopy</td>
<td>352</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4.4 $^1$H N.M.R.</td>
<td>352</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4.5 $^{13}$C N.M.R.</td>
<td>352</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5 SOLID STATE STUDIES</td>
<td>354</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5.1 Electrical Spectroscopy</td>
<td>354</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5.1.1 D.C. Measurements</td>
<td>354</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.6 POLYMERISATION OF A FERROCENE MACROCYCLE</td>
<td>356</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.6.1 Polymerisation of Ferrocene</td>
<td>357</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.6.2 Functionalisation of a Piperazine Cryptand</td>
<td>362</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. CONCLUSIONS AND FUTURE WORK</td>
<td>366</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1 RESULTS AND DISCUSSION (PART I)</td>
<td>367</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2 RESULTS AND DISCUSSION (PART II)</td>
<td>368</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.3 RESULTS AND DISCUSSION (PART III)</td>
<td>369</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. GENERAL EXPERIMENTAL</td>
<td>371</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1.1 Instrumentation</td>
<td>372</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1.2 Solvent Purification</td>
<td>374</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2 EXPERIMENTAL PART I (Chapter 3)</td>
<td>377</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.3 EXPERIMENTAL PART II (Chapter 4)</td>
<td>394</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.4 EXPERIMENTAL PART III (Chapter 5)</td>
<td>424</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. APPENDICES</td>
<td>447</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APPENDIX I Dynamic N.M.R. Studies</td>
<td>448</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APPENDIX II X-Ray Crystallographic Data</td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APPENDIX III Conductivity Experiments</td>
<td>465</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APPENDIX IV Langmuir-Blodgett Technique</td>
<td>470</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. REFERENCES</td>
<td>474</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
0.1 ABBREVIATIONS

(12C4) = [12]-crown-4 (15C5) = [15]-crown-5
(18C6) = [18]-crown-6 (DB18C6) = Dibenzo-[18]-crown-6
(DA18C6) = Diaza-[18]-crown-6
(DDA18C6) = Dibenzyl Diaza-[18]-crown-6
Ts− or Tos− = Tosylate Anion
Cp = Cyclopentadienyl Anion
Fe(Cp.X)2 = Disubstituted Ferrocene (X = Substituent)
FeCp(CpX) = Monosubstituted Ferrocene
(Cp)2Fe or Fc = Ferrocene
Fc[2.2]M = 1,1′-(1,4,10,13-tetraoxa-7,16-diaxacyclododecane-7,16-diylidicarbonyl)ferrocene
Fc[2.2]D = 1,1′,1″,1‴-bis(1,4,10,13-tetraoxa-7,16-diaxacyclododecane-7,16-diylidicarbonyl) bisferrocene
TCNQ = 7,7,8,8-Tetracyanoquinodimethane
TTF = Tetrathiofulvalene
Mn+(TCNQ−) = Tetracyanoquinodimethane Salts
Mn+(Ox−)n = Hydroxypyridone Trimethine Oxonol Dyes
(PDB18C6) = Polydibenzo-[18]-crown-6
(DADB18C6) = Diacetyl Dibenzo-[18]-crown-6
(DHDB18C6) = Dihexyl Dibenzo-[18]-crown-6
(DODB18C6) = Dioctanyl Dibenzo-[18]-crown-6
(DDDB18C6) = Didecanyl Dibenzo-[18]-crown-6
(DTDB18C6) = Di-(trimethylacetyl)Dibenzo-[18]-crown-6
(Cyclam) = 1,4,8,11-Tetra-azacyclotetradecane
### Table of Ionic Radii

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic Radii (Å)*</th>
<th>Ion</th>
<th>Ionic Radii (Å)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>0.6</td>
<td>Cu⁺</td>
<td>0.96</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.95</td>
<td>Cu²⁺</td>
<td>0.92</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.33</td>
<td>Ag⁺</td>
<td>1.26</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>1.48</td>
<td>Zn²⁺</td>
<td>0.74</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>1.69</td>
<td>Mg²⁺</td>
<td>1.10</td>
</tr>
<tr>
<td>Be²⁺</td>
<td>0.31</td>
<td>Mn²⁺</td>
<td>0.80</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.65</td>
<td>Co²⁺</td>
<td>0.72</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Pauling's ionic radii.
CHAPTER 1

INTRODUCTION

1.1. CROWN ETHERS

Crown ethers are macrocyclic compounds containing several oxygen atoms in a regular pattern. Analogues of such structures, which contain nitrogen and sulphur as the heteroelements have also been prepared. These compounds all have the property of forming complexes with positive ions and have varying degrees of binding selectivity, depending on the size of the macrocyclic ring and the nature of its component heteroelements.

A project was initiated in 1961, by Charles A. Pedersen, who was seeking to develop cyclic acetylenic esters (1) which could modify the properties of a vinyldene group to be more cis-stilbene-like than cinnamaldehyde or salvinol. His experimental approach involved the reaction between the phenyl ether (acenaphthylene ether), diethyleneglycol dichloride and sodium hydride. The intended reaction Scheme 1.1 is shown below. After a failed Williams-Led SOCIAL reaction had occurred, it was Pedersen's intention to cleave the trihydroxybenzene ether leaving him with (12). At first no unsaturated "one" was collected. From which small quantities of (11) were isolated. Pedersen also obtained a small amount of white crystals, on purification, which melted at 165°C and showed no hydroxyl absorption.
1. INTRODUCTION
1.1 CROWN ETHERS

Crown ethers are macrocyclic compounds containing several oxygen atoms in a regular pattern. Analogues of such structures which contain nitrogen and sulphur as the heteroatoms have also been prepared. These compounds all have the property of forming complexes with positive ions and show varying degrees of binding selectivity, depending on the size of the macrocyclic ring and the nature of its component heteroatoms.

A project was initiated in 1961, by Charles J. Pedersen, who was seeking a phenolic complexing agent (1) which could modify the properties of a vanadyl group to be used for the catalysis of olefin polymerisation. His experimental approach involved the reaction between the phenol ether (monotetrahydropyranyl ether), diethylene glycol dichloride and sodium hydroxide. The intended reaction Scheme 1.1 is shown below. After a double Williamson reaction had occurred, it was Pedersen's intention to cleave the tetrahydropyranyl ether leaving him with (1). At first an unattractive "goo" was collected, from which small quantities of (1) were isolated. Pedersen also obtained a small amount of fluffy white crystals, on purification, which melted at 164°C and showed no hydroxyl absorption in
the infra red. It was observed that these white crystals were insoluble in methanol unless sodium hydroxide was present. It was subsequently found that any sodium salt greatly increased the solubility of the crystals under these conditions.

\[
\begin{align*}
\text{OH} & + O(\text{CH}_2\text{CH}_2\text{Cl})_2 \xrightarrow{\text{NaOH}} \text{THP} \text{THP} \\
\text{OH} & \quad \text{HO} \quad \text{HO} \\
(1) & + (2)
\end{align*}
\]

Scheme 1.1 Pedersen's Intended Preparation of Bis[2-(ortho-hydroxyphenoxy)ethyl]ether (1)

Pedersen reasoned that there must have been a small amount of catechol present which had not been protected properly. This must have led to the formation of (1) \textit{in situ} followed by cyclisation to form (2). The amount of catechol in the reaction mixture was so small that the efficiency of cyclisation which led to (2) must have been remarkably high. This efficiency was especially notable since the cyclisation leading to a large ring
was conducted in concentrated solution. Furthermore, (2) seemed to interact with, or to complex alkali metal cations despite the fact that it contained no hydroxyl groups. These unexpected results led Pedersen to prepare many examples of the compounds known as "crown ethers".  

1.1.1 Nomenclature.

The term "crown" was first suggested by Pedersen and has now been widely adopted. Although it is assumed by some that the term arises from the appearance of the molecular models, as shown below (Figure 1.1) Pedersen reported that the term was suggested by the fact that these macrocycles "crowned" cations "just as a regal crown adorns a Monarch's brow".

![Figure 1.1 Showing the "Crown" Structure of [15]-crown-5](image)

The term "crown" generally refers to macrocyclic polyethers having the ethyleneoxy unit as the basic repeating structure. For the simple compounds the
molecular convention involves two numbers (for example [15]-crown-5). The first of these indicates the total number of atoms in the macrocycle. The second indicates how many heteroatoms are present in the ring. Compound (2) was given the name of dibenzo-[18]-crown-6, essentially [18]-crown-6 onto which two benzene rings have been fused. Figure 1.2 shows several examples of crown ethers.

![Crown Ether Structures](image)

Figure 1.2 Typical Crown Ether Structures.

1.2 SYNTHESIS OF CROWN ETHERS.

It has been axiomatic for many years that large rings must be prepared under high dilution conditions so that the probability of the two ends meeting exceeds the probability of linear polymer formation. It therefore seems remarkable that many of the syntheses of macrocyclic polyethers which have been reported involve less than dilute if not very concentrated conditions. The success of these large-ring intramolecular SN2 reactions is thought to
be attributed to the operation of a "template" effect during crown synthesis.

1.2.1 Operation of the Template Effect

Many of the crown ether syntheses are one form or another of the Williamson ether synthesis. Although the simplest example of such a reaction would involve a ω-haloethylene glycol oligomer which undergoes intramolecular cyclisation, it is more common for two new bonds to be formed in crown synthesis. An early example of the formation of a crown by a double-Williamson can be found in Dale's synthesis of [18]-crown-6 (Scheme 1.2)\(^5\).

\[
\begin{align*}
\text{OTs} & \quad -O \quad -O \\
O & \quad + \\
O & \quad \text{t-BuO}^+K^+ \\
\text{DMSO} & \quad \rightarrow \\
\text{Scheme 1.2 Dale's Synthetic Route to [18]-crown-6 (5)}.
\end{align*}
\]

In Dale's early synthesis of [18]-crown-6 (5), there is no mention of the template effect. However, one finds the comment: "High-dilution techniques are not needed". The first suggestion of a "template" effect was offered in the literature by Greene in 1972\(^6\). Greene presented several pieces of evidence
in addition to the concept itself. First, he noted that when the final concentration of [18]-crown-6 in a reaction mixture (Me₂SO) was increased from 0.04M to 0.09M, the yield of crown dropped only slightly (84% to 75%). Secondly, in a competition experiment, equal amounts of [18]-crown-6 and [21]-crown-7 were formed when one molar equivalents of triethylene glycol and tetraethylene glycol were allowed to compete for triethylene glycol ditosylate (t-BuOK/THF). Equal amounts of the two crown were also formed when (Bu₄N)⁺(OH)⁻ was used as a base. However, both rate and yield were considerably reduced. Greene noted that such a template effect would actually involve binding between the open-chained intermediates and cations and these interactions are known to be weak relative to crown-cation interactions.

One of the prime tenets of the "template effect"⁶ is that a cation of appropriate size coordinates with the heteroatom binding sites in the incipient ring system. All the evidence presented in the literature⁶⁻¹⁰ is based on the approximate ring sizes of the crown versus the known ionic diameters of metal cations shown in Table 1.1 below.
Table 1.1 Relationship Between Crown Hole Sizes and Cation Diameters.

<table>
<thead>
<tr>
<th>Crown Ether (hole size, Å)</th>
<th>Favoured Cation (ionic diameter, Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]-crown-4 (1.2)</td>
<td>Li⁺ (1.20) Mg2⁺ (1.30)</td>
</tr>
<tr>
<td>[14]-crown-4 (1.2-1.5)</td>
<td>Na⁺ (1.90) Ca2⁺ (1.98)</td>
</tr>
<tr>
<td>[15]-crown-5 (1.7-2.2)</td>
<td>K⁺ (2.66) Sr2⁺ (2.26)</td>
</tr>
<tr>
<td>[18]-crown-6 (2.6-3.2)</td>
<td>Rb⁺ (2.96) Ba2⁺ (2.70)</td>
</tr>
<tr>
<td>[21]-crown-7 (3.4-4.3)</td>
<td>Cs⁺ (3.38) —</td>
</tr>
<tr>
<td>[24]-crown-8 (4.5)</td>
<td>—</td>
</tr>
</tbody>
</table>

1.3 AZA-CROWN ETHERS.

This terminology is a logical extension of the nonsystematic nomenclature described for the crown ethers. Although either amino-crown or azacrown might note the presence of a nitrogen atom in place of oxygen in the macrocycle ring structure, the latter has more often been used. The structures below are monoaza-[18]-crown-6 (6) and 1,10-diaza-[18]-crown-6 (7). This class of compounds was developed by Simons and Park.11
1.4 CRYPTANDS.

Topologically, macrocycles (1-5) already discussed may be defined by a one dimensional circular cavity. However, ligands developed by Lehn and his group\textsuperscript{13} show three-dimensional cavities. This is the case for the compounds shown in Figure 1.3 below; (8) shows the macrobicyclic structure, (9) a cylindrical structure and (10) is a spheriod.

Such ligands form inclusion complexes in which the substrate is contained inside their molecular "crypt" (cavity). It is from this terminology that these series of ligands derived the names of "cryptands", and their complexes "cryptates".

![Various Cryptand Structures](image)

\textbf{Figure 1.3} Various Cryptand Structures
In/In Out/Out In/Out

Figure 1.4 Isomers of the Cryptand (8)

The key step in the design of a cryptand is the recognition that nitrogen atoms are required at the bridgehead (Figure 1.4) in order to provide the necessary trivalent substitution patterns. The nitrogen atoms may be turned in or out with respect to the molecular cavity leading to three isomers in/in, out/out or in/out.

Emil Fischer's "lock and key" theory of enzyme substrate interaction and Paul Ehrilich's search for bactericidal "magic bullets" were early demonstrations of an awareness that there is need for recognition by a receptor molecule\(^{12}\). The requirements for recognition indicate that the larger the number of substrate-ligand interactions, in a generalised "lock and key" relationship not limited to steric fit alone, the higher the selectivity. The cryptands have the ability not only to complex but to encapsulate a substrate. Hence complexes involving bi- or polydentate ligands (3 dimensional) cavities have an enhanced stability when compared with their
unidentate counterparts. This will be discussed in more detail below.

1.4.1 Nomenclature.

The simple cryptands are assumed to be macrobicyclic and nitrogen is assumed to be the bridgehead atom. The different cryptands are designated by assigning numbers according to the number of heteroatoms in each ethyleneoxy chain. The three cryptands shown below are designated [1.1.1]cryptand (11), [2.2.1]cryptand (12) and [3.2.2]cryptand (13) respectively.

As with the crown, the situation becomes more complicated when there are other heteroatoms or substituents in one of the cryptand bridges. The disadvantages of these names are manifest, but "one shudders to think about naming them systematically!"
1.5 SYNTHESIS OF DIAZA CROWNS AND CRYPTANDS.

Macrocyclic diamides may be readily prepared from diacid chlorides and diamines. The diamides may then be reduced to form the aza-crown (Scheme 1.3). Such compounds may also contain sulphur and/or oxygen heteroatoms in the ring.

Scheme 1.3 Preparation of Diaza-[18]-crown-6 (7).

An alternative route to these compounds proceeds by reaction of the glycolditosylate, e.g. triethylene glycol ditosylate, with the sodium salt of the glycoldiamineditosylate, e.g. tetraethyleneglycol-diamine ditosylate (Scheme 1.4).
Scheme 1.4  Alternative Preparation of Diaza-[18]-crown-6 (7)

The cryptand may then be prepared by treatment with a polyether bis acid chloride (Scheme 1.5) and reduction of the resulting bis amide with lithium aluminium hydride¹⁸.

Scheme 1.5  Preparation of [2.2.2]cryptand (8)

1.6  NOVEL CROWN ETHER/CRYPTAND STRUCTURES.

1.6.1  Lariat Ethers.

This is a term introduced by Gokel and co-workers¹⁹. The compounds included in this class
are those which have single macrocyclic rings like crowns but with additional pendant donor groups which make them similar in some respects to cryptands. The presumption from which the name derives is that a complexed cation will be bound by both the macrocyclic ring and the side chain in much the same fashion as a lasso snares an animal. The compounds are named as simple crown derivatives and examples are illustrated below.

1.6.2 Crown Esters.

The crown esters are actually macrocyclic lactones the bulk of whose rings are ethyleneoxy units. By far, the largest number of such compounds have been prepared by Bradshaw and his co-workers. Representative examples are shown below.
1.6.3 Polypodes and Octopus Molecules.

\[ R = (\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3 \]

Both structures above are open-chained compounds corresponding to crown ethers in function if not exactly in structure. They have repeating ethyleneoxy side-chains generally terminated in a methyl group. The polypodes were developed by Montanari and co-workers\textsuperscript{21} as phase transfer catalysts (Section 1.8.5). The first "octopus molecules" were prepared by Vögtle and Weber\textsuperscript{22}.

1.6.4 "Host-Guest" Chemistry.

All the examples quoted above fit into the category of "Host-Guest" molecules. A host is any molecule which can complex, encapsulate or otherwise bind a substrate. Further examples of this rapidly growing category of host guest molecules are listed below.

1. **CASCADES\textsuperscript{23}**
2. **SPHERANDS\textsuperscript{24}**
3. **CYCLODEXTRINS\textsuperscript{25}**
4. **CRYPTOPHANES\textsuperscript{26}**
5. CORONAND*:- any medium sized or macrocyclic system having only one ring and containing any heteroatom(s).
6. PODAND*:- open-chained (acyclic) analogues of coronands or cryptands.
7. CALIXARENE
8. CYCLIDENE.

* These are not really distinct classes of structures but the names have been included for the sake of completeness. Indeed, Collete coined the term cryptophane because "it was the only vacant name, still left in the inclusion field".

1.7 STRUCTURE AND SELECTIVE ION-BINDING IN CROWN ETHERS.

The structures of many macrocyclic compounds have already been investigated by X-ray crystallography. In general alkali and alkaline earth metal cations prefer to reside in a symmetrical coordination sphere which reflects their surface charge distribution. For example, in the potassium cation dibenzo-[30]-crown-10 complex the flexible crown ring encapsulates the cation with all ten oxygen atoms coordinating to the metal ion. Where the ligand does not provide sufficient donor atoms or is inflexible, additional coordination from another crown ether is observed. For example, with small
crown ethers e.g. dibenzo-[15]-crown-5, the potassium cation forms a 1:1 complex with one molecule of water coordinated to the potassium. While sodium forms a 1:2 complex, the cation being sandwiched between two rings (Figure 1.5). No evidence has yet been obtained for the 3:2 complex in the solid state. Examples of the crystalline crown ether complexes are shown in Figure 1.6 below.

![Diagram of crown ether complexes](image)

Figure 1.5 Represents the Various Crown Ether Complexes.

- **M⁺** = Bound Metal Ion
- 1:1 Complex
- 2:1 Complex
- 3:1 Complex
Figure 1.6 Crystallographic Structures of Crown Ether Complexes. (Includes 1:1, 1:2 and 2:1 Complexes).

The heteroatoms in macrocyclic complexes are capable of replacing most, if not all of the ions in the solvation sphere. The degree of complex formation is quantified in terms of the equilibrium constant for the equation (1.1). The equilibrium constant $K$ is the stability constant $K_s$ (reverse reaction), or the association constant $K_a$ (forward reaction).
EQUATION 1.1

\[ \text{M}^{n+} + \text{L} \rightleftharpoons K \text{L}^{n+} \]

Ks reverse reaction

\[ \text{L} = \text{Ligand} \]

It is seen that crown ether cation complexes have larger association constants (Ka) than their open chain analogues because of the greater degree of encapsulation, i.e. "The macrocycle effect" vs. "The chelation effect", (Table 1.2)\(^{30,31}\). A three-dimensional encapsulation gives rise to an even greater association constant and this can be seen with cryptands, for example \( \text{K}^+[2.2.2] \) cryptate is more stable than the \( \text{K}^+ \)-complexes of its corresponding monocyclic coronand by a factor of \( 10^5 \) and even \( 10^4 \) times more stable than the \( \text{K}^+ \)-complex of valinomycin "a natural ionophore" (Section 1.9). This is known as "The cryptate effect"\(^{30}\).

It has been suggested that the unfavourable entropy decrease which the open chain compounds must suffer in order to match the conformations of their cyclic analogues is responsible for the difference in complex stabilities. However, it has been shown that for cryptates there is a large favourable enthalpy increase and that the internal entropy actually decreases due to increased structuring of the solvent upon complex formation. The selectivity of the
Table 1.2 Showing Values of $K_a$ in Methanol at 25°C.

A macrocycle will depend upon the charge and size of the heteroatoms, and the ligand structure and complexation. The extent of complex formation between a cation and a macrocycle reflects the compatibility of the ligand cavity size with the size of the ion, i.e. the cation which fits best into the cavity is the most strongly bound. This is clearly shown in Table 1.3. Therefore [18]-crown-6 (5) which has a cavity diameter of 2.6-3.2 Å most efficiently complexes with potassium ion. The limited flexibility of smaller ligands ensures that only cations within a narrow size range can be accommodated in the cavity. Larger more flexible
macrocycles, while showing a preference for large cations, are much less discriminating. For maximum stability the ion-size to crown-size ratio

Table 1.3 Stability Constants for Crown Alkali Cation Complexes

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>INSIDE DIA. OF CAVITY crown Å</th>
<th>LOG$_{10}$ KA IN CH$_3$OH $@$ 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]-crown-4 (4)</td>
<td>1.2-1.5</td>
<td>2.2 1.3  -</td>
</tr>
<tr>
<td>[15]-crown-5 (3)</td>
<td>1.7-2.2</td>
<td>3.7 3.6  3.8</td>
</tr>
<tr>
<td>[18]-crown-6 (5)</td>
<td>2.6-3.2</td>
<td>4.3 6.1  4.6</td>
</tr>
<tr>
<td>[21]-crown-7</td>
<td>3.4-4.3</td>
<td>2.4 4.3  4.2</td>
</tr>
<tr>
<td>DIAMETER OF ION Å</td>
<td>1.94 2.66 3.34</td>
<td></td>
</tr>
</tbody>
</table>

for univalent cations is about 0.9. For divalent ions, the stability constant is larger than that for univalent ions because of the greater polarising power of the cation. The optimum ratio for the divalent ions is about 0.8 rather than 0.9 or 1.0, which reflects the larger enthalpy changes for the ligation of divalent ions than for monovalent ions (Figure 1.7).
It is important to note that when discussing the binding properties of crown ethers, reference is made to the solvent in which the experiments are being run. If similar experiments are run in aqueous and methanolic solutions, it is found that the crown ether is less cation-selective in aqueous solutions. The reason is that solvation enthalpies (ΔH) for the ions are much larger in water than in methanol. Therefore, the crowns compete much better with methanol than with water for the cations. Methanol has another effect on the crown ether complexes; because the crown ligands are large lipophilic
molecules, their metal ion complexes are appreciably soluble in organic solvents e.g. toluene. If even a small amount of methanol is present the solubility increases greatly. This could result from methanol molecules binding to the ions thus resulting in a more spherically symmetrical distribution of ligands and therefore increased solubility in organic media (14).

![Diagram of MeOH binding to ions](14)

1.7.1. Structure and Selective Ion-Binding in Cryptands.

The complexation of cryptands with alkali and alkaline earth cations is even more selective than that for crown ethers and their complexes show enhanced stabilities with respect to the crown ethers (Table 1.4). The $K^+$ complex of [2.2.2] cryptand is more stable by a factor of $10^5$ than the corresponding diaza-[18]-crown-6 (7) complex and by a factor of 4 when compared with the valinomycin complex (an ionophorous antibiotic), Section 1.9. The cryptand also exhibits a peak selectivity for metal cations.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Radius</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Sr²⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size</td>
<td>0.86</td>
<td>1.12</td>
<td>1.44</td>
<td>1.58</td>
<td>1.84</td>
<td>-</td>
<td>1.18</td>
<td>1.32</td>
<td>1.49</td>
</tr>
<tr>
<td>[2.1.1]</td>
<td>0.80</td>
<td>4.3</td>
<td>2.8</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>-</td>
<td>2.8</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>[2.2.1]</td>
<td>1.15</td>
<td>2.5</td>
<td>5.4</td>
<td>4.0</td>
<td>2.6</td>
<td>2.0</td>
<td>&lt;2</td>
<td>7.0</td>
<td>7.4</td>
<td>6.3</td>
</tr>
<tr>
<td>[2.2.2]</td>
<td>1.40</td>
<td>2.0</td>
<td>3.9</td>
<td>5.4</td>
<td>4.4</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>4.4</td>
<td>8.0</td>
<td>9.5</td>
</tr>
<tr>
<td>[3.2.2]</td>
<td>1.80</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>2.2</td>
<td>2.1</td>
<td>2.2</td>
<td>&lt;2</td>
<td>2.0</td>
<td>3.4</td>
<td>6.0</td>
</tr>
</tbody>
</table>
which agrees with the ion-cavity size i.e. the cation that fits best into the ligand cavity will be most tightly bound.

Apart from the cavity geometry the nature of the donor heteroatoms of the ligand has a large effect on the cation-selectivity\(^{15}\). When oxygen (hard) is replaced by sulphur (soft), the ligands show an increased preference for metals with more covalent bond character (soft transition metals ions e.g. Ag\(^+\)) and a weakening of binding to alkali and alkaline earth (hard) metal cations\(^{35,36}\). Nitrogen as a heteroatom plays the role of a mediator by promoting the complexation of transition metal ions, and Ag\(^+\) without discriminating against alkali metals as well\(^{35}\) (Table 1.5).

Table 1.5 A Comparison of Various Log \(K_s\) Values\(^{14}\).

| LIGAND | \(K^+\) | \(\text{CH}_3\text{OH}\) | \(\text{Ag}^+\) | \(\text{H}_2\text{O}\) |
|--------|--------|-----------------|-----------------|
|        | 6.1    | 1.15            | 3.90            | 2.04            |
|        | 1.6    | 4.34            | 3.30            | 7.80            |

\(^{14}\) Log \(K_s\) values for the binding of various cations to different ligands.
Further possibilities for new binding sites and controlled cation selectivities may be found by the incorporation of phosphorous or arsenic donor atoms into the ligand rings of which only a few cases have been reported.37,38.

1.7.2 The Effect of the Ligand on the Properties of the Cation.

The effects of neutral macrocyclic ligands on the properties of the cation, other than solubility in organic media (i.e. acting as a super-heavy alkali cation which stabilizes unusual anionic species) has not received much attention.

Busch28 has investigated square planar tetra-azamacrocyclic complexes of neutral, mono and dianionic ligands with transition metals. These complexes show a relationship between the macrocyclic ligand field strengths and the difference between the normal or preferred metal-donor distance (acyclic systems) and the metal-donor distance imposed by the ring size. When the metal ion is a perfect fit in the ligand cavity, the complex is stable and relatively inert to reactions involving a change in ring size. But when the cation and ligand cavity sizes do not match, reactions leading to a more favourable ionic size (i.e. oxidation-reduction, change in spin state or movement of the cation out of the plane of the ligand), are promoted by relief of
the strain. It is this last observation that can be exploited to great advantage in electrochemistry by changing chemical potentials and thus permitting unusual reactions.

The potential of Ni^{II}/Ni^{III} couples of various tetra-azamacrocyclic complexes were shown to vary over a wide range (ca. 1.8 V). Similar behaviour has been reported for Fe^{II}/Fe^{III} and Co^{I}/Co^{II} systems.

Peter and Gross^39 have reported reduction potentials for Na^+, K^+ and Rb^+ cryptates in polycarbonate solution. The complexes were all more difficult to reduce than the free ion, e.g. the reduction potential for the K^+ cryptate of (15) was 0.9 V more negative than for K^+(aq).

![Diagram](image)

(15)

1.7.3 Anion Receptor Molecules^40,41.

In view of the fundamental role played by anions in chemical as well as biological processes, the binding of anions by organic ligands would be expected to provide a multitude of novel structures
with properties of wide significance. However, it has received little attention in comparison with cation coordination, which has been the subject of numerous studies. Only in recent years has anion coordination chemistry been developed as a new area of coordination chemistry. This arose from the design of anion receptor molecules of various types, especially macrocyclic and macropolycyclic polycations capable of forming strong and selective complexes with inorganic anions and with negatively charged functional groups (such as carboxylate or phosphate of organic or biological substrates). The binding strength and selectivity of the receptors are provided by electron-deficient interaction sites (like the positively charged sites of the polyammonium and polyguanidinium cations, which may establish multiple $N^+-H \cdots X^-$ bonds), suitably arranged around an intramolecular cavity of a shape and size adapted to the anionic substrate to be bound\textsuperscript{11,42-44}. Polyammonium macrocycles of various ring sizes (for instance (16) $\rightarrow$ (18)) act as anion receptors towards organic polycarboxylates, displaying stabilities and selectivities that result from both electrostatic and structural effects. The binding of complex anions of transition metals, such as the hexacyanides $M(CN)_6^{n-}$, markedly affects their redox
and photochemical properties\textsuperscript{45,46}. The strong complexation of adenosine mono-, di- and triphosphates (AMP, ADP and ATP) is particularly significant in view of their role in bioenergetics. It presents the possibility of devising molecular catalysts and carriers for these substrates. Substances like (16) and (17) are cyclic analogs of biological polyamines and could thus interact with biomolecules; indeed several macrocyclic polyamines induce efficient polymerisation of actin.

Protonated macrobicyclic diamines form katapinates by inclusion of halide ions. Tetraprotonated macrotricycles such as (19) are geometrically suitable receptors for spherical anions and form anion cryptates with halides. Therefore, (19) yields a chloride cryptate of high stability, and it shows a high selectivity for chloride over bromide, but does not complex other type of anions.
1.7.4 Electrides.

Electrides are the first examples of ionic salts in which all the anionic sites are occupied solely by electrons. Within this new kind of crystalline matter, the electrons are trapped in cavities within a framework of regularly stacked cations. Electrons can in some way be viewed as the simplest anions possible, however, unlike normal anions electrons do not behave as if they were simple charged spheres. In particular because of their low mass and their quantum-mechanical tendency to interact with one another over great distances, electrons cannot be "pinned down" to any one location as normal anions can. One cannot expect a trapped electron to spend all its time within the cavity; rather, it will wander close to and among the atoms lining the cavity and interact with electrons in nearby cavities, perhaps changing places with them. Electrides therefore have a number of unusual optical,
The discovery of electrides by J.L. Dye came about as a direct consequence of earlier work on alkalides. These are structures based on alkali metals which are extremely electropositive. In certain circumstances alkali metals can be induced to gain an electron, thereby forming a negative ion. An alkalide then, is an ionic salt in which both the cations and the anions are derived from alkali metals.

Alkalides require a third component as well. The anions of alkali metals are highly reactive; if alkali anions and alkali cations were simply placed close together, the anions would donate electrons to the cations, thereby neutralising both kinds of ions and producing a normal alkali metal. To forstall such a reaction, neutral molecules that are not very reactive are required to isolate the positively charged ions. The positive ions are "caged" in crown ethers or cryptands.

The first electride produced was prepared simply by dissolving the alkali metal in solvents in which they release electrons forming an electron solution. Adding crown ether/cryptand envelops the positively charged alkali metal and after allowing the solvent to evaporate, a fine powder or, sometimes, a thin film of electride is collected.
1.8 USES OF CROWN ETHERS AND CRYPANDS IN CHEMISTRY

Macrocyclic compounds have potential use in a wide variety of fields including industry, medicine, chemistry and analytical studies. However, molecules like the macrocyclic polyethers currently show much more potential than accomplishment; they are expensive to synthesize and therefore have limited commercial value. Most of the research has tended to focus on new types of complexes of higher and higher selectivity rather than on methods of cheap synthesis suitable for industrial use. Therefore as a direct result, what follows represents in the main a guide to possible further use rather than a summary of accomplishments. Macrocyclic molecules can selectively solubilize ions and because of this they have considerable potential for ionic separation. This selectivity characteristic of the molecules may be illustrated by some of the following uses.

1.8.1 Liquid-Liquid Extractions.

Liquid-liquid extractions consist of the contacting of two immiscible liquids so that the desired species is preferentially extracted into one of the liquids. Traditional countercurrent contacting is used to obtain several stages of separation. The liquid-liquid system usually consists of an aqueous phase in contact with an
organic phase containing the macrocyclic ligand. However, due to the great expense of these macrocyclic ligands, it is necessary to separate materials of sufficient value to justify the expense. One of the most promising areas of application is isotope separation. The use of crown ethers have for calcium isotope enrichment has been studied in detail. For example the separation of calcium-48 from calcium-40 is outlined below:

(Equation 1.2)

\[ ^{40}\text{Ca}^{2+}(\text{aq}) + ^{48}\text{CaL}^{2+}(\text{org}) \leftrightarrow ^{48}\text{Ca}^{2+}(\text{aq}) + ^{40}\text{CaL}^{2+}(\text{org}) \]

L - macrocyclic polyether

The process is based upon the exchange between a metal ion in the aqueous phase and the metal ion-macrocyclic polyether complex in the organic phase. This reaction tends to go preferentially to the right as written, and therefore, calcium-44 is preferentially enriched in the organic phase. For dicyclohexyl-[18]-crown-6, the equilibrium separation factor is 1.008±0.0016. Almost any commercially available counter current extractors can be used to obtain multiple-stage separation. For example, six columns 60 foot long and 1.5-6 inches in diameter would enrich approximately 1 Kg of calcium per year.
from natural abundance to the enrichments presented in Table 1.6. Closed reflux of these columns can be accomplished by removing the calcium from the calcium polyether complex at one end of the column and reforming the complex at the other end of the column. In a system containing an aqueous solution of calcium chloride and a chloroform solution of dicyclohexyl-[18]-crown-6 calcium complex. The organic phase is more dense and the bottom reaction is: $\text{CaL}^2\text{(org)} + \text{H}_2\text{O} \rightarrow \text{L(org)} + \text{Ca}^{2+}\text{(aq)}$. This occurs because the calcium ions prefer the dilute aqueous environment to the polyether complex in the organic solution. The equilibrium ratio of $[\text{Ca}^{2+}\text{aq}]$ to $[\text{CaL}^2\text{(org)}]$ was found to be 20:130. The calcium-polyether complex is formed in the separation column by using high calcium concentrations 5M in the aqueous phase compared to 0.2M in the organic phase. The reaction at the top of the column is: $\text{Ca}^{2+}\text{(aq)} + \text{L(org)} \rightarrow \text{CaL}^2\text{(org)} + \text{Ca}^{2+}\text{(aq)}$. Before recycling of the aqueous calcium chloride some reconcentration is required before complexation with the polyether (Table 1.6).

This theoretical cascade system has many advantages over other calcium isotope separation methods. It is easier to operate than the mercury amalgam approach and avoids the toxicity problems. It is also superior to an ion exchange
method in that it is simpler and the single-stage separation factor is considerably larger.

Table 1.6 Calculated Calcium Isotope Enrichment from a Six Column Production Cascade Using Dicyclohexyl-[18]-crown-6.

<table>
<thead>
<tr>
<th>ISOTOPE</th>
<th>NATURAL ABUNDANCE %</th>
<th>% PRODUCT CONCENTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcium-48</td>
<td>0.185</td>
<td>10</td>
</tr>
<tr>
<td>calcium-46</td>
<td>0.0033</td>
<td>0.1</td>
</tr>
<tr>
<td>calcium-44</td>
<td>2.06</td>
<td>40.0</td>
</tr>
<tr>
<td>calcium-43</td>
<td>0.145</td>
<td>1.8</td>
</tr>
<tr>
<td>calcium-42</td>
<td>0.64</td>
<td>2.0</td>
</tr>
<tr>
<td>calcium-40</td>
<td>96.97</td>
<td>46.0</td>
</tr>
</tbody>
</table>

1.8.2 Other Separation Processes.

Besides isotope separation, liquid-liquid extractions have possible application for expensive chemical separation, e.g. lanthanides, amino acids and optically active isomers. Because of pollution and increases in the prices of raw materials, the purification and recovery of metals from waste is becoming more important.

Many of the liquid-liquid extraction systems may
be applied to chromatographic separations; Column chromatography; Extraction; Elution; Exchangers; Thin-layer chromatography and Thin-layer electrophoresis. The macrocycle may be in the stationary phase or in a mobile phase. Silica gel is employed as a solid support for dibenzo-[18]-crown-6 in the separation of radioactive ions. The elution is accomplished with 0.01 mol dm\(^{-3}\) NH\(_4\)SCN in water at 40°C and pH7. The alkali ions appear in the eluate in the order Li\(^+\) > Na\(^+\) > Rb\(^+\) > K\(^+\) > Cs\(^+\) 54.

Crown ethers and cryptands have proved valuable in the treatment of heavy metal poisoning and for decontamination from radioactive metals. The cryptand [2.2.2] binds with Sr\(^{2+}\), Ba\(^{2+}\), Pb\(^{2+}\), Ca\(^{2+}\) and has been tested on rats to remove strontium-85 and radium-224; it is also effective for the removal of lead. Cryptand (20) displays a very high selectivity (10\(^6\) to 10\(^7\)) for Cd\(^{2+}\) with respect to Zn\(^{2+}\) and Ca\(^{2+}\), with even higher ratios for lead and mercury. This striking feature is due to the operation of a double-parameter discrimination (cavity size and binding sites). Whilst the nitrogen sites favour both Cd\(^{2+}\) and Zn\(^{2+}\) over Ca\(^{2+}\), its cavity is too large for any strong complexation of Zn\(^{2+}\). At present there seems to be no other ligand displaying such high selectivity for the heavy metal cations. "Cryptatotherapy"\(^{13,40}\) offers a very important
approach for the medical treatment of heavy metal poisoning.

\[
\text{(20)}
\]

1.8.3 Separation of Optically Active Amino Acids.

One method that has been described is for primary amino ester salts to be adsorbed on silica gel from an aqueous solution. They are then separated by elution with chloroform solutions of different derivatives of di/binaphthyl-[18]-crown-6. The enantiomers are completely separated in this process\cite{55}. A similar method employed by Cram and Cram\cite{53} successfully used liquid-liquid chromatography to separate the enantiomers of \(\alpha\)-phenylethylamine salts. These authors also suggested the resolution of racemic amino acids with an optically active cyclic ether by either liquid-liquid extraction or chromatography.

1.8.4 Membrane Separations.

Membranes containing macrocyclic polyethers can effect rapid selective separation of ionic solutes. These membranes can concentrate the solute of interest, converting a dilute mixture into a concentrated solution of the one desired component.
However, matching empirical membrane technology and a relatively sophisticated membrane mechanism is difficult. Because of this, they have not been as completely developed as the more conventional extractions that are discussed above.

There are two basic types of membranes that are macrocyclic molecules: liquid membranes and solid membranes. Liquid membranes currently offer high selectivity, but solid membranes promise greater stability. Most research to date has concentrated on the development of liquid membranes and they are now suitable for large-scale application. Much less has been done on solid membranes which require more careful chemical formulation.

1.8.5 Ion Selective Electrodes.

Ion-selective electrodes may be divided into three classes: liquid-ion exchangers, solid-ion exchangers and neutral sequestering agents. The liquid-ion exchangers are based on a liquid membrane containing a mobile carrier. Examples of mobile carriers include phosphate ester, fatty acids and amines. The first commercial liquid membrane electrode was calcium selective and used didecylphosphate. The selectivity of these electrodes is based on the specific reaction between the carrier and the solute being studied. The mobile carriers in this case are charged and macrocyclic
molecules may be effectively used as mobile carriers in these electrodes.

The solid-ion exchangers, include glass electrodes and solid-state crystal electrodes. The glass electrodes are made from mixtures of silicon oxides with other metal oxides. The selectivity of the electrode results from the type of defect in the glass and is modified by varying the glass composition. Macrocyclic additives will not have a marked affect on these electrodes.

Neutral sequestering electrodes also use membranes containing a mobile carrier. However this carrier is uncharged. Their selectivity depends totally on the specificity of the reaction between the carrier and the solute being studied. Macrocyclic additives which act as mobile carriers promise to be most useful for this type of electrode.

Whether they are the ion exchangers or neutral carrier type, liquid membrane ion-selective electrodes have two major problems: mechanical stability and reasonable response times. The stability problem is overcome by use of an inert support for the liquid e.g. a porous glass frit (Figure 1.8). If the support is thin enough there will be a rapid establishment of the potential across the membrane. To minimise contamination, the electrode is usually designed for some outward
leakage from the membrane. The electrical contact for the membrane electrode is normally established by having an internal aqueous electrolyte and an internal reference electrode.

Natural macrocycles as well as synthetic macrocycles have also been used in these electrodes. Most of the work with natural macrocycles (Section 1.9), "ionophorous antibiotics", has centred on cation-selective electrodes for the alkali and alkaline earth ions. The earliest type of electrode was based on valinomycin which showed a selectivity for potassium over sodium 10-100 times greater than the commercial glass electrode. Other neutral antibiotics nonactin, actin, enniatins, gramicidin and tetralactones show potassium selectivity. Nonactin was found to have a selectivity of 750 for potassium over sodium with a glass frit support membrane. Charged antibiotics behave in a similar manner, nigericin is selective for sodium and monensin is selective for potassium. Since synthetic macrocycles complex ions selectively, they can be substituted for antibiotics. Again the selectivity of the resulting electrode depends on two main factors; the relative equilibrium constant for formation of the ion-macrocyclic complex and the membrane solvent. Only crown ethers have been studied extensively. Nitrobenzene solutions of
dicyclohexyl-[18]-crown-6 were found to have equilibrium constants for complexation, with potassium, which agreed with the selectivity for the electrode. However, the selectivity of potassium over sodium was found to be much less than that of the analogous antibiotic valinomycin electrode. Mascini and Pallozi repeated the same experiment using a different support, polyvinylchloride, and they found the same result when they compared dibenzo-[18]-crown-6 with valinomycin. Since then Simon has developed a calcium-selective electrode that can be used in the presence of sodium, potassium and magnesium (Table 1.7). The selectivity of the carrier (B) for Ca$^{2+}$, compared to those for Mg$^{2+}$ and
Zn\(^{+}\), is very striking, and important for the differentiation of blood sera\(^6\). Particularly favourable is the fact that the membrane electrode does not interact with Na\(^{+}\) and K\(^{+}\) under physiological conditions. For similar reasons carriers which are selective for Na\(^{+}\) (A) in the presence of protons are interesting, (C) permits the intracellular determination of Ca\(^{2+}\) in blood serum\(^6\). Only a few macrocyclic ligands have so far been tried but their potential is greater than the natural antibiotic because they can be synthesized with properties specific to the ions to be measured.

Table 1.7 Selectivity Constants of Carrier Molecules in P.V.C. Matrices in Acidic Solution\(^6\).

<table>
<thead>
<tr>
<th></th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^{+}) Selective</td>
<td>Ca(^{2+}) Selective</td>
<td>Ba(^{2+}) Selective</td>
<td></td>
</tr>
</tbody>
</table>

1.8.6 Catalysis by Macrocyclic Compounds.

Catalysis reduces the cost of commercial chemical processes by increasing the efficiency of chemical reactions. Catalysts are either homogeneous or
heterogeneous. Most heterogeneous catalysts are metals present either at an interface or as a finely divided dispersion. Because they have the advantage of being readily separable or allowing flow-through processing, they are widely used for industrial applications. Homogeneous catalysts, normally more efficient than heterogeneous ones, are used for the liquid phase reactions. They can, however, be more difficult to separate and recover than heterogeneous catalysts.

The major chemical changes effected by catalysis are listed in Table 1.8. Cyclic polyethers will be of little industrial importance for the first three types of catalysis because satisfactory catalysts are already in use. Macrocyclic catalyst may, however, prove useful for nitrogen fixation. The main objective would be to supplement the enzyme, nitrogenase in the soil. At present, several groups have succeeded in this by using macrochelates of ruthenium, titanium and iron, but the yield is low because the reaction is not reversible. The ammonia remains bound to the metal ion.
Table 1.8  Major Types of Catalysis.

<table>
<thead>
<tr>
<th>TYPE</th>
<th>EXAMPLES OF CATALYSTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid-base</td>
<td>$H^+$, $OH^-$</td>
</tr>
<tr>
<td>hydrogenation-dehydrogenation</td>
<td>platinum metals</td>
</tr>
<tr>
<td>polymerisation</td>
<td>free radicals</td>
</tr>
<tr>
<td>nitrogen fixation</td>
<td>enzymes, transition metal complexes</td>
</tr>
<tr>
<td>oxidation-reduction (electron transfer)</td>
<td>tetraazas, polyelectrolytes</td>
</tr>
<tr>
<td>synthesis-decomposition</td>
<td>enzymes, crown ethers</td>
</tr>
</tbody>
</table>

Electron transfer is a second promising area for possible commercial applications of macrocycles as catalysts. Electron transfer can be accelerated with a macrochelated transition metal ion. In most cases, the macrochelates employed are cyclic tetraaza compounds or similar heterocyclic macrocompounds where the coordination occurs between the transition metal ion and the nitrogens. Table 1.9 shows accelerations of times 300 for the oxidation of Co(III) compounds when tetraaza ligands replace ammonias. The acceleration of the electron transfer results from the alteration of the electronic energy levels of the metal through the coordination. These chemical changes parallel those in biological systems.
where bound metal ions can activate the protein. Ferredoxin, haemoglobin and carbonic anhydrase are some examples of this.

Table 1.9 Rates of Electron Transfer of Macrocyclic Co III Complexes with Rn(NH₃)₆²⁺.

<table>
<thead>
<tr>
<th>OXIDANT</th>
<th>k (M⁻¹ sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NH₃)₅ NH₃³⁺</td>
<td>0.01</td>
</tr>
<tr>
<td>Co(trans-(14)-diene)(NH₃)₂³⁺</td>
<td>3.0</td>
</tr>
<tr>
<td>Co(trans-(14)-diene)(OH₂)₂³⁺</td>
<td>8x10²</td>
</tr>
<tr>
<td>Co(NH₃)₅(OH₂)³⁺</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The greatest potential for macrocyclic catalysis lies in the synthesis of specialised chemicals that otherwise could not be made, or could be made only at prohibitive costs. Because catalysts are recoverable, the cost of the macrocycles does not dominate their use in commercial production. The ability of those materials to solubilise charged species in apolar solvents makes them especially useful in this regard. Many organic reactions make use of alkali and alkaline earth salts, but their efficiency is impaired by low solubility. Cyclic polyethers have been used to solubilise permanganate
salts. By complexing the cation, macrocycles can also enhance the reactivity of the counterion. One example is the use of a cyclic polyether to catalyse the reaction of carbanions. Other possible areas of application will be found in alkyllithium compounds, Grignard reagents, and alkali metals. In the presence of macrobicycles (cryptates), alkali metal solutions give solvated electrons.

Macrocycles could also serve as catalysts by altering the solvation of a compound or by causing a conformational change once the ligand is in the microcavity.

1.9 NATURALLY OCCURRING MACROCYCLES (BIOLOGICAL IONOPHORES).

The essential metals of the human body may be divided into two categories; "Bulk" metal - sodium, potassium, magnesium and calcium, which constitutes about 1% of the human body weight and "trace" metals - iron, manganese, copper, iron, cobalt, zinc, vanadium, chromium and molybdenum, which constitute less than 0.01% of the human body. However, it is the trace metals that have been studied most during recent investigations of metal ions in biological processes. This is because the bulk metals have very few spectroscopic properties. They have no unpaired electrons and cannot be studied by magnetic measurements or electron spin resonance.
spectroscopy. However some complexes of $^{23}\text{Na}$ and $^{44}\text{Ca}$ can be studied by nuclear magnetic resonance spectroscopy. The alkali metal cations are concerned "in vivo" with the maintenance of normal water balance, the conduction of nerve impulses, and neuromuscular activity. Sodium and potassium have a great difference in their location and this is easily seen in mammalian blood cells. $\text{Na}^+$ is principally extra-cellular (143 mM Kg$^{-1}$ $\text{Na}^+$ compared with 5 mM Kg$^{-1}$ $\text{K}^+$ for blood plasma) and $\text{K}^+$ in intra-cellular (105 mM Kg$^{-1}$ $\text{K}^+$ compared with 10 mM Kg$^{-1}$ $\text{Na}^+$ for red blood cells). There is, therefore, a discriminatory mechanism (a selective ion pump) which controls the selective uptake of $\text{K}^+$ across the membrane into the cell from the extracellular fluid. Calcium and magnesium ions are involved in activating several enzyme systems. Calcium is particularly important in the activation of heart and skeletal muscle contraction. Elevation of calcium levels activates the proteases in cells and this is believed to be the basis of degenerating diseases such as muscular dystrophy and Alzehiemer disease. In medicine therefore there is a need to measure and to modify the concentration of ions within the cells. If a macrocycle can be found which can achieve five simple requirements; (1) selective cation binding; (2) ability to cross or span the cell membrane; (3) water
solubility; (4) an indicator change when bound to a cation; and (5) non-toxicity; it should be possible to measure and alter accurately the internal concentration of various free cations. One immediate use would be in detecting tumour cells since tumour cells have much higher concentrations of Ca\(^{2+}\) than normal cells.

### 1.9.1 Macrocyclic Antibiotics and their Alkali Metal Complexes.

In 1964, an American physiologist, B.C. Pressman found that certain antibiotics could induce the selective movement of K\(^+\) into rat liver mitochondria. These antibiotics, now collectively termed ionophoric (or ion-bearing) antibiotics could also increase the permeability of synthetic lipid bilayers to K\(^+\). Such compounds are neutral at physiological pH and so may act as discriminatory cation carriers by forming complexes with the alkali metal cations. This discussion concerns these species although a further class of antibiotics containing carboxylic acid functions have also been found to exercise discriminatory powers. This class can react with alkali metal cations to give 1:1 salts and so act as anionic carriers or provide negatively charged pores.

Valinomycin is a cyclic dodecadepsipeptide, an atypical peptide having alternate amino- and hydroxy-
carboxylic acids linked by amide and ester bonds [L-valine-D-hydroxy isovaleric acid-D-valine-L-lactic acid]. It was first isolated from streptomycetes sources and has been shown to have a high ion selectivity towards K⁺ ions. This selectivity has been retained to a lesser extent, in numerous synthetic analogues of valinomycin. It was first proposed that the ion selectivity arose as a consequence of the size of the cavity in the antibiotic molecules. In valinomycin the cavity was large enough to accommodate the hydrated alkali metal ion. However, X-ray structural determination of the K⁺-complex showed that it is the water-free K⁺ ion that is incorporated (Figure 1.9).

The studies show that it exists in essentially the same conformation in both solid and solution states with inwardly orientated ester carbonyls binding to the metal. The skeletal atoms wrap round the central cation just like three sine waves and are held in position by hydrogen bonds (Figure 1.10) which impart rigidity to the molecular frame.

A second group of antibiotics neutral at physiological pH and capable of alkali metal complexation, is the enniatins. They are isolated from fusarium sources and it is interesting to note that the fusarium species have been shown to attack silicate minerals such as orthoclose releasing
Figure 1.9  The Valinomycin-Potassium Complex

potassium. These soil fungi not only liberate metallic ions from minerals, but can also provide antibiotics which will complex with alkali and alkaline earth metals. Enniatin B is a
cyclohexadepsipeptide and the structure of the enniatin B-K⁺ complex (Figure 1.11) resembles a charged disc with lipophilic boundaries, the metal being found at its centre. The molecules stack one above the other and if such a process should occur in a membrane then it is possible to envisage the formation of an ion-carrying pore.

The third group of neutral ionophores consists of the macrotetrolide actins which are isolable from actinomycyes species. Nonactin, so-named, it is said because of its inactivity in early tests for biological activity, is depicted in Figure 1.12.
Figure 1.10  Schematic Diagram of a Cyclododecapeptide Folded to Produce a Cavity Lined with Six Carbonyl Donors (Arrows) and Stabilized by H-Bonding (Broken Lines).

Figure 1.11  The Enniatin B-K⁺ Complex

The X-ray structure of free nonactin\textsuperscript{89} shows a large cavity to be present and in the K⁺ complex\textsuperscript{90} this is occupied by the metal. This ligand wraps itself around the metal as the seam of a tennis ball, Figure 1.13, shows the way in which the four furanyl and four carbonyl oxygen atoms interact with the
Certain common features may be found for the alkali metal complexes of the three groups of ionophores:

1. the alkali metal sits in the ligand cavity at a centre of optimal electron density provided by the donor atoms of the ligand,
2. a lipophilic exterior is presented to facilitate cation transport,
3. a flexible ligand is required to effect the energetically favoured stepwise removal of the solvation sheath,
4. a best-fit situation is required with regard to
the cavity diameter and the diameter of the incoming ligand, but ligand-ligand repulsions must be minimised.

(5) the difference between the energy of ligation and energy of solvation must be maximised.

Figure 1.13 The Nonactin-Potassium Complex and the Schematic Representation of this Molecule. 

1.9.2 Binding Properties of Other Natural Products.

Crown ether and cryptand analogues can also be seen in carbohydrates, polysaccharides, enzymes and proteins. Indeed, nature has provided us with one of
the most intensively investigated enzyme model systems to date in the shape of the cycloamyloses. This group of homologous oligosaccharides, which are comprised of α-1,4-linked D-glucopyranosyl residues in a cyclic constitution are called cyclodextrins

\[ \alpha-CD; \ n=6 \]
\[ \beta-CD; \ n=7 \]
\[ \gamma-CD; \ n=8 \]
\[ DM\beta-CD; \ n=7; R=Me \]

The best known and studied representatives are those built up from six and seven glucose units. X-ray crystallographic studies reveal that cyclohexa-amylose (24) is a doughnut-shaped molecule in which (i) the six D-glucopyranosyl residues are in the \( \text{C}_1 \) chair conformation, (ii) the six glycosidic oxygens surrounded by four hydrogens (on C-3 and C-5 of neighbouring residues) are all pointing into the centre of the cavity, (iii) the hydroxymethyl groups on C-5 line one rim of the cavity, and (iv) the secondary hydroxyl groups (on C-2 and C-3) line the other rim. As a result of the work of Cramer in Germany, and Bender and Breslow in the United States
and others, it is now well established that cyclohexa-amylose (24) serves as a host molecule in aqueous solution for a whole range of organic guest molecules including aliphatic and aromatic hydrocarbons, alcohols, phenols, ethers, carboxylic acids, esters, amines, and so on. Since the cavity of 4.5 Å in (24) is just sufficient to accommodate a benzene ring, these inclusion complexes, e.g. (25) and (26), can be viewed as owing their existence to a kind of hydrophobic bonding. Association constants are moderately high (10^2-10^4 mol⁻¹) and they have shown, for example, to exhibit covalent catalysis with maximal rate enhancement of the order of several hundred times that of the uncatalysed reaction (e.g. the hydrolysis...
of meta(t-butyl)phenyl acetate can be accelerated 260-fold) as well as non-covalent catalysis. The p-chlorination of anisole with hypochlorous acid proceeds 5.3 times faster with high regioselectivity (para:ortho 96:4) when 72% of the anisole is bound in (24) 

\[ \text{OMc} \]

\[ \text{Me} \]

\[ \text{Me} \]

\[ \text{Me} \]

\[ \text{OMc} \]

\[ \text{Me} \]

\[ \text{Me} \]

\[ \text{Me} \]

\[ \text{OMc} \]

(25) (26)

Although the cyclodextrins, \( \alpha^- \), \( \beta^- \) and \( \gamma^- \) are promiscuous in their role as receptors for a range of chemical species, only relatively few examples of adduct formation with organometallic compounds have been described in the literature. For example ferrocene forms a 1:1 adduct with \( \beta^- \)-cyclodextrin and a 2:1 adduct with \( \alpha^- \)-cyclodextrin (Figure 1.14). Further investigations in this area with ruthenocene, cobalt (III), platinium complexes are still being carried out. 

Research aimed at uncovering the potential of the cyclodextrins as enzyme models will no doubt continue to thrive, it would appear that rapid progress in this area is going to be hampered by a number of
factors, not least of them (i) the lack of sufficient structuring of the guest in their binding sites, (ii) the low degree of chirality inherent in their axial symmetry (despite the fact the α-cyclodextrin contains 30 chiral centres!) and (iii) the constraints of always having to start with the same one or two basic building blocks.

Figure 1.14  The Proposed Structures for the Adducts of (A) [Cp₂Fe((α-CD)₂)]  (B) [Cp₂Fe(β-CD)]  (C) [Cp₂Fe(γ-CD)]

The design of certain types of crown compounds (27) and (28) which are capable of binding ammonium salts, having been shown to imitate enzyme protease and transacylase by introducing sulphur nucleophiles at the proper position to attach an activated carbonyl group in the ammonium substrate e.g. ammonium salts of activated amino acid esters (Equation 1.3 below)
Other exciting possibilities of enzymic activity can be seen in binuclear complexes like (29a and b), which is capable of complexing two copper ions. The cavity between the two copper ions (29a) should be large enough to accept a substrate and thereby provide a model for oxygenase activity.

One of the major contributing factors to enzyme catalysis is the polarisation of the carbonyl group by an electrophile in metabolic processes. This occurs by an imidazole group or a zinc ion in a peptide chain. Synthetic dihydropyridines have been used in these processes.
with complexed magnesium ions are the best synthetic electrophilic catalysts and are now being incorporated into crown ethers (30) and (31).

\[ \text{NADPH} + \text{NAD}^+ \xrightleftharpoons{\text{Enzyme}} \text{NADP}^+ + \text{NADH} \]

The resultant compounds are found to have some hydrogenase activity and are therefore of great biochemical interest since a transhydrogenase enzyme is essential for the interconversion of NADH and NAD (P)H, Equation 1.4.

EQUATION 1.4.

"I have a dream we shall be able to make molecules which will vie with Nature's receptor molecules in their ability to exhibit selective binding and to display recognition functions towards chosen target molecules" (J.F. STODDART)\(^93\).
CHAPTER 2

AIMS AND OBJECTIVES

This project is an investigation of the preparation and properties of a novel class of electrically active clay-based and organo-clay composites. The objective chosen for the study incorporates a novel clay composite that provides potential edge corner for interaction with a bond material. The work falls into a number of distinct categories.

2.1 SYNTHESIS AND STRUCTURAL ANALYSIS OF A REACTABLE CLAY

Hail and coworkers have been studying to design an ion-binding structure containing a forebond unit that adopted the following selecting a synthetic surrogate.

The ion-binding moiety should be a central

The size of the binding cavity, the number and nature of the heterocycles, and hence the specificity towards different cations can be varied during the construction of a macrocycle without major changes in the synthetic approach.

(a) Large rings should form one edge of a macrocycle,

(b) A polymeric chain should form one edge of a macrocycle,

The simplest form of this type of molecule would
2. AIMS AND OBJECTIVES.

This project is an investigation of the preparation and properties of a series of electrically active crown ether and cryptand complexes. The cryptand chosen for the study incorporates a metallocene unit as one bridge which provides a potential redox centre for interaction with a bound metal ion. The work fell into a number of distinct categories.

2.1 SYNTHESIS AND STRUCTURAL ANALYSIS OF A REDOXABLE CRYPTAND.

Hall and co-workers\textsuperscript{106}, in attempting to design an ion-binding structure containing a ferrocene unit, adopted the following criteria when selecting a synthetic target:

(a) The ion-binding moiety should be a neutral crown ether or related macrocyclic ligand.

This class of ligands is exceptionally versatile (Chapter 1). The size of the binding cavity, the number and nature of the heteroatoms and hence the specificity towards different cations can be varied during the construction of a macrocycle without major changes in the synthetic approach.

(b) Ferrocene should form one edge of a macrocycle, i.e. be joined through each cyclopentadienyl ring to the same molecule.

The simplest form of this type of molecule would
be a monocycle (Figure 2.1) where ferrocene is linked through some "bridgehead" atom B to a \((\text{CH}_2\text{CH}_2\text{X})_n\) chain \((\text{X} = \text{heteroatom})\).

Any complexed metal ion might be expected to reside in the cavity in the plane of the bridge and benefit from any interaction due to its position adjacent to the iron atom.

\[
\text{B} = \text{Bridgehead} \\
\text{\(\text{X} = \text{heteroatom}\)}
\]

Figure 2.1 Ferrocene Macrocyle.

The syntheses and metal cation complexing abilities of macrocyclic compounds containing a ferrocene and ruthenocene unit as an integral part of the macrocyclic skeleton have been reported\(^9\)\(^8\)-\(^1\)\(^0\)\(^2\). The ferrocenophanes have received much attention because the iron atom of a ferrocene nucleus may play a role as a coordinatable heteroatom. Oepen and Vögtle\(^1\)\(^0\)\(^5\) were the first to report a preparation of a ferrocene-containing cryptand and this concept was subsequently developed by Bell and Hall\(^1\)\(^0\)\(^6\), and later by Grossel and Knychal\(^1\)\(^0\)\(^7\) who also prepared a series of ruthenocene analogues. Hall and his co-workers prepared a whole series of macrocyclic ligands attached to the ferrocene moiety by the condensation
of an acid chloride with an amine. The first ferrocene amides (32) (33) showed only weak if any complexing capacity for Li\(^+\), Na\(^+\) or K\(^+\) ions. It was for this reason that they went on to investigate the preparation of a cryptand attached to the ferrocene unit (Fc[2.2]M + Fc[2.2]D).

\[
\begin{align*}
(32) & \quad n = 0, 1, 2 \\
(33)
\end{align*}
\]

As a direct consequence of the work reported above, Akabori and others\(^{103,104}\) synthesised several polyoxa (n), polythia (n), and mixed oxathia (n) ferrocenophanes. These showed the ability to bind transition metal cations more effectively than the corresponding crown ethers. These crown ether ferrocenophane included (34), (35) and (36).
Grossel and co-workers have collaborated with Hall on the preparation of ferrocene amide cryptands Fc[2.2]M and Fc[2.2]D and their ruthenocene analogues. It was decided to extend this work to investigate their complexing ability and selectivity towards different metal ions. As a starting point, (even though considerable progress had been achieved by Hall and his colleagues) we wished to carry out a detailed structural study of Fc[2.2]M and Fc[2.2]D and any other cryptand that could be prepared. In particular, it was hoped that the study of these in the solid state (n.m.r. and X-ray crystallography) would provide further information about their ion binding ability.

One proposed application for metallocene crown ether ligands such as (34) is the electrochemical transport of an ion across a liquid membrane. Recently, the enhancement of binding consequent upon electrochemical reduction of redox active crown ethers and cryptands has been reported. Saji and Kinoshita have noted an abrupt decrease of ion
binding efficiency of pentaoxa-[13]-ferrocenophane (37) upon electrochemical oxidation. They investigated the behaviour of (37) as a carrier in a liquid membrane and found that such an electrochemically switched cation transport system offers an efficient method for the conversion of electrical energy into a chemical concentration gradient. They demonstrated that Na⁺ transport was greatly enhanced in the presence of the redox active macrocyclic polyether (37).

The mechanism of electrochemical redox-driven metal ion transport is shown in Figure 2.2 below. At the left interface, (37) extracts a metal ion to form a complex (37)M⁺. This complex diffuses to the right interface whereupon it becomes oxidised at electrode W¹. Then, the metal ion must be lost to the aqueous phase. The (37)⁺ diffuses back to the left interface, whereupon it becomes reduced at electrode W² and the cycle recommences.
Figure 2.2 Electrochemical Transport with Redox Active Crown Ether.

W₁, W₂: mini grid platinum working electrodes.
C₁, C₂: platinum working electrodes.
C₁, C₂: platinum plate counter electrodes.
R₁, R₂: saturated calomel reference electrodes.

2.2 ELECTRICALLY ACTIVE CROWN ETHER COMPLEXES.

As already discussed in Chapter 1, in 1967 Pedersen¹⁰⁹ demonstrated the ability of macrocyclic polydentate ligands to solubilise inorganic and organic salts in polar and non-polar solvents, with the production of chemically active anionic species². A simplistic view of the solubilisation process is shown in Figure 2.3. Since the complex has a hydrophobic "greasy" exterior, it is readily solubilised by the non-polar or dipolar aprotic solvent. In order to preserve electrical neutrality, the anion must accompany the cation-crown complex into solution. Since a non-polar aprotic solvent such as benzene or a dipolar aprotic solvent such as
acetonitrile should not have a high affinity for the anion. When compared with protic media, the anion is not expected to be highly solvated. Such anionic species have been termed "naked" anions.

![Figure 2.3 The "Naked Anion".](image)

A further aspect of this project has been to investigate the effects of crown ether encapsulation on the properties (particularly electrical) of organic materials in the solid state. From a viewpoint of solid state chemistry, the "naked anion" of the crown ether complex may show unusual properties under the influence of an electric field since it is bound much more weakly to the metal cation than in the original salt. However, little information concerning this has been available until now.

### 2.2.1 Conduction Mechanisms in Crown Ether/TCNQ Complexes.

Nogami et al have carried out an extensive study on conduction mechanism in a variety of crown ether/TCNQ salts. They were interested in how the presence of crown ethers would effect the
intermolecular interaction between TCNQ-anions, stacked in one-dimensional columns. These workers synthesised about 100 different crown ether/cation-TCNQ complexes and measured the electrical resistivities of these materials, mainly as compacted samples, at room temperature.

However, the results reported in the literature are of questionable value since the d.c. measurements were made at only one temperature and a.c. dielectric response studies measurements were only carried out at one frequency. For these reasons we decided to try to understand the electrical behaviour of such compounds. Accordingly, temperature-dependent d.c. conductivity measurements and a.c. dielectric response studies have been carried out over a wide range of frequencies on a number of these materials.

2.2.2 Novel Photographic (Oxonol) Dyes and their Crown Ether Complexes.

Following their work on the crown ether/TCNQ complexes Nogami and Newman studied conduction mechanisms in crown ether/alkali-metal iodide complexes. They found that the crown ethers enhanced the conductivity of the metal iodides and suggested that these materials represent a new kind of anionic conductor.

In order to gain further insight into the
behaviour of such materials we compared the electrical properties of a number of crown ether/alkali metal halide complexes with an analogous group of anionic dye salts (38). Edwards and Grossel have shown that simple oxonol dye salts (e.g. (38)) behave as semiconductors and semi-insulators. In the current project a number of crown ether/oxonol dye complexes have also been prepared in order to compare their behaviour with the semiconducting and metallic crown ether/TCNQ salts. It was also of interest to incorporate photographic dyes into electrochemically active molecular stacks in the hope of obtaining unusual photoelectrical and electro-optical properties.

\[ \text{(38)} \]

2.3 SYNTHESIS OF SUBSTITUTED AND POLYMERIC MACROCYCLIC SYSTEMS.

The final part of this study falls into three small sections;

2.3.1 Electrically Active Substituted Crown Ethers.

To our knowledge no study has been carried out on
substituted crowns, although Nogami et al.\textsuperscript{120} have prepared a series of polymeric crown ether/alkali-metal TCNQ complexes. For several years Bradshaw\textsuperscript{121} has been engaged in a study of the structural parameters that affect the ability of a macrocyclic ligand to bind cations, catalyse phase-transfer reactions, and transport ions across liquid membranes.

A primary concern of ours was how substituted crown ethers might be used to control electrical conduction processes in solids as outlined in the previous Section 2.2. Lehn\textsuperscript{122} considers a polyfunctional macrocyclic K\textsuperscript{+} complex as providing a solid state model of a K\textsuperscript{+} channel. Molecular channels are thought to be important in ion exchange processes across membranes, and biophysical and physiological data point to the existence of an ion-specific Na\textsuperscript{+} and K\textsuperscript{+} pores. Figure 2.4 shows the crystal structure of the potassium complex (KBr/H\textsubscript{2}O) of the tetracarboxamide of [18]-crown-6 (39). Molecular channels such as these could be envisaged in electrically active materials and the crystal structure of Figure 2.4 shows similar likeness to the presently known organic superconductors (Chapter 4).
Figure 2.4 Lehn's Crystal Structure of Tetracarboxamide of [18]-crown-6.

The controlled aggregation of molecules is an important problem within chemistry. Many methods have been devised to combine atoms by chemical bonds in a controlled manner, but no similar control exists of Van der Waals bonding, nor can molecules of different kinds be arranged in a solid in any planned order. The superimposition of monomolecular layers
can lead to the arrangement of molecules in a specific planned structure ABCD (Figure 2.5). We have been interested in the production of monolayer systems and, in particular, the design and synthesis of molecules which could form a conducting monolayer. By adding long aliphatic chains to the crown ethers it was hoped that the crown ether/TCNQ complexes might form highly conducting monolayers. However, this aspect of the project is still in its infancy and work continues on the development of electrically active monolayers.

![Figure 2.5 Assembling Monolayers of Molecules A,B,C,D.](image)

2.3.2 Electrically Active Polymeric Crown Ethers.

A further step from the substituted crown ether/TCNQ complexes is the synthesis of analogous crown ether polymer/TCNQ complexes. Nogami has carried out electrical measurements on the TCNQ complexes of a crown ether polymer. These were d.c. measurements taken only at room temperature and thus do not provide any insight into the conduction
mechanisms occurring in such materials. We have prepared similar materials and have carried out more detailed electrical measurements on these.

2.3.3 Development of a Polymeric Metalloocene Cryptand.

The final part of this project involved preliminary investigation into the possibility of preparing a polymeric metalloocene cryptand. This involved developing a model system by which Fc[2.2]M and Fc[2.2]D could eventually be polymerised. These types of materials might offer exciting and interesting uses as ion-selective electrodes (Chapter 1).
CHAPTER 3

RESULTS AND DISCUSSION (I)

The synthesis and properties of some redoxable cryptands and cryptates.
3. RESULTS AND DISCUSSION (I)

3.1 INTRODUCTION TO FERROCENE CHEMISTRY

Ferrocene was discovered by accident in 1951 by Kealy and Pauson\textsuperscript{124}, who were attempting to synthesize fulvalene by oxidation of the cyclopentadienyl Grignard reagent (Equation 3.1). The synthesis of fulvalene was unsuccessful, but a stable orange compound was isolated from the reaction mixture which was subsequently characterized and named ferrocene. The iron (III) is first reduced by the Grignard reagent to iron (II) which then reacts with cyclopentadienyl anion to form ferrocene (Equation 3.2).

\[ \text{CpMgX} \xrightarrow{\text{Fe}^{3+}} \text{CpFe} \]

Equation 3.1.

\[ \text{Fe}^{3+} \xrightarrow{\text{CpMgX}} \text{Fe}^{2+} + e^- \xrightarrow{2\text{CpMgX}} \text{Cp}_2\text{Fe} \]

Equation 3.2.

Original structures of ferrocene were based on the ability of each of the cyclopentadienyl rings to become aromatic by gaining an electron (Equation 3.3) and a planar structure was suggested for this
material. However, such a planar structure could not explain the exceptional stability of ferrocene and an alternative was proposed in which the rings are symmetrically placed around the iron (II) nucleus.

![Diagram of prismatic and antiprismatic structures](image)

Equation 3.3.

Key pieces of evidence for a sandwich structure include X-ray studies, as well as a variety of other physical and chemical evidence. For example there is a single sharp infra red absorption at 3.25μ which indicates the presence of only one type of C-H bond highlighting a symmetrical structure. The structure was finally confirmed by X-ray analysis in 1952 \(^{125}\). In the solid state both monoclinic (staggered) antiprismatic structures and orthorhombic (eclipsed) prismatic structures of ferrocene have been found\(^{126}\). The orthorhombic form is thermodynamically
stable below 242 K but at higher temperatures the monoclinic form is preferred. 126

Ferrocene  Fe-C of ring 2.05Å
         C-C of ring 1.40Å
         Cp-Cp  3.32Å

An electron diffraction study of ferrocene 127, 128 in the gas phase indicates an eclipsed prismatic geometry with a barrier to rotation of only 3.8±1.3 kJ mol⁻¹. Hence the rings are almost free to rotate and the conformation adopted in the crystal is susceptible to packing forces. The bonding structure of ferrocene may be understood as involving overlap of one or more d-orbitals of the metal atom and the π-electron clouds of the cyclopentadienyl rings. This gives an ideal number of electrons for the ferrocene molecule as each cyclopentadienyl ligand is a six-electron donor which together with the six electrons of Fe²⁺ leads to a stable 18-electron configuration. 129

The main feature of the chemistry of the cyclopentadienyl ring in ferrocene is its ability to undergo aromatic substitution. Typical reactions 130 include Friedel-Crafts acylation, alkylation, arylation and sulphonation. However, in ferrocene the iron nucleus is in the iron (II) state and is
therefore oxidisable to iron (III) to form the ferricenium ion. Indeed attempted nitration or halogenation, only result in oxidation of the iron nucleus\textsuperscript{130}. This generates a positive ion, the ferrocenium ion, and prevents any further electrophilic attack. The ferricenium ion (Scheme 3.1) has a characteristic blue-green colour and is water soluble.

![Ferricenium Ion](image)

Scheme 3.1 Redox Reactions of Ferrocene/Ferricenium.

3.1.1 Applications of Ferrocene Compounds.

Ferrocene derivatives have been found to have a wide range of applications. Some examples are given below:

(i) Catalysis.

Ferrocene has been used to catalyse the decomposition of aryldiazonium salts, \( X.C_6H_4N_2^+BF_4^- \), where \( X = H, \ p-MeO \) to form the radicals \( X.C_6H_4^- \) which have been used in organic reactions\textsuperscript{131}.

Ethanol and acetaldehyde were prepared from methanol, carbon monoxide and hydrogen under pressure at 50\(^\circ\)-350\(^\circ\)C in the presence of a catalyst system
containing cobalt carbonyl and a suitable promoter, 
1,1'-bis(diphenylphosphino) ferrocene (40)\textsuperscript{131}.

\begin{center}
\includegraphics[width=0.2\textwidth]{ferrocene.png}
\end{center}

(ii) \textit{Photosensitisation.}

Improved electrostatic and imaging properties of an electrophotographic photoreceptor have been found using ferrocene and dimethylferrocene mixed with a polycarbonate in a protective layer over a selénium light sensitive layer\textsuperscript{133}. The importance of charge transfer interaction between the ferrocene and the polycarbonate has been emphasised\textsuperscript{134}. The protective layer is not uniform but carries a higher proportion of ferrocene at the face adjacent to the light sensitive layer\textsuperscript{135}.

A secondary battery has been developed containing ferrocene. The battery consisted of a polyethylene outer casing, stainless steel current collector and a semipermeable membrane separating the anode and cathode compartments. The anode compartments contained polypyrrole and ferrocene in an electrolyte of lithium perchlorate, methyl cyanide and propylene carbonate\textsuperscript{136}. The electrical and physical properties of a silver-iodine battery containing ferrocenium
polyiodide have also been investigated\textsuperscript{137}.

(iii) \textit{Ferrocene Stabilisers and Improvers.}

Highly porous, low density spheres based on inorganic materials have been formed for use in the preparation of hygroscopic, flammable or radioactive articles. The spheres were formed from a mixture of powdered copper, polystyrene binding agent and napthalene with ferrocene and were then sintered at 600-700\textdegree{}C to give the product with density 0.4-0.7 g/cm\textsuperscript{3}\textsuperscript{138}.

The addition of ferrocene to the components used in the manufacture of carbon fibre increases the tensile strength of the carbon fibre\textsuperscript{134}. A small quantity of ferrocene has also been used as one of the additives in an anaerobic two component adhesive\textsuperscript{139}.

(iv) \textit{Combustion Control.}

The incorporation of ferrocene compounds as burning rate modifiers into ammonium perchlorate has been regarded as a potentially hazardous operation. Isothermal and dynamic thermogravimetry have been used to determine the stability and half-life of a ferrocene additive under processing conditions. Exothermic decomposition peaks are observed at lower temperatures in the mixture than for the pure compounds\textsuperscript{140}.

The flammability of polystyrene and polypropylene
has been studied in the presence of metal chelates, chlorinated hydrocarbons and ferrocene; flammability was reduced, char was increased and the formation of smoke was suppressed\(^{141}\).

(v) **Biological Applications**

The oxidation of ferrocytochrome C by six ferrocenium ion derivatives and the reduction of ferricytochrome C by decamethylferrocene has been investigated. The rates of these reactions show first order dependence on both protein and in ferrocenium ion or ferrocene concentrations\(^{142}\).

The growth of Ehrlich ascites tumours in rats is inhibited by ferrocenium salts \([\text{CpFe}]^+ X^-\), where \(X^- = \text{FeCl}_4^-; 2,4,6-(\text{NO}_2)_3\text{C}_6\text{H}_2\text{O}^-; \text{CCl}_3\text{CO}_2^-\). However, ferrocene and tetrachloroferrate salts, \([\text{R}_4\text{N}]^+ [\text{FeCl}_4]^-\), show little activity. Carbamate derivatives of ferrocene have been used as prophylactic agents in the soman poisoning of mice. Administration of the ferrocene carbamate 30 min before dosing with soman gives a six-fold decrease in acute toxicity. The ferrocene carbamates inhibit the brain acetylcholinesterase\(^{144}\).

### 3.1.2 Synthesis of Ferrocene and its Derivatives.

Numerous synthetic procedures for the preparation of ferrocene itself have appeared since the compound was first characterised\(^{124, 145, 146}\). Most of these involve the treatment of cyclopentadiene with a base
to give the resonance stabilized cyclopentadienyl anion, which then reacts with an anhydrous iron salt to give ferrocene (Equation 3.4).

\[
\text{Equation 3.4.}
\]

The bases employed can range in strength from diethylamine to metallic sodium\(^{147}\). Use of the base facilitates the removal of the acidic hydrogen of cyclopentadiene and is sufficient to allow the formation of ferrocene from iron at lower temperatures (Equation 3.5).

\[
\text{Fe} + 2\text{R}_3\text{NH}^+\text{Cl}^- \rightarrow \text{FeCl}_2 + 2\text{R}_3\text{N} + \text{H}_2
\]

\[
\text{FeCl}_2 + 2\text{C}_5\text{H}_6 + \text{R}_3\text{N} \rightarrow \text{Fe(C}_5\text{H}_5)_2 + 2\text{R}_3\text{NH}^+ + \text{Cl}^-
\]

\[
\text{Equation 3.5.}
\]

The preparation of substituted ferrocenes can in general involve either "direct" or "indirect" methods. In the latter, the ferrocene molecule serves as the starting point, substituents are introduced, and the products are then converted to
the desired material. The "direct" route to substituted ferrocenes is from the appropriately substituted cyclopentadiene, the anion of which is treated with a ferrous or ferric salt. This type of reaction needs a stronger base (e.g. metallic sodium) to give a good yield. Simple alkyl derivatives have been made this way but there are problems with selective substitution of the cyclopentadiene rings. These do not arise in the "indirect" method.

3.1.3 Reactions of Ferrocene and 1,1'-Disubstituted Derivatives.

There are only two efficient methods available for the preparation of symmetrical 1,1'-disubstituted ferrocenes:127,148,149:

i) Friedel-Crafts acylation and ii) Lithiation. Both of these approaches have been investigated in the course of this project.

i) **Friedel-Craft acylation and subsequent reactions.**

This is discussed in detail in Chapter 5.

ii) **Lithiation and subsequent reactions.**

Treatment of ferrocene with excess n-butyl-lithium complexed with tetramethylethylene diamine (TMEDA) in a 1:1 ratio gives 1,1'-dilithioferrocene (41). This is precipitated as a fine orange suspension and can be used without any further purification due to its high reactivity (Equation 3.6a). The easy formation of this intermediate
could, in principle, be exploited to great advantage in preparative routes to ferrocenyl macrocycles, but, the only reaction which has so far been attempted\textsuperscript{107} (Equation 3.6b) was unsuccessful, ferrocene being recovered after hydrolysis together with unreacted bis chloroether. A number of other leaving groups have been used in an attempt to overcome the lack of reactivity e.g. bromide and tosylate but, as yet, these reactions have not been successful.

\[
\text{Fe}^+ \underset{n-C_4H_9Li, \text{TMEDA.}}{\xrightarrow{\text{dilution \text{in benzene}}}} \text{Fc}^\text{Li}
\]

Equation 3.6a.

\[
\text{Fc}^{\text{Li}} + X^- + O^- \xrightarrow{\text{high \text{dilution \text{in benzene}}}} \text{Fc}^{\text{Li}}
\]

Equation 3.6b (\(X = \text{Cl, Br or Ts}\)).

However, the reaction of 1,1'-dilithioferrocene with carbon dioxide and \(N,N\)-dimethylformamide have provided the key steps in the synthesis of ferrocene cryptands\textsuperscript{107}. 1,1'-dilithioferrocene reacts with \(N,N\)-dimethylformamide to give, after hydrolysis, 1,1'
-ferroacenedicarboxaldehyde (42). This bis-aldehyde (42) was expected to be suitable starting material for condensation with diamines to give macrocycles since the imine (43) is readily prepared and other examples of bis-aldehyde $\alpha,\omega$-diamine condensations are known.

Bell and Hall have demonstrated that this is a viable route (Scheme 3.2) to macrocyclic compounds but yields are low (~10%). These preparations were also limited by the difficulty in preparing large quantities of the bis-aldehyde because of its tendency to polymerise in organic solutions giving a red oil. In the solid state it is sensitive to oxygen and light. Further investigation of the Bell and Hall method for preparing the bis-aldehyde (42), by Grossel and Kynchala, has shown that, if the addition of 1,1'-dilithioferrocene is carried out at lower temperature (-55° to -60°C), a significantly higher yield of 1,1'-ferroacenedicarboxaldehyde (42) is obtained. Accordingly the above route could offer a viable method of preparing ferrocene macrocycles.
Scheme 3.2 Bell and Halls Original Route to Macrocyclic Compounds.

10% yield overall
Carbonation is achieved by the addition (via a syringe) of an ether/tetrahydrofuran suspension of 1,1'-dilithioferrocene into a carbon dioxide/ether slush to give dilithium ferrocene 1,1'-dicarboxylate (Scheme 3.3). This is easily converted into 1,1'-ferrocenedicarboxylic acid by acidification with dilute acid. The acid could be used to prepare ferrocene macrocycles but is, however, insoluble in most organic media and therefore of limited use. It can be readily dehydrated to the anhydride (44), but more usefully dilithium ferrocene 1,1'-dicarboxylate is readily converted into 1,1'-ferrocenedicarboxyl chloride (45), when treated with oxalyl chloride\textsuperscript{151}. This is a stable, easily purified crystalline solid, which is soluble in benzene and more polar solvents.

Bell and Hall\textsuperscript{106}
Scheme 3.3 Preparative Routes to Ferrocene Derivatives via the Lithiation of Ferrocene.

3.1.4 Condensation of Metallocene bis Acid Chlorides with Amines.

The reaction of acid chlorides with amines has been extensively studied and the mechanism is well understood. In such reactions the amine serves as a nucleophilic reagent, attacking the carbonyl group and displacing chloride ion (Equation 3.7). A proton is then lost from nitrogen by transfer to a second molecule of amine or another base present in the
reaction mixture. Both primary and secondary amines can be used to prepare other substituted amides. However tertiary amines fail to yield amides, because they cannot lose a proton after initial addition to the carbonyl group.

\[
\begin{align*}
R-C + RNH_2 & \rightarrow R-CCl^- \rightarrow R-C + HCl \\
\end{align*}
\]

Equation 3.7.

3.1.5 Preparation of Ferrocene Amides.

1,1'-Ferrocenedicarboxyl chloride was found to react rapidly with amines to give amides and relatively slowly with alcohols and water. In this work a series of simple amines were condensed with 1,1'-ferrocenedicarboxyl chloride, under anhydrous conditions and in the presence of a tertiary amine (triethylamine). In all cases the reaction proceeded quickly (5 minutes) and the yields were high (80-100%). The tertiary amine acted as a base removing a proton from the intermediate and forming an insoluble hydrochloride salt in the organic solvent. Once the hydrochloride complex was filtered off, the subsequent purification of the amide was easily achieved.
3.1.6 Preparation of Ferrocene Macrocyclic Amides.

In just the same manner adopted for the condensation of simple amines with 1,1'-ferrocenedicarboxyl chloride, so it was possible to condense diaza crown ethers to form macrocyclic amides. As the resultant amide is stable and the reaction is rapid, it is clear that a high dilution technique is required to prevent polymer formation. The 1,1'-ferrocenedicarboxyl chloride is therefore the ideal precursor for reactions with α, ω-diamines and diaza crown ethers and it is with this type of reaction that the synthesis of macrocyclic metallocenes has been achieved (Scheme 3.4).

Scheme 3.4 Preparative Route of Ferrocene Macrocycles.

3.1.7 Preparation of Binding Ligands.

Kynchala and Grossel successfully prepared a whole series of ferrocene crown ethers and cryptands
by reaction with the appropriate primary and secondary diamines. Since few of these ligands are commercially available it was necessary to prepare them prior to use.

The aliphatic diamines (Scheme 3.5); diaminodiethylene ether, diaminetriethylene ether and diaminotetraethylene ether are readily prepared from the corresponding alcohols following Lehn's method\textsuperscript{152}. Great care must be taken with the storage of the diaminooethylene ethers as they are very hygroscopic and must therefore be distilled from potassium hydroxide prior to use. The solvent used in any subsequent reaction must be "super-dry" as any traces of water will cause hydrate formation and thus impede the condensation reaction with the metallocene bis(acid chloride) to give macrocyclic product.

There are two general routes by which diaza crown ethers may be prepared; (i) the intramolecular nucleophilic displacement of tosyl or halide groups by an anion; and (ii) the condensation of acid derivatives with diamines (Scheme 3.5). The cyclisation state for both routes gives approximately 20-30\% yield. However, due to the relatively large quantities of ferrocene [2.2] cryptand required for much of the work reported here. This cryptand was prepared from diaza-[18]-crown-6 which was obtained commercially.
Scheme 3.5 Preparation of Diaza Crown Ethers.
3.2 SYNTHESIS OF FERROCENE CRYPTANDS

Bell and Hall\textsuperscript{106} have shown that the condensation of diaza-[18]-crown-6 with 1,1'-ferrocene dicarboxyl chloride under high dilution conditions results with the formation of two main products: a monomer Fc[2.2]M (40%), and a dimer Fc[2.2]D (26%) (Scheme 3.6). More recently it has been found that the relative proportions obtained for these two products are somewhat temperature dependent\textsuperscript{153}, the formation of the monomer being favoured at low temperatures and the dimer at higher temperatures. The monomer was also reported by Vogtle\textsuperscript{105} but no detailed spectroscopic data was described and the dimer was apparently not observed.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{high_dilution_apparatus.png}
\caption{High Dilution Apparatus Used for the Preparation of Ferrocene Cryptands.}
\end{figure}
Scheme 3.6 Preparation of the Ferrocene Cryptand Fc[2.2]M and Fc[2.2]D.
3.2.1 Spectroscopic Analysis of the Ferrocene Amides.

Much spectroscopic work has been carried out on both the ferrocene amides\textsuperscript{\ref{107}} and the ferrocene macrocyclic amides (Fc\textsubscript{[2.2]}M and Fc\textsubscript{[2.2]}D)\textsuperscript{\ref{106}}, and this greatly simplified characterisation of the amides prepared in the course of this project.

3.2.2 Mass Spectrometry and Element Analysis.

All the amides prepared showed a stable molecular ion by mass spectrometry (electron ionisation) and gave good combustion analyses (Chapter 7).

3.2.3 Infra Red Analysis.

Workers\textsuperscript{\ref{107}} who have characterised the ferrocene amides and the ferrocene macrocyclic amides using infra red spectroscopy have not reported detailed spectroscopic data. Table 3.1 below gives a direct comparison of the ferrocene amide carbonyl shifts with those found in other analogous ferrocene derivatives. It is clear that the lone pair electrons on the nitrogen in the amide function are capable of producing a lengthening (weakening) of the C=O bond. This leads to a lower frequency than the corresponding ketone, acid and ester derivatives.

More detailed infra red data may be found in Chapter 7.
Table 3.1 Comparison of Carbonyl Stretching Frequencies in the Infra Red.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Assignment</th>
<th>Stretching Frequency cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CpCONHMe)₂</td>
<td>C=0</td>
<td>1633</td>
</tr>
<tr>
<td>Fe(CpCON(Me)₂)₂</td>
<td>C=0</td>
<td>1625</td>
</tr>
<tr>
<td>Fe(Cp(CON(CH₂)₄O)₂)</td>
<td>C=0</td>
<td>1625</td>
</tr>
<tr>
<td>Fe[2:2]M</td>
<td>C=0</td>
<td>1620</td>
</tr>
<tr>
<td>Fe(CpCOCH₃)₂</td>
<td>C=0</td>
<td>1662</td>
</tr>
<tr>
<td>Fe(CpCOOH)₂</td>
<td>C=0</td>
<td>1765</td>
</tr>
<tr>
<td>Fe(CpCOOMe)₂</td>
<td>C=0</td>
<td>1720</td>
</tr>
</tbody>
</table>

3.2.4 Mössbauer Spectroscopy (Structural Probe of Organometallic Compounds).

Mössbauer spectroscopy has been a particularly valuable technique for the study of the structural properties of some types of organometallic compounds. Valuable information may be gained about the oxidation state (valence) of an iron atom in various structures, the symmetry of its electronic environment and the nature of the chemical bonds involved.

The ferrocene type "sandwich" complex has always excited interest because of the unusual nature of the bonding involved. The Mössbauer spectrum of the parent ferrocene (Figure 3.2a), shows a large temperature-independent quadrupole splitting, in
close agreement with work reported in the literature. Large amounts of data are available for substituted ferrocenes. However, these results show that the iron environment is very insensitive to substitution in the cyclopentadienyl rings since this primarily affects the \( \sigma \)-bonding of the ring. The ranges which are typical for ferrocene derivatives (Q.S. \( \Omega \) 2.3 mm/s @ I.S. \( \Omega \) 0.51 mm/s) indicate that they belong to the most strongly covalent compounds of iron. The Mössbauer spectra of the ferrocene amides and Fc[2.2]M (Figure 3.2b) showed no variation in the patterns reported for the substituted ferrocene derivatives. The Mössbauer parameters are listed below (Table 3.2).

![Figure 3.2a Mössbauer Spectrum of Ferrocene](image-url)
Figure 3.2b Mössbauer Spectrum of Fc[2.2]M.

Table 3.2 Mössbauer Parameters.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Isomer</th>
<th>Quadrupole Shift mm/s</th>
<th>Quadrupole Shift mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocene (Fc) 298K</td>
<td>0.53</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>Ferrocene (Fc)* 298K</td>
<td>0.68</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>Fc(CON(Me)₂)₂ 298K</td>
<td>0.52</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>Fc(CON(Bt)₂)₂ 298K</td>
<td>0.515</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>Fc(CON(CH₂)₄O)₂ 298K</td>
<td>0.53</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>Fc(COCH₃)₂ 298K</td>
<td>0.6</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>Fc[2.2]M 298K</td>
<td>0.52</td>
<td>2.36</td>
<td></td>
</tr>
</tbody>
</table>

* Literature values.
Ferrocenium Salts

Oxidation of ferrocene results in the formation of the ferrocenium ion (Scheme 3.1). While the isomer shift of ferrocenium salt is only a little more negative than that of ferrocene itself at 2.42 mm/s, the quadrupole splitting changes remarkably to 0-0.2 mm/s. Ferrocenium iodide (Figure 3.3a) was prepared as a reference for comparison with the ferrocenium[2.2] monomer iodide (Figure 3.3b). The Mössbauer spectrum of Fc\(^{3+}\)[2.2]M I\(^{-3}\) is identical with that of the parent ferrocenium salt. Parameters are listed in Table 3.3 below.

Table 3.3 Ferrocenium Mössbauer Parameters

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Isomer Shift mm/s</th>
<th>Quadrupole Shift mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocenium Iodide</td>
<td>298K</td>
<td>0.56</td>
</tr>
<tr>
<td>Ferrocenium Bromide*</td>
<td>298K</td>
<td>0.7</td>
</tr>
<tr>
<td>Ferrocenium[2.2]Iodide</td>
<td>298K</td>
<td>0.565</td>
</tr>
</tbody>
</table>

* Literature values

Bell and Hall\(^{157}\) reported the oxidation potential for the conversion Fc\(^{II}\)[2.2]M to Fc\(^{III}\)[2.2]M is +0.2 volts. It will become clear why it was important to have a record of the Mössbauer spectra in future Sections.
Figure 3.3a Mössbauer Spectrum of Ferrocenium Iodide.

Figure 3.3b Mössbauer Spectrum of $\text{Fc}^{3+}[2.2]\text{M I}^{-3}$. 
3.2.5 \(^1\)H n.m.r. Studies on Ferrocene Amides.

Detailed \(^1\)H n.m.r. studies have been carried out on both ferrocene amides (Chapter 7) and the ferrocene cryptands. The Fc[2.2]M cryptand has an extremely complex \(^1\)H n.m.r. spectra, for which Hall and co-workers\(^{150}\) carried out a complete assignment using \(^{13}\)C and \(^1\)H heteronuclear and homonuclear decoupling techniques (Appendix I).

3.2.6 \(^{13}\)C n.m.r. and Dynamic n.m.r. Studies on Ferrocene Amides.

As well as extensive \(^1\)H n.m.r. studies, \(^{13}\)C n.m.r. experiments have been carried out on both the ferrocene amides (Chapter 7) and the ferrocene cryptands (Appendix I). It was found that the spectra of these systems are temperature dependent and therefore dynamic phenomena were also investigated (generally by \(^{13}\)C n.m.r.).

Restricted rotation about the carbon-nitrogen bond in amides is the classical example of a rate process that can be studied by dynamic n.m.r.\(^{159}\) Resonance theory describes the electronic structure of amides by a hydrid (Equation 3.8) which suggests a certain amount of double bond character for the carbon nitrogen bond and therefore an increase of its rotational barrier above that for simple C-N single bonds, e.g. those found in amines (\(\Delta G^\#\) for MegN 7.5 kcal mol\(^{-1}\)). Since R' and R'' reside in different
magnetic environments (R" being more shielding than 
R') in the "frozen" structure and become 
time-averaged on rapid rotation, it is possible to 
calculate the free energy of activation (ΔG⁺)\textsuperscript{159}. 
This may be done for the rotation from the 
coalescence temperature, Tc(K), and the frequency of 
separation, Δν H\textsubscript{z}, of the two exchanging signals in 
the "frozen" condition (Appendix I).

\[
\begin{align*}
\text{R}^\circ & \quad \text{C} \quad \text{O} \\
\text{R} & \quad \text{N} \quad \text{C} \quad \text{O} \\
\text{R} & \quad \text{R} \\
\end{align*}
\]

Equation 3.8

In the case of the metallocene amide derivatives 
there is another rotation barrier which can be 
investigated by n.m.r. spectroscopy. The rotation 
barrier between the cyclopentadienyl ring and the 
carbonyl group. When this process is slow on the 
n.m.r. time scale, the ortho protons and carbons on 
the metallocene ring become non-equivalent. It has 
sometimes proved possible to measure both rotational 
activation barriers. It would be expected that these 
two energy barriers should show some mutual 
dependence for increased interaction between the 
nitrogen lone pairs and the carbonyl group might be
expected to reduce the degree of conjugation within the cyclopentadienyl ring.

Kynchala\textsuperscript{107} carried out a detailed study on a series of simple ferrocene and ruthenocene amides using variable temperature (both $^1\text{H}$ n.m.r. and $^{13}\text{C}$ n.m.r.) spectroscopy. Table 3.4a below gives a list of some typical $\Delta G^\ddagger$ values seen in the amides. The table also includes data on 1,1'-bis($N$-methylamido)-ferrocene (46) which was prepared in the course of this work. Table 3.4b shows the $^1\text{H}$ n.m.r. spectral assignments of 1,1'-bis($N$-methylamido)ferrocene (46) during a variable temperature n.m.r. experiment.

Table 3.4 $\Delta G^\ddagger$ Values for a Series of Amides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^\ddagger$ Kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCON(CH$_3$)$_2$</td>
<td>20.6 (lit.162)</td>
</tr>
<tr>
<td>CH$_3$CON(CH$_3$)$_2$</td>
<td>18-20 (lit.162)</td>
</tr>
<tr>
<td>Disubstituted Ferrocene Amides</td>
<td></td>
</tr>
<tr>
<td>Fe(CpCON(CH$_2$CH$_3$)$_2$</td>
<td>a 14.5</td>
</tr>
<tr>
<td></td>
<td>b 14.2</td>
</tr>
<tr>
<td>Fe(CpCON(CH$_3$)$_2$</td>
<td>14.31</td>
</tr>
<tr>
<td>Fe(CpCONHCH$_3$)$_2$</td>
<td>14.25 (this work)</td>
</tr>
</tbody>
</table>
Table 3.4b Variable Temperature $^1$H N.M.R.

Assignments of 1,1'-bis(N-Methylamido)ferrocene (46) (90 MHz, CDCl$_3$).

\[
\begin{array}{c|c|c|c|c|c}
\text{Assignment} & -10^\circ & -5^\circ & 0^\circ & 5^\circ & 22^\circ \\
\hline
H_{2,5} & 4.84 & 4.84 & 4.84 & 4.84 & 4.84 \\
H_{3,4} & 4.42 & 4.42 & 4.42 & 4.42 & 4.42 \\
\text{CH}_3 & 3.90 & 3.90 & 3.90 & 3.90 & 3.90 \\
& 3.72 & 3.72 & 3.72 & 3.72 & 3.72 \\
\end{array}
\]

\(T_c^* = 278^\circ\quad \Delta \nu = 16.2\text{Hz}\)

(*Appendix I)

3.2.7 $^{13}$C N.M.R. and Dynamic N.M.R. Studies in Ferrocene Macroyclic Amides.

The simple ferrocene amides provided a good model with which to compare the more complex metallocene cryptands. The $^{13}$C n.m.r. spectra of Fc[2.2]M$_{160}$ (Section 3.3.7) shows 12 different signals arising from 5 ferrocenyl carbons (C$^{1'}$-C$^{5'}$), 1 carbonyl carbon, 4 different carbons attached to oxygen and 2 carbons attached to nitrogen. Each signal represents 2 equivalent carbon atoms and the implications of this spectrum are two-fold. Firstly, there must be a
degree of rigidity within the molecule since freedom of rotation about the 2 carbonyl groups, as observed in the non-bridged acyl ferrocenes, would mean fewer than 12 non-equivalent carbons. Secondly, there must be an element of symmetry within the molecule since total asymmetry would lead to 24 non-equivalent carbons. One can envisage two possible configurations; Fc[2.2]M-trans and Fc[2.2]M-cis both of which are consistent with the n.m.r. data and in which the 12 pairs of equivalent carbons are designated (a) - (l).

It has been proposed that both Fc[2.2]M trans and Fc[2.2]M-cis have the carbonyl groups co-planar with the ferrocene rings since this conformation allows maximum conjugation. Furthermore, in Fc[2.2]M-trans the 2 bridges of the diaza crown ether unit each contain the same 6 non-equivalent carbons, and as shown in (47) below, the C23 symmetry and hence the carbon and proton equivalencies are retained whatever the angle of twist (θ) between the two rings. In
Fc[2.2]M-cis however, the $^{13}$C and $^1$H data are only satisfied when the ferrocene rings and amide groups are, on average, eclipsed, since then each ferrocene ring contains the same 5, non-equivalent carbons and each bridge of the crown contains 3 different pairs of equivalent carbons. The eclipsed conformation is however, energetically unfavourable due to the parallel dipoles of the carbonyl groups. This interaction can be alleviated by twisting the ferrocene rings, as in (48), but the plane of symmetry through the molecule is then lost: (a) is no longer equivalent to (a'), and the carbon and proton equivalences of the eclipsed conformer are removed. This would give rise to n.m.r. spectra of greater complexity than those observed for Fc[2.2]M.
In exactly the same way as for the ferrocene amides, Hall et al. have shown that dynamic n.m.r. phenomena exist in metallocene cryptands. However, in these larger molecules the molecular motion associated with the amide group leads to much more complex spectral changes as all groups seem to be involved. The activation energies associated with such rotation in several ferrocene cryptands are shown in Table 3.5 below.

Table 3.5 Activation Energies of the Ferrocene Cryptands.

<table>
<thead>
<tr>
<th>Cryptand</th>
<th>$\Delta G^\ddagger$ kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m = 2, n = 1</td>
<td>15.1</td>
</tr>
<tr>
<td>m = 3, n = 2</td>
<td>15.1</td>
</tr>
<tr>
<td>m = 3, n = 3</td>
<td>15.0</td>
</tr>
</tbody>
</table>

It is evident that the free energy of activation for the fluxional process is the same for each of the monomers (Table 3.5) and has a value very similar to that associated with rotation about the amide bond of 1,1'-ferrocene bis amide (Table 3.4). The n.m.r.
spectra at low temperatures of the cryptands indicate only one configuration for each compound and by analogy with earlier work it has been suggested this configuration is that in which the carbonyl groups are trans to each other. No coalescence phenomena are observed in the $^1\text{H}$ and $^{13}\text{C}$ n.m.r. spectra of the [1.1] monomer ($m=n=1$) and the [2.2] monomer ($m=n=2$, Fc[2.2]M) over the temperature range 254–354 K. This may suggest that the molecules are rigid on the n.m.r. time scale over this temperature range and that the fluxional behaviour is dependent not only upon the size of the diaza crown macrocycle but also upon there being an unsymmetrical structure.

However, inspection of models reveals that in the trans-carbonyl configuration the [1.1] and [2.2] monomers have no difficulty in achieving co-planarity between the π-orbitals of the carbonyl group and the lone pair on the nitrogen. Such co-planarity is not so easily accomplished in the unsymmetrical [2.1] and [3.2] cryptands and there appears to be a considerable dihedral angle between at least one of the π-orbitals of the carbonyl and the lone pair of the nitrogen. The same argument is not applicable to the [3.3] monomer since the size of the macrocyclic ring makes the system inherently more flexible.

Further insight into the energy minimum conformations of ferrocene amides, in solid state, is
provided by solid state $^{13}$C n.m.r. spectroscopy and X-ray structural studies.

3.3 SOLID STATE STUDIES OF FERROCENE AMIDES.

A literature search$^{162}$ suggested that even though considerable work has been carried out on ferrocene and its derivatives, no X-ray structural studies have, until now, been reported on ferrocene amides.

3.3.1 X-Ray Crystallography of a Simple Ferrocene Amide.

Our investigations on the solid state geometries of ferrocene amides began with the study of a simple compound (46). This amide was recrystallised from chloroform/hexane, as orange cubes. A crystal of approximate dimensions $0.09 \times 0.18 \times 0.44$mm was selected and used for data collection. Full details of this and the subsequent refinements of the structure are described in Appendix II.

Several views of the solid-state structures of the amide are shown in Figure 3.5. The atomic number scheme employed is detailed in Figure 3.6 and the appropriate bond lengths are shown in Table 3.6 below.
Figure 3.5  Crystallographic Views of 1,1′-Bis
(N-Methylamido)ferrocene (46).
Figure 3.6 Numbering Scheme Adopted Throughout this Study.

Table 3.6 Bond Lengths Found in 1,1'-Bis(N-Methylamido)ferrocene (46) (Appendix II).

<table>
<thead>
<tr>
<th>Ring</th>
<th>C11-C15</th>
<th>C21-C24</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C11</td>
<td>1.485(6)</td>
<td>C2-C21</td>
</tr>
<tr>
<td>C1-N1</td>
<td>1.327(6)</td>
<td>C2-N2</td>
</tr>
<tr>
<td>C1-O1</td>
<td>1.201(6)</td>
<td>C2-O2</td>
</tr>
<tr>
<td>C3-N1</td>
<td>1.444(6)</td>
<td>C4-N2</td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.417(6)</td>
<td>C21-C22</td>
</tr>
<tr>
<td>C11-C15</td>
<td>1.422(7)</td>
<td>C21-C25</td>
</tr>
<tr>
<td>C12-C13</td>
<td>1.420(7)</td>
<td>C22-C23</td>
</tr>
<tr>
<td>C13-C14</td>
<td>1.416(8)</td>
<td>C23-C24</td>
</tr>
<tr>
<td>C14-C15</td>
<td>1.422(7)</td>
<td>C24-C25</td>
</tr>
</tbody>
</table>

Average Fe-C bond = 2.0448Å (Lit.\textsuperscript{163} = 2.044Å)
Table 3.7 shows a direct comparison of the bond lengths in the 1,1'-bis(N-methylamido)ferrocene (46) and those found in other ferrocene derivatives. Clearly the interatomic distances obtained for the 1,1'-bis(N-methylamido)ferrocene (46) give good agreement with the values quoted from crystallographic studies on analogous ferrocene structures. The average C-C bond is close to the value cited by Wheatley\textsuperscript{163}, but shorter than values found by Palenik\textsuperscript{164} on the 1,1'-diacetylferrrocene (51) and the 1,1'-ferrocenedicarboxylic acid (52). Therefore, the 1,1'-bis(N-methylamido)ferrocene (46) has molecular dimensions consistent with other ferrocene molecules and no unusual intramolecular interactions are present.

Table 3.7 Crystallographic Data Found in Ferrocene and its Derivatives.

<table>
<thead>
<tr>
<th>Ferrocene Derivatives</th>
<th>C-C Bonds in Rings</th>
<th>Fe-C Bonds</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(Cp)\textsubscript{2}</td>
<td>1.419Å</td>
<td>2.045Å</td>
<td>165</td>
</tr>
<tr>
<td>Fe(Cp)\textsubscript{2}*</td>
<td>1.431Å</td>
<td>2.058Å</td>
<td>166</td>
</tr>
<tr>
<td>Fe(CpCOCH\textsubscript{3})\textsubscript{2}</td>
<td>1.426Å</td>
<td>2.046Å</td>
<td>164</td>
</tr>
<tr>
<td>Fe(CpCOOH)\textsubscript{2}</td>
<td>1.424Å</td>
<td>2.043Å</td>
<td>167</td>
</tr>
<tr>
<td>Bis(\pi-azulene)iron</td>
<td>1.430Å</td>
<td>2.044Å</td>
<td>168</td>
</tr>
<tr>
<td>Fe(CpCONHMe)\textsubscript{2}</td>
<td>1.4207Å</td>
<td>2.0448</td>
<td></td>
</tr>
</tbody>
</table>

* Electron Diffraction.
The structural angles of particular interest are defined in Figure 3.7. These angles $\alpha$, $\beta$, and $\gamma$ may be defined in the following manner:

$\alpha$ – measures the extent to which the cyclopentadienyl rings are non-parallel and is found by considering one ring to be flat and comparing the tilt of the second ring relative to this.

$\beta$ – measures the angle of rotation of the carbonyl plane relative to the cyclopentadienyl ring (Cp).

$\gamma$ – is a measure of the relative orientation of the cyclopentadienyl rings (i.e. the extent to which they are eclipsed).

![Figure 3.7a Defining Angle $\alpha^\circ$.](image)

![Figure 3.7b Defining Angle $\beta^\circ$.](image)
Figure 3.7c  Defining Angle $\gamma^o$

Figure 3.7a, b and c  Illustrating Angles of Crystallographic Interest.

Table 3.8 below compares some of the angles found in other ferrocene derivatives with those found in the $1,1'$-bis(N-methylamido)ferrocene (46). A detailed list of angles found in the $1,1'$-bis(N-methylamido)ferrocene (46) may be found in Appendix II.

Table 3.8 Structural Angles Found in Ferrocene Derivatives as Compared with $1,1'$-Bis(Methylamido)-Ferrocene (46).

<table>
<thead>
<tr>
<th>Ferrocene Derivative</th>
<th>$\alpha^o$</th>
<th>$\beta^o$</th>
<th>$\gamma^o$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CpCOOH)</td>
<td>1.28</td>
<td>0.8</td>
<td>4.67</td>
<td>1.6</td>
</tr>
<tr>
<td>Fe(CpCOCH$_3$)</td>
<td>1.15</td>
<td>11.15</td>
<td>8.80</td>
<td>139.2</td>
</tr>
<tr>
<td>Fe(CpCONHMe)</td>
<td>1.4</td>
<td>15.59</td>
<td>5.99</td>
<td>141.5</td>
</tr>
</tbody>
</table>
Even though considerable work has been carried out on a whole range of ferrocene derivatives, a literature search\textsuperscript{162} suggests that only the disubstituted 1,1'-diacetylferrrocene\textsuperscript{164} (51) and the 1,1'-ferrocenedicarboxylic\textsuperscript{167} acid (52) would provide analogous structures with which to compare the 1,1'-bis(methylamido)ferrocene (46). The dependence of the conformation of ferrocene derivatives upon the nature of the substituents on the cyclopentadienyl rings is, as yet, unclear. In 1,1'-ferrocenedicarboxylic acid (52), the cyclopentadienyl rings are almost completely eclipsed and so are the substituents. This conformation may be understood as a consequence of dimerisation of the molecules through hydrogen bonding between carboxylic groups within pairs of molecules (Figure 3.8).

![Figure 3.8 Showing Hydrogen Bonding in 1,1'-Ferrocenedicarboxylic Acid (52).](image)
This prompted Palenik to investigate the crystallography of 1,1'-diacetylferrocene\(^\text{164}\) (51) (Figure 3.9) since hydrogen bonding between molecules is not possible for this compound. The results provide information regarding the preferred conformation of substituted ferrocenes and the relationship between the rotation of the cyclopentadienyl rings and intermolecular forces. It also provided an excellent example with which to compare the 1,1'-bis(N-methylamido)ferrocene (46).

![Figure 3.9](image)

Figure 3.9  A View Down the Ring Centres Showing the Nearly Eclipsed Conformation of the 1,1'-Diacetylferrocene (51).

It is clear from Table 3.8 that the angles in the 1,1'-bis(N-methylamido)ferrocene (46) correspond closely to those in the diketone (51). It is also interesting to note that the angle \(\gamma\) is very similar in both structures showing a virtually eclipsed 1,3'
(position 1 on the upper ring aligned with position 3 on the lower ring) conformation. Churchill and Wormald discuss this angle \( \gamma \) by developing an angle \( \omega \) which can extend from \( 0^\circ-36^\circ \). The angle \( \omega \) expresses how eclipsed the rings sit with respect to each other, i.e. if the rings have an angle \( \omega = 36^\circ \) then they are perfectly staggered to each other and consequently when \( \omega = 0 \) the rings are eclipsed (since in ferrocene itself the eclipsed conformation repeats every \( 72^\circ \)). Churchill and Wormald go on to discuss that in the solid state, certain substituted ferrocenes have a strictly staggered conformation (i.e. \( \omega = 36^\circ \)) and that others are obviously forced by steric requirements to take up a conformation other than the strictly staggered conformation. Use of this angle \( \omega \) ignores the fact that as two substituted ferrocene cyclopentadienyl rings mutually rotate, they go through a number of energetically different staggered and eclipsed conformations. In other words, the energy of two substituents sitting in a 1,1 position will be totally different from that when the substituents are sitting in a 1,2 position. It is therefore not sufficient to use the angle \( \omega \), which can expresses how eclipsed ferrocene itself is in ferrocene derivatives. The angle \( \gamma \) not only gives an indication of the conformation (diacetylferrocene is 1,3-eclipsed) but also by
subtracting from $\frac{2}{5}$ths of regular pentagon expresses the extend of "eclipsedness".

\[ \text{1,2' Conformation} \quad \text{1,3' Conformation} \]

3.3.2 Packing Arrangements and Stereochemistry

Adopted in 1,1'-Diacetylferrocene (51) and 1,1'-Bis(N-Methylamido)ferrocene.

The packing relationships for both 1,1'-bis(N-methylamido)ferrocene (46) (Figure 3.10a) and 1,1'-diacetylferrocene (51) (Figure 3.10b) show great similarities. In order to understand the packing arrangement adopted by the diacetyl derivative, a computer simulation of the atomic co-ordinates has been carried out using Chem-X. In Palenik's structural analysis of 1,1'-diacetylferrocene, the unit cell arrangement of the molecules was not discussed.

It is clear from the packing diagrams that there is only one orientation for the C=O bonds in both the amide and the acetyl structures. The amide function could adopt two possible conformations which are shown below in Figure 3.11. In this study, it would appear that the preferred conformation is the E isomer in which the carbonyl oxygens (in just the
same manner adopted in the diacetylferrrocene) are anti with respect to one another.

Figure 3.10a  Packing Arrangements in 1,1' -Bis(N-Methylamido) Ferrocene.

Figure 3.10b  Packing Arrangements in 1,1' -Diacetylferrrocene.
As already stated, the free rotation of the ferrocene carbonyl bond and the peptide bond may be monitored using variable temperature n.m.r. spectroscopy. As well as having a typical amide rotation barrier, the bond lengths in the amide group of (46) compare closely with those for related compounds already in the literature (Table 3.9).

Table 3.9 Comparison of Bond Lengths of 1,1'-Bis(N-Methylamido)ferrocene (46) with Typical Literature Values\(^{170}\).

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Recorded Values</th>
<th>Typical Compounds</th>
<th>Literature Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_2C'N )</td>
<td>1.444(6)</td>
<td>Methylamine</td>
<td>1.472(5)</td>
</tr>
<tr>
<td>( O=C'N )</td>
<td>1.337(6)</td>
<td>Acetamide</td>
<td>1.322(3)</td>
</tr>
<tr>
<td>(-C'=0)</td>
<td>1.1995(6)</td>
<td>Formamide</td>
<td>1.23(10)</td>
</tr>
</tbody>
</table>

(\( \dagger \) Bonds of Interest)
Plates (3.1 and 3.2) below which were generated using Chem-X\textsuperscript{69} show the full crystallographic structure of 1,1'-bis(N-methylamido)ferrocene (46).
3.3.3 Solid State N.M.R. Studies on the Ferrocene Amides.

Wasylishen\textsuperscript{171} and Yannoni\textsuperscript{172} have recently reviewed the interpretation and methods of acquisition of high resolution solid state n.m.r. spectra. A common feature of solid state spectra is that they give rise to line multiplicities not observed in solution. In a single phase (not a mixture of polymorphic forms) peak multiplicities arise through a number of different effects. The splitting observed in the solid state $^{13}$C spectrum of 2,4-dinitrotoluene\textsuperscript{173} arises from the presence of two independent molecules in the crystallographic unit cell whilst benzo-[15]-crown-5 shows splitting which arises because packing within the crystal renders chemically equivalent pairs of atoms magnetically inequivalent\textsuperscript{174}.

To our knowledge no solid state n.m.r. study has yet been reported on the ferrocene amides. Pines and coworkers\textsuperscript{175} have studied the chemical shielding parameters for a series of metalloccenes. However, this only included information on one substituted ferrocene derivative (decamethylferrocene).

In order to gain experience in correlating solid state n.m.r. data with X-ray structural information, a solid state n.m.r. spectrum was recorded for 1,1'-bis(N-methylamido)ferrocene (46) using
cross-polarisation magic-angle spinning (C.P.MAS) techniques\textsuperscript{176} (Figure 3.12a). This may be compared with the corresponding solution spectrum shown in Figure 3.12b. The n.m.r. data is assigned in Table 3.10.

The solid state spectrum of 1,1'-bis(N-methyl-amido)ferrocene (46) shows 1 carbonyl signal, 1 methyl signal and 4 independent signals from the cyclopentadienyl rings. Non-quaternary suppression experiments show that the ipso carbon $C_1/C_1'$ has a chemical shift of $\delta 78.65$ ppm. Removing this signal leaves three signals which represent the carbons $C_2/C_2'$, $C_5/C_5'$, $C_3/C_3'$ and $C_4/C_4'$. The relative intensities of the peaks in the spectrum suggest that two signals due to $C_2/C_2'$ and $C_5/C_5'$ merge into one broad peak. The other two less intense resonances are a result of $C_3/C_3'$ and $C_4/C_4'$ signals.

The features of this spectrum agree closely with those found by crystallographic analysis. Both spectrum and structure, show only one carbonyl and one methyl environment. If the spectrum is then compared with that for 1,1'-bis(N,N-dimethylamido)-ferrocene (49) Figure 3.12a, the presence of the second methyl group is highlighted. An obvious interpretation would be that this arises from the two independent environments of the methyl groups giving restricted rotation about the amide bond (Table 3.11).
Table 13C N.M.R. Data Versus Solution 13C N.M.R. Data for 1,1'-Bis(N-Methylamido)ferrocene (46).

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>Solid State ppm</th>
<th>Solution ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=0</td>
<td>170.05</td>
<td>170.3</td>
</tr>
<tr>
<td>C1/C1'</td>
<td>78.65</td>
<td>79.12</td>
</tr>
<tr>
<td>C2/C2'</td>
<td>76.21</td>
<td>71.23</td>
</tr>
<tr>
<td>C5/C5'</td>
<td>73.79</td>
<td>70.65</td>
</tr>
<tr>
<td>C3/C3'</td>
<td>71.46</td>
<td></td>
</tr>
<tr>
<td>C4/C4'</td>
<td>39.29</td>
<td>51.67</td>
</tr>
<tr>
<td>C6/C6'</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Number scheme refer to structure (46)

Figure 3.12b Solution State 13C N.M.R. Spectrum of 1,1'-Bis(N-Methylamido)ferrocene (46) (MHz; CDCl3).
Figure 3.12a Solid State $^{13}$C N.M.R. Spectrum of 1,1'-Bis(N-Methylamido)ferrocene (46).
Table 3.11  Solid State and Solution $^{13}$C N.M.R. Data for 1,1'-Bis(N,N-Dimethylamido)ferrocene (49).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Solid State ppm</th>
<th>Solution State ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=0</td>
<td>170.052</td>
<td>170.624</td>
</tr>
<tr>
<td>C1,1'</td>
<td>80.718</td>
<td>78.651</td>
</tr>
<tr>
<td>C2,2'</td>
<td>76.211</td>
<td></td>
</tr>
<tr>
<td>C5,5'</td>
<td>76.211</td>
<td>72.850</td>
</tr>
<tr>
<td>C3,3'</td>
<td>73.796</td>
<td></td>
</tr>
<tr>
<td>C4,4'</td>
<td>71.462</td>
<td>71.972</td>
</tr>
<tr>
<td>N-Me</td>
<td>40.027</td>
<td></td>
</tr>
<tr>
<td>N-Me</td>
<td>37.288</td>
<td>38.320</td>
</tr>
</tbody>
</table>

Figure 3.13a  Solid State Spectrum of 1,1'-Bis(N,N-Dimethylamido)ferrocene (49).
The final amide which was prepared for a solid state n.m.r. study was the 1,1'-bis(N,N-morpholine-amido)ferrocene (50). This was chosen not only for comparison with the other ferrocene amides but as a model with which to compare with the ferrocene macrocyclic amides. Figure 3.13b shows the solid state spectrum and Table 3.12 below compares with assignment of the morpholine amide (50) in the solid state and in solution.

Figure 3.13b Solid State Spectrum of 1,1'-Bis(N,N-Morpholineamido)ferrocene (50).
Table 3.12 Solid State and Solution $^{13}$C N.M.R. Data for 1,1′-Bis(N,N-Morpholineamido)ferrocene (50).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Solid State ppm</th>
<th>Solution State ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=0</td>
<td>168.85</td>
<td>169.1</td>
</tr>
<tr>
<td>C$_1$/C$_1'$</td>
<td>78.58</td>
<td>80.9</td>
</tr>
<tr>
<td>C$_2$/C$_2'$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_5$/C$_5'$</td>
<td>76.682</td>
<td>72.2</td>
</tr>
<tr>
<td>C$_3$/C$_3'$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_4$/C$_4'$</td>
<td>72.829</td>
<td>71.3</td>
</tr>
<tr>
<td>O-CH$_2$</td>
<td>68.55</td>
<td>67.1</td>
</tr>
<tr>
<td>N-CH$_2$</td>
<td>50.774</td>
<td></td>
</tr>
<tr>
<td>N-CH$_2$</td>
<td>45.719</td>
<td>45.7</td>
</tr>
</tbody>
</table>

When comparing the solid state and the solution spectral data, it would appear that there are two N-CH$_2$ signals and that the O-CH$_2$ is at about 68.55 ppm. Consequently there remain three resonances due to the cyclopentadienyl carbons suggesting that the carbonyl (Cp - C=0) rotation is fast whereas the amide (O=C-N) rotation is slow on the n.m.r. time scale.
3.3.4 Solid State N.M.R. Studies on Other Ferrocene Derivatives.

After successfully relating the X-ray crystal structure of the 1,1'-bis(N-methylamido)ferrocene (46) with its solid state n.m.r. spectrum, a series of analogous ferrocene derivatives were prepared in order for similar solid state characterisation to be made. 1,1'-Diacetylferrocene (51) provides an excellent model with which to initiate such a study. Figure 3.14a shows the $^{13}$C n.m.r. solid state spectrum and Figure 3.14b the corresponding solution state spectrum of this material. The assignments of these spectra are presented in Table 3.13.

Table 3.13 Solid State and Solution $^{13}$C n.m.r. Data for 1,1'-Diacetylferrocene (51).

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Solid State</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>204.45</td>
<td>201.64</td>
</tr>
<tr>
<td>C$_1$,C$_1$</td>
<td>81.93/80.52</td>
<td>81.15</td>
</tr>
<tr>
<td>C$_2$,C$_2$ /C$_5$,C$_5$</td>
<td>74.27</td>
<td>74.18</td>
</tr>
<tr>
<td>C$_3$,C$_3$ /C$_4$,C$_4$</td>
<td></td>
<td>71.52</td>
</tr>
<tr>
<td>C$_7$,C$_7$</td>
<td>29.23</td>
<td>28.21</td>
</tr>
</tbody>
</table>
Figure 3.14a  Solid State $^{13}$C N.M.R. of 1,1'-Diacetylferrrocene.

Figure 3.14b  Solution State $^{13}$C N.M.R. of 1,1'-Diacetylferrrocene (22.5 MHz; CDCl$_3$).
It is clear from the spectral information presented in Table 3.13 that many of the crystallographic solid state feature (Section 3.3.2) are highlighted by the solid state n.m.r. spectrum. The observation of only one methyl group and one carbonyl group are in agreement with the results presented in Palenik's crystallographic study\(^\text{167}\). However, when this solid state spectrum is compared with those recorded for the ferrocene amides (Section 3.3.3), several different features are seen. Firstly, 1,1'-diacetylferrocene (51) only shows one signal for the ferrocenyl carbons, which unlike the ferrocene amides cannot be easily explained. Secondly, non-quarternary suppression experiments suggest that the ipso carbon \((C_1, C_1')\) splits into two signals but there is at present no satisfactory explanation for this.

The solid state \(^{13}\text{C}\) n.m.r. spectrum of 1,1'-diacetylferrocene (51) agrees closely with that expected from X-ray crystallographic data and solution state n.m.r. However, the spectrum of 1,1'-ferrocenedicarboxylic acid (52) is very unusual in the solid state (Figure 3.15a) when compared with that for it in solution (Figure 3.15b). Palenik\(^\text{164}\) noted that ferrocene and many of its derivatives show high thermal motion at room temperature, thereby reducing the accuracy of crystallographic data.
Within 1,1' -ferrocenedicarboxylic acid (52) hydrogen bonding exists between the two carboxyl groups which greatly reduces thermal motion. From the solid state spectrum of this material, however, it would appear that fluxional motion is taking place leading to considerable line broadening and lack of differentiation of the carbonyl signals. This may indicate the occurrence of a dynamic process with a coalescence close to the probe temperature (298 K). Only one carbonyl signal is seen in agreement with the data obtained from Palenik's crystallography study.

\[
\begin{align*}
\text{COOH} & \quad \text{(52)} \\
\text{COOH} \\
\end{align*}
\]
Figure 3.15a $^{13}$C N.M.R. Solid State Spectrum of 1,1'-Ferrocenedicarboxylic Acid.

Figure 3.15b $^{13}$C N.M.R. Solution State Spectrum of 1,1'-Ferrocenedicarboxylic Acid (22.5 MHz, d$^6$-DMSO).
The final derivative which was prepared for solid state study in this series of related compounds was dimethyl ferrocene 1,1'-dicarboxylate (53). The solid state spectrum of this material shows one carbonyl and one methyl resonance. However, unlike 1,1'-diacetylferrocene only one quaternary carbon resonance is evident at 6 75.163 ppm. In general however, the similarity of the features in both spectra suggest that these materials both have a similar solid state structure. Table 3.14 shows the assignment of dimethylferrocene 1,1'-dicarboxylate in both solid and solution states.

Table 3.14  Solid State and Solution $^{13}$C N.M.R. Data for Dimethyl Ferrocene 1,1'-Dicarboxylate.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Solid State</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>172.42</td>
<td>172.61</td>
</tr>
<tr>
<td>C1, C1'</td>
<td>75.16</td>
<td>80.88</td>
</tr>
<tr>
<td>C2, C2'/C5, C5'</td>
<td>74.29</td>
<td>73.27</td>
</tr>
<tr>
<td>C3, C3'/C4, C4'</td>
<td>72.45</td>
<td>72.29</td>
</tr>
<tr>
<td>C7, C7'</td>
<td>53.37</td>
<td>53.39</td>
</tr>
</tbody>
</table>
3.3.5 X-Ray Crystallography of Fc[2.2]M Dihydrate.

\(1,1'-(1,4,10,13\text{-tetraoxa-7,16\text{-diazacyclo-octadecane-7,16\text{-diyl}}}{\text{dicarbonyl}})\text{ferrocene dihydrate}\)

With a completed structural analysis on a simple ferrocene bis amide, attention focussed onto the Fc[2.2]M. The \(1,1'\text{-bis(N-methylamido)ferrocene (46)}\) not only provided a useful model on which to start the X-ray analyses, it also provides a reference with which to compare Fc[2.2]M.

Initial work started by attempting to grow good quality crystals. With the experience of the simple amide this proved to be relatively straightforward. An orange crystal of approximate dimensions 0.11 x 0.33 x 0.33 mm (similar size to the bis(methylamido) ferrocene) was collected, and preliminary photographs indicated it was of good quality. Figures 3.16a and 3.16b show various views of the Fc[2.2]M.

Several months after the refinement of this X-ray crystallography study, the same Fc[2.2]M structure was published by Beer et al.\(^7\). Both the structure presented by Beer and the structure in this study show identical characteristics. The atomic numbering scheme (Figure 3.17) and list of bond lengths may be seen in Table 3.15. From this table the average C-C 1.4187Å distances are seen to be in good agreement with those cited by Beer, and again show an excellent agreement with the values cited by
Wheatley for ferrocene itself. The molecular dimensions of the ferrocene moiety when compared with analogous ferrocene derivatives (Table 3.7) show no unusual properties.

The angles of interest (which were defined in detail in Section 3.3.2) are presented in Table 3.16. A more detailed Table of all the molecular parameters in Fc[2.2]M may be found in Appendix II.
Table 3.15  Interatomic Distances in the Fc[2.2]M Structure (Å e.s.d.).

<table>
<thead>
<tr>
<th>Ring</th>
<th>101-105</th>
<th>201-205</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C101</td>
<td>1.501(8)</td>
<td>C2-C201</td>
</tr>
<tr>
<td>C1-N1</td>
<td>1.343(8)</td>
<td>C2-N2</td>
</tr>
<tr>
<td>C1-O1</td>
<td>1.244(7)</td>
<td>C2-O2</td>
</tr>
<tr>
<td>C101-C102</td>
<td>1.439(8)</td>
<td>C201-C202</td>
</tr>
<tr>
<td>C101-C105</td>
<td>1.430(8)</td>
<td>C201-C205</td>
</tr>
<tr>
<td>C102-C103</td>
<td>1.411(8)</td>
<td>C202-C203</td>
</tr>
<tr>
<td>C103-C104</td>
<td>1.403(9)</td>
<td>C203-C204</td>
</tr>
<tr>
<td>C104-C105</td>
<td>1.402(9)</td>
<td>C204-C205</td>
</tr>
</tbody>
</table>

Ethylene Bridges

<table>
<thead>
<tr>
<th></th>
<th>11-C18</th>
<th>21-C28</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11-C12</td>
<td>1.510(8)</td>
<td>C21-C22</td>
</tr>
<tr>
<td>C11-N1</td>
<td>1.464(6)</td>
<td>C21-N1</td>
</tr>
<tr>
<td>C12-O13</td>
<td>1.414(7)</td>
<td>C22-O23</td>
</tr>
<tr>
<td>C14-C15</td>
<td>1.485(8)</td>
<td>C24-C25</td>
</tr>
<tr>
<td>C14-O13</td>
<td>1.413(6)</td>
<td>C24-O23</td>
</tr>
<tr>
<td>C15-C16</td>
<td>1.424(6)</td>
<td>C25-O26</td>
</tr>
<tr>
<td>C17-C18</td>
<td>1.508(7)</td>
<td>C27-C28</td>
</tr>
<tr>
<td>C17-O16</td>
<td>1.405(7)</td>
<td>C27-O26</td>
</tr>
<tr>
<td>C18-N2</td>
<td>1.481(6)</td>
<td>C28-N2</td>
</tr>
</tbody>
</table>

Average Fe-C bond = 2.0422Å (Lit. 163 = 2.044Å)
Table 3.16  Comparison of Selected Structural Angles

<table>
<thead>
<tr>
<th>Derivative</th>
<th>Angle $\alpha^\circ$</th>
<th>Angle $\beta^\circ$</th>
<th>Angle $\gamma^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cpl</td>
<td>Cp2</td>
<td></td>
</tr>
<tr>
<td>Fc[2.2]M</td>
<td>1.2</td>
<td>15.55</td>
<td>50.23</td>
</tr>
<tr>
<td>Fc[2.2]M</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(CpCONHMe)$_2$</td>
<td>1.4</td>
<td>15.59</td>
<td>5.99</td>
</tr>
</tbody>
</table>

It is well known$^{178}$ that the tilt angle ($\alpha$) between two cyclopentadienyl rings varies greatly with the number of bridging methylenes of the ferrocenophanes. A deformation strain resulting from an interannular bridge shorter than four carbons in length can not be accommodated in the ferrocene nucleus without distortion of the preferred co-planar molecular geometry by ring tilting. Akabori et al.'s$^{179}$ X-ray analysis of a polyoxaferrocenophane in which the interannular bridge contains thirteen atoms has an angle $\alpha$ of 3.3$^\circ$. The bridge unit in the Fc[2.2]M structure has 12 atoms.

Angle of twist, $\beta$, between the cyclopentadienyl plane $C(101) \rightarrow C(105)$ and the plane $C(101)$, $C(1)$, $O(1)$, $N(1)$ is 15.55$^\circ$. Whereas the angle $\beta$ between cyclopentadienyl plane $C(201) \rightarrow C(205)$ and plane $C(201)$, $C(2)$, $O(2)$, $N(2)$ is 50.23$^\circ$. The values for
the bis amide were 5.99° and 15.59°. It is interesting to note that the amide function in Fc[2.2]M makes a similar angle to the Cp ring in the C(1), O(1), N(1), whereas the other amide function is forced to an angle of 50.23° due to the tight packing of the macrocycle unit. The amide function forced into such an angle means that it is not possible for it to conjugate with the cyclopentadienyl ring. It also means that the unit cell packing comprises of two differently orientated carbonyls moieties which have trans (antiperiplanar) conformations.

The two rings are rotated from the eclipsed orientation by 12.5°, whereas Beer et al. find a value of only 6.4°. These parameters are similar to those found in, inter alia, the low temperature triclinic and orthorhombic forms of ferrocene, 1-acetyl-1'-benzoylferrocene, acetylferrocene, 1,1'-diacetylferrocene and ferrocene-1,1'-carboxylic acid. In these compounds, the cyclopentadienyl ring orientations range from precisely eclipsed through to a staggered conformation.

The amide bonds have bond lengths in good agreement with those suggested in the literature (Table 3.17), the C-N bond having significant double character with the electron delocalisation between the nitrogen lone pair and the carbonyl oxygen atoms.
The amide function of the 1,1'-bis(N-methylamido)ferrocene (46) is also presented in Table 3.17 to give a good reference with which to compare the Fc[2.2]M structure.

Table 3.17 Comparison of the Bond Lengths of Fc[2.2]M, and 1,1'-bis(N-methylamido)ferrocene with Typical Literature Values\(^{170}\) (Å e.s.d.).

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Recorded Values</th>
<th>Literature Values(^{170})</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(_3)C=NN</td>
<td>1.465(7)Å 1.444(6)Å</td>
<td>1.472(5)Å</td>
</tr>
<tr>
<td>O=C=NN</td>
<td>1.348(8)Å 1.337(6)Å</td>
<td>1.322(3)Å</td>
</tr>
<tr>
<td>-C(_2)O</td>
<td>1.234(6)Å 1.199(6)Å</td>
<td>1.23(10)Å</td>
</tr>
</tbody>
</table>

3.3.6 Size of the Binding Site in Fc[2.2]M Dihydrate.

One of the most important features, from the viewpoint of function in Fc[2.2]M, is its ion-binding ability which is related to and its cavity size. From the X-ray crystallographic study it was hoped that a little more light would be thrown on the ability of Fc[2.2]M to bind metal ions and in particular provide an assessment of the best ion for this purpose.

From the crystallographic views present in Figure 3.16 it is clear that the four ether oxygens (O(13), O(16), O(23) and O(26)) adopt a rather twisted
conformation. Figure 3.18 below gives the distances of the oxygen from each other in the heterocyclic ring.

![Diagram of Oxygen-Oxygen Distances](image)

**Oxygen-Oxygen Distances (Å)**

1. 1.705 Å
2. 1.115 Å
3. 1.974 Å
4. 2.239 Å

average = 2.1065 Å

5/6 O O Å

Figure 3.18 Binding Site of Fc[2.2]M.

(* Free space (Å) between oxygen atoms in the polyether bridges of Fc[2.2]M (assuming a Van der Waals radius for O of 1.5 Å)).

The values (3/4), indicated in Figure 3.18, show that the central cavity between the four oxygens has a diameter of the order of 2.1 Å. This value is smaller than the value quoted for [18]-crown-6 (5) (2.6-3.2 Å), which on the basis of molecular models suggest that diaza-[18]-crown-6 (7) should be of similar size. The distances between the oxygens on the same ether chair (5/6) is less than the sum of their Van der Waal radii suggesting that the ethylene bridges are in a very compressed conformation. The ether bridges are separated by an average distance (1/2) of 1.41 Å.

From these values and that for diaza-[18]-crown-6 (7) it is clear to see that the binding cavity in Fc[2.2]M is relatively small. The
ferrocene bridging unit forces the flexible crown into a restricted orientation. The 7,16-diphenyl derivative of diaza-[18]-crown-6 is also highly puckered and unsymmetrical and this has been attributed to the steric requirements of the phenyl substituents, but the effects of packing forces may also be important.

In terms of binding ions (Table 0.2) the cavity dimension calculation suggest that lithium, sodium, magnesium and calcium from groups I and II should fit. As well as metals from groups I and II listed above, a few transition elements should also fit, indeed any metal ion which has an ionic radii of less than 1.05Å should be suitable.

As suggested by Beer et al and as seen in this study, all the crystals suitable for X-ray structural analysis had water of crystallisation associated with them, which could be easily detected using infra red spectroscopy. However, recent attempts at growing reasonable crystals without the presence of water molecules proved successful and on examination of the unit cell for this material suggested that a different packing arrangement was present. At the moment this structure is still being refined.

Plates (3.3 and 3.4) below were generated using Chem-xl69 showing the full crystallographic structures of Fc[2.2]M dihydrate.
Plates 3.3

Plates 3.4
In the light of work carried out on the simple ferrocene amides and related ferrocene derivatives, and the X-ray crystallographic study on Fc[2.2]M, a solid state $^{13}$C n.m.r. spectrum of this material was recorded. This is shown together with a resolution enhanced spectrum presented in Figures 3.19a and 3.19b. For comparison, Figure 3.19c shows the solution spectrum for this compound, with the assignment of all these spectra given in Table 3.18.

From the results presented in the table of n.m.r. data it is clear that there are several outstanding features which endorse the crystallography data. The most prominent of these features is the number of carbonyl signals present. The crystallographic study suggests that the carbonyl groups of the amide function sit in two independent environments within the unit cell. The solid state n.m.r. spectrum clearly demonstrates this, though on resolution enhancement of the spectrum a third signal looks to be present. Close examination suggests that the two major signals have relative intensities of 50:50 supporting the crystallography data. Similar spectral features have been observed in trans-azobenzenes and p-alkoxybenzoic acids where the absence of exchange between different
Table 3.18  Solid State $^{13}$C N.M.R. and Solution $^{13}$C N.M.R. Data for Fc[2.2]M Dihydrate

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Solid State</th>
<th>Solution State</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>169.05/168.29</td>
<td>170.05/168.29</td>
</tr>
<tr>
<td>C1'</td>
<td>84.92</td>
<td>78.5</td>
</tr>
<tr>
<td>C2'</td>
<td>79.43</td>
<td>73.3</td>
</tr>
<tr>
<td>C3', C4'</td>
<td>77.87</td>
<td>72.9</td>
</tr>
<tr>
<td>C4, C3</td>
<td>76.41</td>
<td>72.9</td>
</tr>
<tr>
<td>C4', C3'</td>
<td>74.03</td>
<td>71.5</td>
</tr>
<tr>
<td>C5'</td>
<td>72.03</td>
<td>71.0</td>
</tr>
<tr>
<td>C3, C4</td>
<td>70.47</td>
<td>70.5</td>
</tr>
<tr>
<td>C5</td>
<td>69.84</td>
<td>70.1</td>
</tr>
<tr>
<td>C2</td>
<td>67.28</td>
<td>69.5</td>
</tr>
<tr>
<td>C6</td>
<td>49.97</td>
<td>51.5</td>
</tr>
<tr>
<td>C1</td>
<td></td>
<td>50.1</td>
</tr>
</tbody>
</table>
Figure 3.19a  $^{13}$C CPMAS Spectrum of Fc[2.2]M.

Figure 3.19b  $^{13}$C CPMAS Spectrum of Fc[2.2] Resolution Enhanced.
Figure c Solution State $^{13}\text{C} \text{N.M.R. of Fc[2.2]M}$ (CDCl$_3$; $\alpha$ 62.5 MHz).

...conformers has given rise to similar peak multiplicities.

Work by Hall and co-workers has made it possible to make a complete assignment of all the carbon signals in the Fc[2.2]M molecule (Appendix I). From this data it was relatively straightforward to propose an assignment of the solid state spectrum. It is clear that the solid state and solution data agree very well. The only real exception being seen in the signals due to carbons C$_6$ and C$_1$ which, in the solid state, merge into one broad hump.

3.3.8 Discussion of the Solid State Features of Fc[2.2]M and the Comparison with other Ferrocene Cryptands.

One of the most notable features of the solid...
state study on Fc[2.2]M is seen when the results are compared with the work carried out by Hall and Grossel. Hall suggests that the [1.1] and [2.3] monomers are rigid (Section 3.2.7) and that from models a trans arrangement for the carbonyl group provides a likely low energy conformation. This is somewhat at variance with the solid state n.m.r. data which as already discussed shows several carbonyl signals. An attempt to freeze the carbonyl rotation in solution by a $^{13}$C n.m.r. study at low temperatures (-100°C), still only resulted in one carbonyl signal being observed. This simply indicated a low barrier of inversion and freezing out of this would be hampered by the small frequencies of separation of the interconverting sites in the cis and trans conformations (Section 3.2.7).

When considering the other ferrocene cryptands in the series, the [2.1] monomer has several distinct conformations (Figure 3.20). The carbonyl group may be cis to the single oxygen bridge, cis to the two oxygen bridge and trans. These three structures are structurally different from each other and one would expect to see markedly different chemical shifts for each. A similar argument may be applied in the case of the [3.2] monomer.
Figure 3.20 Possible Conformation for the Unsymmetrical Ferrocene Cryptands.

The [3.3] monomer, however, is a special case. The large macrocyclic ring can adopt a number of distinct conformations as it is significantly compressed by its anchoring points to the ferrocene moiety. It is unlikely therefore that this structure would favour a high symmetry conformation.

The intriguing question still remains as to why there are only two resonances observed at low temperature in solution for the [2.1] and [3.2] monomers? It is hoped in due course that solid state and X-ray crystallographic studies may throw further light onto this situation.
Finally the other prominent feature highlighted in this solid state study is that the conformation of the macrocyclic ring. The X-ray crystallography suggests that the 18-membered ring is more puckered than that of the parent diaza-[18]-crown-6 (7). The consequence of this on the ability of the cryptand to bind ions will be discussed in the following section of this chapter.

3.4 PHYSICAL PROPERTIES OF THE FERROCENE MACROCYCLE Fc[2.2]M.

3.4.1 Cation Binding Properties.

The cation binding properties of the Fc[2.2]M cryptand were originally tested by Bell and Hall\textsuperscript{157}, using a method originally employed by Pedersen\textsuperscript{158} and later used extensively by Frensdorf\textsuperscript{186}. This method involved the mixing of a dichloromethane solution containing a macrocycle with an aqueous solution containing a metal picrate. As suggested in Chapter 1, the macrocycle extracts the cation from the aqueous phase and in order to preserve electrical neutrality so the transfer of the picrate anion also takes place. This process may be detected easily as picrate anion absorbs at 389 nm in dichloromethane. No picrate is phase- transferred in the absence of a dichloromethane soluble binding ligand.

When Bell and Hall\textsuperscript{157} attempted this experiment
on the Fc[2.2]M macrocycle they found that the
extraction of picrates followed the sequence Ca^{2+} \gg \ni \ni Li^{+} > Na^{+} = Mg^{2+} > K^+, with the transfer of potassium
ions being only just detectable. This sequence of
ions is unusual for a number of reasons. Firstly,
the order of alkali-metal binding suggests a small
cavity (Table 0.2) comparable to [12]-crown-4 which
prefers small alkali metal cations. The strong
binding of Ca^{2+} which is similar in ionic size to K^+
is therefore incongruous and does not parallel any
previous observations seen in [12]-crown-4. Bell and
Hall\textsuperscript{157} also suggested that calcium picrate
is unstable in aqueous solution and that it may have
formed calcium hydroxide and picric acid. If this is
the case, they propose that rather than seeing Ca^{2+}
ions transferred what is actually occurring is the
transfer of solvated H^+ into the dichloromethane
accompanied by picrate anion. Hence the sequence of
ion binding ability now gives the sequence were: H^+ > 
Li^+ > Na^+ = Mg > > K^+, Ca^{2+} = 0. In solvents of low
dielectric constant, binding ligands with a large
lyophilic character favour complex formation with
ions of lower charge. However, the relatively strong
binding of Mg^{2+} by Fc[2.2]M is unusual because the
small size and high charge density of Mg^{2+} means that
it usually forms much less stable complexes than
Na^+. Again this maybe a phenomenon of the stability
of the picrate and not the binding ability of the macrocycle. The binding sequence would be more informative if a run had been made against picric acid itself. Consequently Bell and Hall drew no conclusions from these observations, but felt that it was possible for a π cloud interaction of the ferrocene moiety to contribute to the degree of binding of the cation within the macrocyclic ligand.

3.4.2 Extraction Experiments with Oxonol Dyes

(Chapter 4).

It was our intention to attempt to unravel the confusing results recorded by Bell and Hall$^{157}$ when trying to assess the ion binding ability of Fc[2.2]M. It was because of the success of complexing simple crown ethers with oxonol dyes (Chapter 4) and also because of the experience within the research group of synthesising oxonol dyes$^{115,188}$, that they were used to study the ion binding ability of Fc[2.2]M. To our knowledge these photographic bleachable dyes have never been used in this way before.

This system for studying the extraction ability of a macrocyclic ligand was favourable in several ways. As photographic dyes they have a high extinction coefficient ($= 10^5$) and can be easily detected as they absorb at 598 nm in dichloromethane. Furthermore they do not carry the
potential hazard associated with the formation of picrate salts. The only real disadvantage of these compounds over the picrate salts is that they are more difficult to synthesise and to purify.

Table 3.19 shows the extinction coefficient of the various oxonol dyes used in these experiments. Before they were used many of the dyes had to be recrystallised 4-5 times until the extinction coefficient remained constant. In order to check the oxonol dye extraction system fully, a control experiment was carried out using dibenzo-[18]-crown-6. The method employed by Pedersen when trying to demonstrate the complexation of crown ethers with picrate salts, was followed very closely. Solvent extraction was carried out at room temperature (25-26°C) by shaking vigorously (approximately one hundred times) with equal volumes of aqueous and organic solutions. The phases were allowed to settle out and then separated in a separation funnel. The concentration of the coloured anion left in the aqueous phase was determined (any solvent interaction at 589 nm was blanked prior to the experiment) and the results are shown in Table 3.20. Previously run controls showed that no oxonol dye is transferred without a dichloromethane soluble ligand present. It is important to point out that Pedersen monitored the picrate extractions by
Table 3.19  Extinction Coefficients of the Oxonol Dyes Used in the Extraction Experiments.

<table>
<thead>
<tr>
<th>c(max)</th>
<th>( \lambda_{\text{max}} )</th>
<th>Concentration</th>
<th>( \epsilon(\text{max}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{n} \text{Mn}^+ )</td>
<td>(mol dm(^{-3}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(^+)</td>
<td>598</td>
<td>1.48 x 10(^{-5})</td>
<td>1.22 x 10(^5)</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>598</td>
<td>1.491 x 10(^{-5})</td>
<td>1.26 x 10(^5)</td>
</tr>
<tr>
<td>K(^+)</td>
<td>598</td>
<td>1.511 x 10(^{-5})</td>
<td>1.23 x 10(^5)</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>598</td>
<td>1.513 x 10(^{-5})</td>
<td>1.107 x 10(^5)</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>598</td>
<td>1.506 x 10(^{-5})</td>
<td>1.08 x 10(^5)</td>
</tr>
<tr>
<td>NH(_4)(^+)</td>
<td>598</td>
<td>1.487 x 10(^{-5})</td>
<td>1.15 x 10(^5)</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>598</td>
<td>1.475 x 10(^{-5})</td>
<td>0.985 x 10(^5)</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>598</td>
<td>1.514 x 10(^{-5})</td>
<td>1.25 x 10(^5)</td>
</tr>
</tbody>
</table>

determining the concentration of anion in the dichloromethane layer.

The model experiment with the oxonol dyes proved to give good agreement with the literature reports on picric acid extractions described by Pedersen\(^{185}\).

With the success of these results the next stage was to repeat the work of Bell and Hall\(^{157}\), and to assess the ability of Fc[2.2]M to bind specific ions. The
results of these findings are shown in Table 3.21.

Table 3.21 The Percentage of Oxonol Transferred with Fc[2.2]M (1.5 x 10^{-5} \text{ mol dm}^{-3}).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Percentage Transferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>7.74%</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>3.76%</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0%</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>3.82%</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.2%</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0%</td>
</tr>
</tbody>
</table>

From the sequence of these results it is clear that they agree generally with the work of Bell and Hall. However, the oxonol extraction experiments do not show enhanced Ca$^{2+}$ binding by the macrocycle.

The oxonol extraction experiments also gave good literature agreement with the work of Shamsipur and Popov$^{189}$ who found that the formation constants of the complexes between Li$^+$, Na$^+$ and Cs$^+$ with diaza-[18]-crown-6 (7) decreased in the following order: Li$^+$ > Na$^+$ > Cs$^+$. This is markedly different from that observed for the analogous [18]-crown-6 (5) derivative: Cs$^+$ > Na$^+$ > Li$^+$.

Frensdorf$^{35}$ showed that the substitution of nitrogen or sulphur for oxygen in [18]-crown-6 (5) and dibenzo-[18]-crown-6 (2) greatly influences the complexing ability of these macrocycles. The complexation of K$^+$ is weakened appreciably by nitrogen and by sulphur substitution, the stability constant falling in the order of decreasing...
electronegativity $O > NR > NH > S$. This is just as expected: as the negative charge on the heteroatom drops so the electrostatic attraction between it and the cation is diminished.

When comparing the binding ability (i.e. the (\%) transfer of anion across phases) of Fc[2.2]M with the work reported by Frensdorf on diaza-[18]-crown-6 (7), it is clear that Fc[2.2]M is a considerably poorer complexing agent. This may be explained in several ways. Firstly, Fc[2.2]M is an amide, and hence the lone pair of electrons on the nitrogen is less available for ion-binding, whereas the amine lone pairs in diaza-[18]-crown-6 (7) are comparatively more available to bind to a cation. The low basicity of the Fc[2.2]M nitrogens compared with those in diaza-[18]-crown-6 (7) explains its apparent lack of efficiency to bind cations. Secondly, in the light of the X-ray crystallographic study, the Fc[2.2]M macrocyclic unit is forced into a highly puckered and compressed conformation. The anchoring of the diaza-[18]-crown-6 to a ferrocene bridge reduces the size of the binding site and hence its ability to bind cations as effectively as the parent diaza-[18]-crown-6 (7).

As already noted the oxonol experiments do not show preferential Ca$^{2+}$-binding ability originally suggested by Bell and Hall. The solvated proton
extraction idea also seems rather unsatisfactory for, if this explanation is to be accepted why is a similar effect not seen with magnesium picrate? Would the stability of magnesium and calcium picrate differ to such an extent?

Possibly a more reasonable explanation for the observations of Bell and Hall, is that they in fact monitored a 2:1 complex of Fc[2.2]M and calcium. Poonia showed (Chapter 4) that when the cavity size of a crown ether is smaller than the size of the bound cation, a 2:1 complex forms. Since Bell and Hall did not report any working concentrations when carrying out these experiments it is possible that they observed two molecules of Fc[2.2]M encapsulating one calcium ion.

However, the intriguing question remains as to whether the bound cation sits within the cryptand cavity provided by Fc[2.2]M or whether it sits externally to it? If we are to believe the explanation just presented about Ca\textsuperscript{2+} binding then we would expect it to sit external to the cryptand cavity so that a 2:1 complex could form. In order to answer the question more fully the following chain of experiments and spectroscopic studies were carried out.
3.5 SYNTHESIS OF FERROCENE CRYPTATE COMPLEXES.

A series of cryptate salts were prepared \((\text{Fc}[2.2]\text{M})_m(M^+x)_n\) \((m=1, n=1)\) by a generally accepted method for crown ether/cryptate complexes reported in the literature\(^1\) and are shown in Table 3.22.

Table 3.22 Complexes Prepared From \(\text{Fc}[2.2]\text{M}\).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Molecular Weight</th>
<th>Element Analysis</th>
<th>Yields</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Fc}[2.2]\text{M})(\text{LiClO}_4))</td>
<td>606.5</td>
<td>C: 47.37, H: 5.20, N: 4.51</td>
<td>45%</td>
<td>Tan Solid</td>
</tr>
<tr>
<td>((\text{Fc}[2.2]\text{M})(\text{LiI}))</td>
<td>634</td>
<td>C: 45.27, H: 5.00, N: 4.31</td>
<td>49%</td>
<td>Tan Solid</td>
</tr>
<tr>
<td>((\text{Fc}[2.2]\text{M})(\text{LiCF}_3\text{SO}_3))</td>
<td>656</td>
<td>C: 45.49, H: 4.81, N: 4.11</td>
<td>39%</td>
<td>Tan Solid</td>
</tr>
<tr>
<td>((\text{Fc}[2.2]\text{M})(\text{Ca CF}_3\text{SO}_3))</td>
<td>Poor Results</td>
<td>838</td>
<td>12%</td>
<td>Tan Solid</td>
</tr>
<tr>
<td>((\text{Fc}[2.2]\text{M})(\text{AgI}))</td>
<td>Pending Results</td>
<td>725</td>
<td>53%</td>
<td>Brown Solid</td>
</tr>
</tbody>
</table>

TCNQ Salts see Next Chapter.

3.5.1 Spectroscopic Analysis of \(\text{Fc}[2.2]\text{M}\) Cryptate Complexes.

The preparation of the lithium salts proved...
relatively straightforward and were characterised by a number of spectroscopic techniques. The alkaline-earth metal salts gave not only poor yields but also poor combustion analyses.

3.5.2 Mass Spectrometry.

Attempts to show the complex formation of Fc[2.2]M and a simple salt (M⁺X⁻) by electron ionisation mass spectrometry proved unsuccessful. Under these conditions the complexes fell apart, showing evidence of only the parent ion of Fc[2.2]M and of the respective anion.

Work by Johnstone and Rose¹⁹¹ and more recently Beer¹⁹², have shown that fast atom bombardment (f.a.b.) mass spectrometry may be used to study the ion selectivity of monocyclic crown ethers. It was due to the success by these workers that f.a.b. mass spectrometry was attempted on the (Fc[2.2]M)(LiClO₄) complex. The spectrum was recorded by dissolving the sample in a matrix liquid (3-nitrobenzyl alcohol) without the aid of a co-solvent. The source was operated at room temperature and the data system was calibrated with perfluoroheptatriazine.

The spectrum is shown in Figure 3.21 and there is clear evidence for a complex ion at m/e = 507 which is due to the (Fc[2.2]M)Li⁺ ion. However, even more surprising is the signal shown at m/e = 1007, which can only be explained by the presence of a
(Fc[2.2]M)Li⁺ complex of a 2:1 ratio. This result suggests that the Li⁺ ion must sit external to the Fc[2.2]M cryptand cavity (otherwise it would be impossible for the dimer to form). These results clearly support the conclusions drawn concerning the ion binding ability of Fc[2.2]M in Section 3.4.2.

Even though combustion analysis data suggest that the (Fc[2.2]M)(LiClO₄) was a 1:1 complex, the f.a.b. results suggest that it is a mixture of 2:1, 1:1 and simple Fc[2.2]M. It is doubtful, though possible that the 2:1 complex forms within the confines of the mass spectrometer. In other words it looks as though
not all the ferrocene cryptand is involved in cation binding and this is an important point to consider when studying the complexes spectroscopically.

3.5.3 Infra Red Spectroscopy.

Infra red mass spectrometry has been used to study the complexation of a macrocyclic ligand, by many workers within the crown ether field. Pedersen for example in his early work noted in a spectrum of dibenzo-[18]-crown-6 complex with potassium thiocyanate complex, several outstanding features: (a) change in the methylene bridges bands with an increase in intensity, and, (b) significant variation in the aromatic bands. It was apparent that the potassium ion was bonded in such a way as to cause a carbon-hydrogen vibration to be more restricted in the complex.

The tell tale signs shown by infra red on complexation between a crown ether and a metal ion, infra red was used to study the complexes of Fc[2.2]M. Table 3.23 reports the characteristic features of the complexes infra red spectrum of this complex.

Fc[2.2]M shows a similar series of spectral changes on complexation to those previously reported by Pedersen. Firstly, the C-H deformations on the methylene bridges in Fc[2.2]M show several more signals in the 1400 cm⁻¹ → 1300 cm⁻¹ region than the
<table>
<thead>
<tr>
<th>Wavenumber/cm⁻¹</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>3457(s)</td>
<td>H-O Stretch</td>
<td>H₂O</td>
</tr>
<tr>
<td>3098(w)</td>
<td>C-H Stretch</td>
<td>Aromatic Cyclopentadienyl Rings</td>
</tr>
<tr>
<td>2862(s)</td>
<td>C-H Stretch</td>
<td>Alkane Bridges of Ether</td>
</tr>
<tr>
<td>1610(s)</td>
<td>C=O Stretch</td>
<td>Tertiary Amide</td>
</tr>
<tr>
<td>1475(m)</td>
<td>C-H Deformation</td>
<td></td>
</tr>
<tr>
<td>1417(m)</td>
<td>C-H Deformation</td>
<td>Methylene Bridges of Ether Rings</td>
</tr>
<tr>
<td>1362(m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1112(vs)</td>
<td>C-O Stretch</td>
<td>Aliphatic Ether</td>
</tr>
<tr>
<td>916(w)</td>
<td>C-H Deformation</td>
<td>Aromatic C-H out of Plane</td>
</tr>
<tr>
<td>876(w)</td>
<td></td>
<td>Deformation</td>
</tr>
</tbody>
</table>
complex does. As Pedersen reported, these signals are shifted closer together and there is a change in intensity. Secondly, there is a dramatic change in the C-O stretching bands of the aliphatic ethers. In Fc[2.2]M this is characterised by two signals at 1140 cm\(^{-1}\) and 1099 cm\(^{-1}\) of similar intensity. However, in the (Fc[2.2]M)(LiClO\(_4\)) complex these signals merge into one extremely intense band at 1112 cm\(^{-1}\). This suggests that the lithium ion is bonded to the Fc[2.2]M and that it causes the vibration to be more restricted in the complex.

3.5.4 \(^1\)H N.M.R.

Work by Live and Chan\(^{193}\) has shown that both proton \((^1\text{H})\) and carbon \((^1\text{C})\) n.m.r. can be used to elucidate the structures of a number of crown ether complexes. In just the same manner adopted by Live and Chan and subsequently by other workers, it was hoped that \(^1\)H n.m.r. shift changes between complexed and uncomplexed Fc[2.2]M would give some indication of the conformation adopted in solution. The \(^1\)H n.m.r. spectrum of Fc[2.2]M may be seen in Appendix I along with the complete structural assignment of this spectrum by Hall and co-workers\(^{158,160}\). This has been compared with that of its lithium perchlorate complex. The assignments of these spectra are shown in Table 3.24.

Work by Akabori et al\(^{199,1979}\) on the polyoxa (n)
ferrocenophanes (Figure 3.22) reported the $^1$H n.m.r. chemical changes when the polyoxa (n) ferrocenophanes were complexed with a series of alkaline metal thiocyanates. They were interested (as we are) to know what kind of interaction could be expected when a cation was complexed with redoxable cryptand. They found only small differences in the proton chemical shifts ($\pm$ 0.05 ppm) and attributed these changes to electronic field effects and conformational changes upon metal-ion complexation.

When reviewing the literature on chemical shift$^{99,179,193}$ changes in complexed and uncomplexed macrocycles, it became evident that solvents affected the strength of interaction between the binding ligands and the metal salts. In fact when comparing the results obtained by Akabori et al (run in CDCl$_3$) it was evident that the chemical shift changes observed for the Fc[2.2]M complex (run in CD$_3$OD) were
Table 3.24 $^1$H N.M.R. Chemical Shifts Differences Between Fc[2.2]M and (Fc[2.2]M)(LiClO$_4$) (400 MHz; CD$_3$OD).

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>Fc[2.2]M</th>
<th>(Fc[2.2]M)(LiClO$_4$)</th>
<th>$\Delta$,$\delta$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>2.92</td>
<td>2.93</td>
<td>0.01</td>
</tr>
<tr>
<td>6A</td>
<td>3.25</td>
<td>3.25</td>
<td>0.00</td>
</tr>
<tr>
<td>2A</td>
<td>3.51</td>
<td>3.53</td>
<td>0.02</td>
</tr>
<tr>
<td>3A,B 4A,B</td>
<td>3.70</td>
<td>3.73</td>
<td>0.03</td>
</tr>
<tr>
<td>5A</td>
<td>3.81</td>
<td>3.82</td>
<td>0.01</td>
</tr>
<tr>
<td>5B</td>
<td>4.06</td>
<td>4.06</td>
<td>0.00</td>
</tr>
<tr>
<td>2B</td>
<td>4.12</td>
<td>4.13</td>
<td>0.01</td>
</tr>
<tr>
<td>6B</td>
<td>4.15</td>
<td>4.15</td>
<td>0.00</td>
</tr>
<tr>
<td>1B</td>
<td>4.27</td>
<td>4.27</td>
<td>0.00</td>
</tr>
<tr>
<td>4'</td>
<td>4.47</td>
<td>4.47</td>
<td>-</td>
</tr>
<tr>
<td>3'</td>
<td>4.48</td>
<td>4.48</td>
<td>-</td>
</tr>
<tr>
<td>5'</td>
<td>4.57</td>
<td>4.57</td>
<td>-</td>
</tr>
<tr>
<td>2'</td>
<td>4.80</td>
<td>4.80</td>
<td>-</td>
</tr>
</tbody>
</table>

(* Numbering scheme refer to Figure 3.23).

very small. For this reason Fc[2.2]M and (Fc[2.2]M)(LiClO$_4$) were also studied in deuterochloroform solution with the results tabulated in Table 3.25 below.

It is clear from the results above that the resonanced of all the methylene protons on the ligand shifted on complexation but, the protons on
the ferrocene rings are not significantly effected. It would therefore seem that the Li⁺ ion is involved only with the macrocycle and not with the bridging ferrocene unit. In order to gain more information ¹³C n.m.r. experiments were also carried out.

Table 3.25 ¹H N.M.R. Chemical Shift Differences Between Fc[2.2]M and (Fc[2.2]M)(LiClO₄) (400 MHz; CDCl₃).

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>Fc[2.2]M</th>
<th>Fc[2.2]MLiClO₄</th>
<th>Δδ, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>2.92</td>
<td>2.96</td>
<td>0.04</td>
</tr>
<tr>
<td>6A</td>
<td>3.25</td>
<td>3.29</td>
<td>0.04</td>
</tr>
<tr>
<td>2A</td>
<td>3.51</td>
<td>3.54</td>
<td>0.03</td>
</tr>
<tr>
<td>3A,B 4A,B</td>
<td>3.70</td>
<td>3.74</td>
<td>0.04</td>
</tr>
<tr>
<td>5A</td>
<td>3.81</td>
<td>3.85</td>
<td>0.04</td>
</tr>
<tr>
<td>5B</td>
<td>4.06</td>
<td>4.08</td>
<td>0.02</td>
</tr>
<tr>
<td>2B</td>
<td>4.12</td>
<td>4.10</td>
<td>0.02</td>
</tr>
<tr>
<td>6B</td>
<td>4.15</td>
<td>4.17</td>
<td>0.02</td>
</tr>
<tr>
<td>1B</td>
<td>4.27</td>
<td>4.30</td>
<td>0.03</td>
</tr>
<tr>
<td>4'</td>
<td>4.47</td>
<td>4.47</td>
<td>-</td>
</tr>
<tr>
<td>3'</td>
<td>4.48</td>
<td>4.48</td>
<td>-</td>
</tr>
<tr>
<td>5'</td>
<td>4.57</td>
<td>4.57</td>
<td>-</td>
</tr>
<tr>
<td>2'</td>
<td>4.80</td>
<td>4.80</td>
<td>-</td>
</tr>
</tbody>
</table>

(* Number scheme refer to Figure 3.23).
3.5.5 $^{13}$C N.M.R.

It is well known\textsuperscript{134} that $^{13}$C n.m.r. chemical shifts are sensitive to conformational changes, and relatively less sensitive to perturbations such as solvent effects, than proton chemical shifts. Therefore, the $^{13}$C n.m.r. spectra of Fc[2.2]M and the (Fc[2.2]M)(LiClO$_4$) complexes were recorded in dueteromethanol. The $^{13}$C n.m.r. spectrum of Fc[2.2]M may be seen in Appendix I and Table 3.26 compared this spectrum with that of the LiClO$_4$ complex (Figure 3.23).

![Figure 3.23 (Fc[2.2]M)(LiClO$_4$) Cryptate.](image)

Work by Hall and co-workers completely who assigned the $^{13}$C n.m.r. spectrum of Fc[2.2]M by homonuclear and heteronuclear decoupling experiments\textsuperscript{158,160}, allows us to deduce which of the carbon atoms (from chemical shifts) are intimately involved with ion binding. From the chemical shift differences reported in Table 3.26 it is clear that...
### Table 3.26 Comparison of Chemical Shift Differences Between Fc[2.2]M and (Fc[2.2]MLiClO₄). (100 MHz; CD₃OD).

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>Fc[2.2]M</th>
<th>Fc[2.2]MLiClO₄</th>
<th>ΔΔS, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>48.53</td>
<td>48.53</td>
<td>0.01</td>
</tr>
<tr>
<td>C-6</td>
<td>50.89</td>
<td>50.96</td>
<td>0.07</td>
</tr>
<tr>
<td>C-2</td>
<td>68.66</td>
<td>68.68</td>
<td>0.02</td>
</tr>
<tr>
<td>C-5</td>
<td>69.16</td>
<td>69.21</td>
<td>0.05</td>
</tr>
<tr>
<td>C-3/C-4</td>
<td>69.60</td>
<td>69.73</td>
<td>0.13</td>
</tr>
<tr>
<td>C-5'</td>
<td>70.37</td>
<td>70.36</td>
<td>0.01</td>
</tr>
<tr>
<td>C-4'/C-3'</td>
<td>71.20</td>
<td>71.23</td>
<td>0.03</td>
</tr>
<tr>
<td>C-4/C-3</td>
<td>71.49</td>
<td>71.37</td>
<td>0.12</td>
</tr>
<tr>
<td>C-3'/C-4'</td>
<td>71.64</td>
<td>71.63</td>
<td>0.01</td>
</tr>
<tr>
<td>C-2'</td>
<td>72.62</td>
<td>72.03</td>
<td>0.01</td>
</tr>
<tr>
<td>C-1'</td>
<td>78.40</td>
<td>78.50</td>
<td>0.10</td>
</tr>
<tr>
<td>C=O</td>
<td>170.86</td>
<td>171.00</td>
<td>0.14</td>
</tr>
</tbody>
</table>

(* Number scheme refer to Figure 3.23).

C-3/C-4 show the greatest changes. This is to be expected if the potential binding site for the Li⁺ ion is within the cavity expressed by the four oxygen atoms. However, as well as the changes to C-3 and C-4, the chemical shifts of C-2 and C-5 should also be affected; this is not the case. The only other detectable chemical shift change is of the carbonyl group, this may be as a result of a reorganisation of
the binding ligands in the Fc[2.2]M structure.

As mentioned in the previous section, solvent effects are important in the strength of complexation in solution for crown/cryptands and metal salts. Accordingly the Fc[2.2]M and (Fc[2.2]M)(LiClO₄) n.m.r. spectra were also recorded in deuterochloroform and the assignments are tabulated in Table 3.27.

Table 3.27 Comparison of Chemical Shift Differences Between Fc[2.2]M & (Fc[2.2]M)LiClO₄. (CDCl₃ @ 100 MHz).

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>Fc[2.2]M</th>
<th>Fc[2.2]MLiClO₄</th>
<th>Δδ, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>C-1</td>
<td>50.064</td>
<td>49.894</td>
<td>0.17</td>
</tr>
<tr>
<td>C-6</td>
<td>51.417</td>
<td>51.429</td>
<td>0.012</td>
</tr>
<tr>
<td>C-2</td>
<td>69.366</td>
<td>69.651</td>
<td>0.285</td>
</tr>
<tr>
<td>C-5</td>
<td>70.017</td>
<td>69.845</td>
<td>0.172</td>
</tr>
<tr>
<td>C-3/C-4</td>
<td>70.473</td>
<td>70.289</td>
<td>0.184</td>
</tr>
<tr>
<td>C-5'</td>
<td>71.103</td>
<td>71.188</td>
<td>0.085</td>
</tr>
<tr>
<td>C-4'/C-3'</td>
<td>71.414</td>
<td>71.316</td>
<td>0.094</td>
</tr>
<tr>
<td>C-4/C-3</td>
<td>72.787</td>
<td>72.401</td>
<td>0.386</td>
</tr>
<tr>
<td>C-3'/C-4'</td>
<td>72.787</td>
<td>72.686</td>
<td>0.101</td>
</tr>
<tr>
<td>C-2'</td>
<td>73.235</td>
<td>73.155</td>
<td>0.08</td>
</tr>
<tr>
<td>C-1'</td>
<td>78.726</td>
<td>79.045</td>
<td>0.319</td>
</tr>
<tr>
<td>C=O</td>
<td>170.695</td>
<td>170.878</td>
<td>0.183</td>
</tr>
</tbody>
</table>

(*Number scheme refer to Figure 3.23).
From the results listed above there is clearly a change in chemical shifts between the complexed and uncomplexed Fc[2.2]M, particularly for C-3/C-4, and to a lesser extent for C-2/C-5. These results tend to suggest that it is plausible for the Li\(^+\) ion to sit in between the four oxygen atoms of the binding ligands. Other significant shift changes are seen in C-1 and C=0; these changes may be a direct result of molecular restructuring in the complexed Fc[2.2]M state.

Even though only speculative assessments may be made between Fc[2.2]M and (Fc[2.2]M)(LiClO\(_4\)), the experiments suggest that some interaction is taking place when Li\(^+\) ion binds with the ligand. At what precise position the Li\(^+\) ion sits is difficult to predict from this type of information. There is no way of deducing whether the Li\(^+\) ion sits exterior to the ligand or interior (Figure 3.24). In the latter case it would be expected to effect the amide rotations present within the structure. For this reason a series of variable temperature \(^{13}\)C n.m.r. spectra were recorded, it being suggested that any carbonyl interaction with the bound Li\(^+\) ion would affect the activation barrier for the amide rotations discussed in an earlier section.

Variable temperature studies run at 50\(^\circ\)C, 0\(^\circ\)C and -50\(^\circ\)C showed no variation in coalescence phenomena.
when comparing Fc[2.2]M bound and unbound. All these spectra were recorded at 100 MHz in deuterochloroform. It therefore seems increasingly likely that the M\(^+\) is located exterior to the ligand.

![Diagram](image)

Figure 3.24 Diagram Showing the Possible Position of the M\(^+\) Ion Either Exterior or Interior to Fc[2.2]M.

3.5.6 \(^7\)Li N.M.R.

It was hoped that more evidence about the nature of the complex might be derived about from \(^7\)Li n.m.r spectroscopy. The ability of macrocyclic polyethers to bind alkali metals has been studied comprehensively by multinuclear n.m.r. Popov et al\(^{189}\) have reported the effects of the formation of lithium cryptates by this technique in several nonaqueous solutions. They also compared the behaviour of complexes of diaza-[18]-crown-6 (7) and of [18]-crown-6 (5).

In an attempt to gauge the ability of Fc[2.2]M to bind Li\(^+\), we have carried out a series of \(^7\)Li n.m.r.
experiments in which the binding ability of Fc[2.2]M's is compared with those of a series of crown ethers, by investigating the chemical shift changes in several different solvents. These results are summarised in Table 3.28.

Table 3.28  Li N.M.R. Study of Lithium Complexes in Various Solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Salt</th>
<th>[Li⁺]</th>
<th>(Crown)/([Li⁺])</th>
<th>Chemical Shift 7Li ppm (±0.0023)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>LiClO₄</td>
<td>0.025</td>
<td>0.0</td>
<td>0.9535</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>1.0657</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>0.0</td>
<td>1.4302</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>1.4583</td>
</tr>
<tr>
<td>THF</td>
<td>LiClO₄</td>
<td>0.025</td>
<td>0.0</td>
<td>0.5890</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.9535</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>0.0</td>
<td>1.5431</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>1.6546</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>0.0</td>
<td>0.4488</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.5013</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.6868</td>
</tr>
</tbody>
</table>

Cont. ...
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Salt</th>
<th>[Li⁺]</th>
<th>(Crown)/[Li⁺]</th>
<th>Chemical Shift (7Li ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyridine</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>0.0</td>
<td>0.9813</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>0.5</td>
<td>1.0561</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>1.0</td>
<td>1.1321</td>
</tr>
<tr>
<td><strong>15C5</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>MeOH</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiClO₄</td>
<td>0.025</td>
<td>0.0</td>
<td>0.9535</td>
</tr>
<tr>
<td></td>
<td>LiClO₄</td>
<td>0.025</td>
<td>1.0</td>
<td>1.0657</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>0.0</td>
<td>1.4302</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>1.0</td>
<td>1.9070</td>
</tr>
<tr>
<td><strong>THF</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiClO₄</td>
<td>0.025</td>
<td>0.0</td>
<td>0.5890</td>
</tr>
<tr>
<td></td>
<td>LiClO₄</td>
<td>0.025</td>
<td>1.0</td>
<td>1.4022</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>0.0</td>
<td>1.5431</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>1.0</td>
<td>2.2436</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>0.0</td>
<td>0.4488</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>0.5</td>
<td>1.0788</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>1.0</td>
<td>1.4988</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>2.0</td>
<td>2.1531</td>
</tr>
</tbody>
</table>

Cont. ...
Table 3.28 (Cont.)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Salt</th>
<th>[Li+]</th>
<th>[Crown]/[Li+]</th>
<th>Chemical Shift 7Li ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>LiI 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>0.9813</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>0.0</td>
<td>1.2627</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>1.8931</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>0.0</td>
<td>2.1732</td>
</tr>
<tr>
<td>18C6</td>
<td>LiClO₄ 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>0.9535</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>1.1218</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4302</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>1.3461</td>
</tr>
<tr>
<td>MeOH</td>
<td>LiClO₄ 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5890</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>1.0377</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>1.5431</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>1.8740</td>
</tr>
<tr>
<td></td>
<td>LiI 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4488</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>0.0</td>
<td>0.6588</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>0.7288</td>
</tr>
<tr>
<td>THF</td>
<td>LiClO₄ 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>Cont. ...</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>Cont. ...</td>
</tr>
<tr>
<td></td>
<td>LiI 0.025</td>
<td>0.0</td>
<td>0.0</td>
<td>Cont. ...</td>
</tr>
</tbody>
</table>
### Table 3.28 (Cont.)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Salt</th>
<th>[Li⁺]</th>
<th>[Crown]/[Li⁺]</th>
<th>Chemical Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7Li ppm</td>
</tr>
<tr>
<td>Pyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>0.0</td>
<td>0.9813</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>1.1241</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>1.1937</td>
</tr>
<tr>
<td>Fc[2.2]M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>LiClO₄</td>
<td>0.025</td>
<td>0.0</td>
<td>0.9535</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>0.0</td>
<td>1.4302</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>THF</td>
<td>LiClO₄</td>
<td>0.025</td>
<td>0.0</td>
<td>0.5890</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>LiTCNQ</td>
<td>0.025</td>
<td>0.0</td>
<td>1.5431</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>LiI</td>
<td>0.025</td>
<td>0.0</td>
<td>0.4488</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
</tbody>
</table>

Cont. ...
As stated earlier the stabilities of the complexes depends on the nature of the solvent. Popov and Shamsipur\cite{189}, when examining the binding ability of diaza-[18]-crown-6 (7) with that of [18]-crown-6 (5), showed that there was an inverse relationship between the stability of the complexes and the donicity of the solvents. The donicity of the solvents is expressed by Gutmann's donor number\cite{195}. In other words, when the donor number was high the stability of the complex was low, with the notable exception of pyridine.

We have used the procedure employed by Popov et al to study the properties of Fc[2.2]M. This involved rigorous pre-drying of all of the solvents, and measuring chemical shift changes with various lithium salts and a series of crown ethers. These simple experiments work on the principal that the bigger the chemical shift changes (from unbound Li$^+$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Salt</th>
<th>[Li$^+$]</th>
<th>[Crown]</th>
<th>Chemical Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^7$Li ppm</td>
</tr>
<tr>
<td>Pyridine</td>
<td>LiI</td>
<td>0.025</td>
<td>0.0</td>
<td>0.9813</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>0.0</td>
<td>1.0560</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>1.1333</td>
</tr>
</tbody>
</table>

Table 3.28 (Cont.)
to bound Li\(^+\) then the larger the interaction between macrocycle and alkali metal (Table 3.28). It is evident from this information that [12]-crown-4 and Fc[2.2]M show virtually the same binding capacity in solution. In solvents such as methanol where the donicity number is high and solvation ability of the solvent great, then the methanol competes with the ligand for binding the Li\(^+\). In solvents such as tetrahydrofuran more stable complexes form. However in comparison with [15]-crown-5 and even with [18]-crown-6, the Fc[2.2]M shows a weak interaction.

Popov\(^{196}\) reported that only one mass-average resonance was observed when studying the lithium cryptates in different solvents. This indicated that the exchange between the free and bound lithium is fast on the n.m.r. time scale. Ceraso and Dye\(^{76}\) have shown recently that at room temperature sodium exchange with [2.2.2]crypt in ethylenediamine solution is slow and separate \(^{23}\)Na resonances are obtained for the complexed and the free sodium ion.

In an attempt to show the lithium ion exchange with Fc[2.2]M, the experimental procedure of Ceraso and Dye has also been investigated. Initially the original experiments of Ceraso and Dye were repeated using [2.2.2] cryptand (11) and following the ion exchange by \(^{23}\)Na n.m.r. spectroscopy. The experiment was found to be easily reproducible and so the method
was repeated using Fc[2.2]M in ethylenediamine and monitoring by $^7$Li n.m.r. There was no evidence from the experiment that exchange between bound and unbound lithium was occurring. Initial attempts at trying to see an exchange process included: (a) variable temperature experiment (i.e. attempting to slow the exchange down) which were hampered by the fact that ethylenediamine has a high freezing point ($8.5^\circ$); (b) the use of a different solvent. However, on both accounts no exchange was seen. Finally attempts to observe sodium exchange by $^{23}$Na n.m.r. with Fc[2.2]M, by analogy with the original Ceraso and Dye experiment, also proved unsuccessful.

These n.m.r. experiments show that Fc[2.2]M behaves more like a crown ether than a cryptand. Its ability to bind lithium compares with that of [12]-crown-4. Though this result may seem surprising, when the size of cavity in Fc[2.2]M is approximately 2.1Å, Popov and Shamsipur also found the same unusual results when comparing [18]-crown-6 (5) to diaza-[18]-crown-6 (7). They showed, as we have here, that diaza-[18]-crown-6 (7) prefers $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. 

The above results strongly emphasize the variability of what factors affect the stability of a macrocyclic complex. While the relative sizes of the cation and of the macrocyclic cavity play an
important role, they are certainly not the unique, and not always the most important factors which determine the stabilities of macrocyclic complexes. The relative donor abilities of the heteroatoms of the macrocyclic rings are of considerable importance. The "hard-soft" character of the ions and of the solvents is also important.

3.5.7 Mössbauer Spectroscopy.

Work by Lesikar\textsuperscript{197} has shown that the electron-attracting substituents decrease the quadrupole splitting of ferrocene and Sano\textsuperscript{198} et al report that some ferrocene derivatives with electron-donating substituents give larger values of quadrupole splitting than that observed for ferrocene itself. Mössbauer spectroscopy could give insight into the effect of a bound ion in the Fc\([2.2]\)M cryptand, the results indicating whether there is any interaction between the iron atom of the ferrocene nuclei and the complexed cation. This phenomena was studied by Akabori and co-workers\textsuperscript{179}, who were interested to know whether there was just such an interaction between a bound alkali metal and the iron atom in a polyoxa \((n)\) ferrocenophane. They looked at the Mössbauer spectra of the compounds \((54a)\), \((54b)\) and \((54c)\) at room temperature. They found that the spectra \((54b)\) and
(54c) gave larger quadrupole splitting than that of the metal-free ferrocenophane (54a) (the isomer shifts change). From these results they suggested that if the alkali metal cation exerts an electron-attracting effect through the Na⁺ • • • O • • • C interaction on the cyclopentadienyl ring, compounds (54b) and (54c) can be expected to give smaller values of quadrupole splitting than that of metal-free ferrocenophane (54a). However, as described above, the complexes which incorporate sodium and lithium cations into the macrocyclic ether of ferrocenophane gave larger values of quadrupole splitting than that of (54a). The results obtained suggest that the larger values of quadrupole splitting estimated for these complexes may be ascribed to some interaction between the complexed alkali metal cation and the iron atom of the ferrocene nucleus, although the possibility of the effect of the counter anion (SCN⁻) on the d-orbital of the ferrocene nucleus can not be ruled out.

In order to assess the effect of a bound alkali metal ion in Fc[2.2]M, we have recorded the Mössbauer spectra for Fc[2.2]M and (Fc[2.2]M)(LiClO₄)
cryptate. In contrast with the work of Akabori and co-workers there was no change in the Mössbauer spectra in this case, reflecting the fact that the Li$^+$ in Fc[2.2]M cryptate has no direct interaction with the ferrocene bridging unit.

3.5.8 X-Ray Crystallographic Study of an Fc[2.2]M Cryptate.

The final and most undisputed evidence of the conformation of an Fc[2.2]M cryptate is from a single crystal X-ray diffraction study. This would show not only whether the Fc[2.2]M macrocycle has changed in conformation but also and most importantly the location of the bound cation. In fact considerable effort was taken to attempt to grow decent cryptate crystals for this purpose. Originally the (Fc[2.2]M)(LiClO$_4$) cryptate was examined, but both poor quality and twinned crystals were all that we managed to isolate. The only decent crystal which was eventually chosen showed no evidence of bound Li$^+$ ions!

Attention was then turned to the isolation of a cryptate complex of lithium trifluoromethanesulphonate. The trifluoromethanesulphonate provides a much better anion for the crystallographer to refine than the perchlorate ion. However, an attempt to isolate decent crystals of the (Fc[2.2]M)(LiSO$_3$CF$_3$) cryptate also proved unsuccessful.
The final effort at isolating decent Fc[2.2]M cryptate crystals, was attempted with silver iodide. Frensdorf\textsuperscript{35} has shown that the effect of substituting a nitrogen or sulphur heteroatom into a crown ether increases its ability to complex Ag\textsuperscript{+} ions. These observations were in agreement with those of Lotz and co-workers\textsuperscript{199} who showed that the relative stability of the silver-non-metal bond increases in the order $0 < S < N$. Evidently, it is not electrostatic forces which matter for the Ag\textsuperscript{+} complexes of nitrogen- and sulphur-containing cyclic polyethers, but rather the type of covalent bonding which is involved in many well-known Ag\textsuperscript{+} complexes.

In view of this attempts were made to isolate an (Fc[2.2]M)(AgI) cryptate. Not only did large cryptate crystals grow during the complexation procedure (Chapter 7), but preliminary photographs using the Lorenz camera suggested that they were of good quality. At the present time a data set is being collected on this material and hopefully a completed refinement will soon follow.

3.5.9 Discussion of Fc[2.2]M Cryptates.

All the spectroscopic evidence presented in this section of work clearly indicates that a bound cation seems to sit external to the cryptand cavity of the Fc[2.2]M macrocycle. However, even if a cryptate structure could be isolated in which the cation sat
inside the cryptand it is highly unlikely that there would be an interaction between the iron atom of the ferrocene moiety and the bound cation. This is endorsed by Akabori et al. who have reported a crystal structure of an alkali thiocyanate complex with a polyoxa (n) ferroceneophane (54c). They suggest that the crystallographic dimensions between the iron atom of the ferrocene and the incorporated sodium cation were too large for any interaction to take place. It was therefore unlikely that the iron atom is involved in any complex formation. In the case of the Fc[2.2]M structure which involves an amide-bridging unit between the ferrocene moiety and the macrocyclic skeleton, it seems even more unlikely that the iron atom could participate in any complex formation.

3.6 THE FERROCENE[2.2]DIMER(Fc[2.2]D).

Having completed a structural analysis of the Fc[2.2]M macrocycle and assessed its ability to bind cations, attention was then turned to its dimeric analogue (Fc[2.2]D). Fc[2.2]D offers an interesting material with which to compare Fc[2.2]M, and for this reason the structural and spectroscopic analysis were carried out following the same pattern defined in the previous section of work.
3.6.1 Synthesis of Fc[2.2]D.

As stated earlier (Section 3.2) the condensation of diaza-[18]-crown-6 (7) with 1,1'-ferrocene dicarboxyl chloride (45) under high dilution, results in the formation of two main products, Fc[2.2]M (40%) and Fc[2.2]D (29%). Even though the relative proportions of these two products are temperature dependent, they are also concentration dependent. Therefore, in order to increase the yield of dimer required for this part of the study, it was necessary to vary the reactant concentrations (Table 3.29).

Table 3.29 Showing the Varying Monomer/Dimer Yields with Varying Concentration.

<table>
<thead>
<tr>
<th>Amount of Solvent</th>
<th>%Monomer</th>
<th>%Dimer</th>
<th>Overall Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300ml</td>
<td>40%</td>
<td>26%</td>
<td>66%</td>
</tr>
<tr>
<td>270ml</td>
<td>36%</td>
<td>30%</td>
<td>66%</td>
</tr>
<tr>
<td>230ml</td>
<td>31%</td>
<td>35%</td>
<td>66%</td>
</tr>
<tr>
<td>200ml</td>
<td>27%</td>
<td>39%</td>
<td>66%</td>
</tr>
</tbody>
</table>
3.6.2 Spectroscopic Analysis of Fc[2.2]D.

As already stated in Section 3.2.1 considerable spectroscopic work has been carried out on the ferrocene macrocyclic amides (Fc[2.2]M and Fc[2.2]D), and this greatly simplifies the characterisation Fc[2.2]D prepared in the course of this project.

3.6.3 Mass Spectrometry and Combustion Analysis.

Mass spectrometry (electron ionisation) confirmed the presence of the dimeric molecule revealing a stable molecular ion (m/e = 1000), and the combustion analysis data were in good agreement with expected values (Chapter 7).

3.6.4 Infra Red Spectroscopy.

The dimeric product showed similar structural stretches and deformations to those seen for the monomeric material.

3.6.5 Mössbauer Spectroscopic Study on Fc[2.2]D.

As already discussed in Section 3.2.4, Mössbauer spectroscopy is a particularly valuable technique for the study of the structural properties of some types of organometallic compounds. In order to understand the Fc[2.2]D structure in relation to the other ferrocene amide derivatives a Mössbauer spectrum was recorded. Table 3.30 below shows that Fc[2.2]D behaves just like other ferrocene derivatives.
Table 3.30 Mössbauer Parameters

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Isomer</th>
<th>Quadrupole Shift mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Shift mm/s</td>
</tr>
<tr>
<td>298K</td>
<td>Ferrocene (Fc)</td>
<td>0.68</td>
</tr>
<tr>
<td>298K</td>
<td>Fe(CpCONHMe)₂</td>
<td>0.52</td>
</tr>
<tr>
<td>298K</td>
<td>Fc[2.2]M</td>
<td>0.52</td>
</tr>
<tr>
<td>298K</td>
<td>Fc[2.2]D</td>
<td>0.517</td>
</tr>
</tbody>
</table>

Table 3.31 ¹H N.M.R. Data of Fc[2.2]D (250 Hz;CDCl₃)

Assignment*  δ(23°)ppm

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0-CH₂</td>
<td>3.4-4.0 broad</td>
</tr>
<tr>
<td>N-CH₂</td>
<td></td>
</tr>
<tr>
<td>3'/4'-H</td>
<td>4.35 br</td>
</tr>
<tr>
<td>2'/5'-H</td>
<td>4.63 br</td>
</tr>
</tbody>
</table>

(* Number scheme refer to Figure 3.25).

3.6.6 ¹H N.M.R.

The ¹H n.m.r. spectrum of Fc[2.2]D (Appendix I) at ambient temperature shows two broad absorptions at δ4.35ppm and δ4.63ppm each representing 8 ferrocene protons and a very broad absorption between δ3.4 and δ4.0ppm representing 48 protons. Unlike Fc[2.2]M a complete assignment of the Fc[2.2]D at ambient temperature is very difficult (Table 3.31), because of the large number of the 48 protons involved.
3.6.7 13C N.M.R.

The 13C n.m.r. spectrum of Fc[2.2]D (Section 3.7.3) shows only 8 signals at ambient temperature of which those at 170ppm (C=O) and 80ppm (ipso carbon on the ferrocene) are sharp whilst the others are broad (as in the 1H n.m.r.). This broadening reflects the conformational flexibility of this material (Table 3.32).

Table 3.32 13C N.M.R. Data of Fc[2.2]D (62.5 MHz; CDCl3).

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>δ(23°C)ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-C</td>
<td>47.3 br</td>
</tr>
<tr>
<td>N-C</td>
<td>49.3 br</td>
</tr>
<tr>
<td>O-C</td>
<td>67.7 br</td>
</tr>
<tr>
<td>Ferrocene C-3'/4'</td>
<td></td>
</tr>
<tr>
<td>O-C</td>
<td>70.4 br</td>
</tr>
<tr>
<td>Ferrocene C-3'/4'</td>
<td></td>
</tr>
<tr>
<td>O-C</td>
<td>72.0</td>
</tr>
<tr>
<td>Ferrocene C-2'/5'</td>
<td>73.9 br</td>
</tr>
<tr>
<td>Ferrocene C-2'/5'</td>
<td>73.9 br</td>
</tr>
<tr>
<td>Ferrocene C(Ipso)</td>
<td>79.6</td>
</tr>
<tr>
<td>C=O</td>
<td>170.1</td>
</tr>
</tbody>
</table>

(* Number scheme refer to Figure 3.25)

3.6.8 Dynamic N.M.R. Studies on Fc[2.2]D.

The 1H and 13C n.m.r. of the Fc[2.2]D were
recorded by Hall and co-workers\textsuperscript{160} over a wide range of temperatures and a detailed analysis of this spectra suggests that two dynamic processes are involved. The coalescence temperature ((Tc) Section 3.2.6) for the rotation of the ferrocenecarbon-carbonyl bond is about \(-10^\circ\text{C}\). \(\Delta G^\ddagger\) for this process being calculated from the Gutowsky equation (Appendix I)\textsuperscript{159} at about 12 k Cal mol\(^{-1}\) (\(\Delta G^\ddagger = 50 \text{ kJ mol}^{-1}\)).

In addition there is a rotational barrier about the amide bond with a coalescence temperature of 60\(^\circ\text{C}\) (N-C signal), \(\Delta G^\ddagger\) for this process being the 16 k Cal mol\(^{-1}\) (\(\Delta G^\ddagger = 67 \text{ kJ mol}^{-1}\)). This is consistent with the barriers of rotation associated with conventional amide links. Hall et al\textsuperscript{160} were in no doubt that two dynamic processes were involved.

In view of this work it seemed logical extension to this work to investigate the solid state conformation of Fc[2.2]D for comparison with the solution data.

3.7 SOLID STATE STUDIES OF Fc[2.2]D.

3.7.1 X-Ray Crystallographical Study of Fc[2.2]D.

With the experience gained by X-ray crystallography on the simple ferrocene bis amide and the Fc[2.2]M structure, the next objective was to complete a crystallographic study on Fc[2.2]D\textsuperscript{200}. The 1,1'-bis(N-methylamido)ferrocene (46) and Fc[2.2]M, not only provided a useful model on which
to start the X-ray analyses, but also provided points of reference with which to compare Fc[2.2]D.

Initial work started by attempting to grow good quality crystals and the experience gained from the previous X-ray structural studies made this a relatively straightforward process. An orange crystal of approximate dimensions 0.18 x 0.24 x 0.35 mm was grown. This was glued to the end of a glass fibre, and preliminary photographs indicated that it was of good quality.

Unfortunately unlike the Fc[2.2]M and the 1,1'-bis(N-methylamido)ferrocene (46) which were monoclinic the Fc[2.2]D had a triclinic unit cell. This meant that a much more extensive data collection was required to give a good convergence refinement. Only a small data set could be collected and a convergence of no better than 9% was achieved (compared with 4.56% in 1,1'-bis(N-methylamido)-ferrocene and 3.44% in Fc[2.2]M). It is for this reason that the crystallographic data are only accurate to two decimal places. Bond lengths and bond angles may be found on microfiche in Appendix II.

The information obtained at this stage does nonetheless give an excellent indication of the crystallographic structure of Fc[2.2]D (Figure 3.26a, b and c). It was hoped that a further data collection would be possible in order to improve the
Figure 3.26a  Shows a Side View of Fc[2.2]D.
Figure 3.26b  Top View of Fc(2.2)D.
Figure 3.26c End View of Fe(2.2]D.
(* Oxygen's of the Carbonyls).
accuracy of some of the crystallographic values. However, on the information available at present it is possible to highlight some of the more interesting features. The average C-C distance (Section 3.3.1) in the cyclopentadienyl ring is 1.40Å which again gives good agreement with the value cited by Wheatley. The molecular dimensions of the ferrocene moiety when compared with analogous ferrocene derivatives suggest that there are no unusual properties.

The angles of interest (Section 3.3.1) are presented in Table 3.32. For comparison these are detailed together with those for the Fc[2.2]M and the 1,1'-bis(N-methylamido)ferrocene (46).

Table 3.33 Comparison of Structural Angles Found in Fc[2.2]D with those Found in Fc[2.2]M and 1,1'-bis(N-Methylamido)ferrocene (46).

<table>
<thead>
<tr>
<th>Derivative</th>
<th>Angle α°</th>
<th>Angle β°</th>
<th>Angle γ°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cp1</td>
<td>Cp2</td>
<td></td>
</tr>
<tr>
<td>Fc[2.2]D</td>
<td>2.55</td>
<td>35°</td>
<td>35°</td>
</tr>
<tr>
<td>Fc[2.2]M</td>
<td>1.2°</td>
<td>15.55°</td>
<td>50.23°</td>
</tr>
<tr>
<td>Fe(CpCONMe)₂</td>
<td>1.4°</td>
<td>1.59°</td>
<td>5.99°</td>
</tr>
</tbody>
</table>

From Table 3.33 it is clear that the cyclopentadienyl rings of each ferrocene unit are tilted towards the centre of the cryptand cavity. These deviations from planarity are in agreement with
some of the structural discussed in the X-ray crystal analysis of Fc[2.2]M (Section 3.3.5). As well as being titled the ferrocene rings adopt a staggered conformation at an angle 45.5°.

As stated in Section 3.6.7, a particularly noteworthy feature of the n.m.r. data for Fc[2.2]D is that two different dynamic processes are observed and it has been suggested that the barrier for rotation about the amide O=C-N bond has a higher activation energy (ΔG° = 67 kJ mol⁻¹) than that for rotation about the ferrocenecarbon-carbonyl bond (ΔG° = 50 kJ mol⁻¹). Consistent with this view, the amide units are approximately planar but each carbonyl group is tilted well away from the plane of the ferrocenyl cyclopentadienyl ring (β ≈ 35°). Each carbonyl group is disposed trans (antiperiplanar) relative to its neighbours, as previously proposed.

3.7.2 Size of the Binding Site in Fc[2.2]D.

Apart from the interesting features already highlighted for Fc[2.2]D, one of the most important aspects of this structure from the point of view of function, is the binding site and its cavity size (Figure 3.27a and Figure 3.27b). Fc[2.2]M showed a two dimensional cavity whereas Fc[2.2]D has a three dimensional cavity and instead of only four chelating oxygen atoms, in Fc[2.2]D there are eight oxygens available for binding. From the X-ray
crystallographic study it was hoped that a little more light would be thrown on the ability of Fc[2.2]D to bind metal ions and in particular, suggest the most suitable ions for complexation.

Whilst the molecular conformation of the cryptand is probably a poor representation of that to be expected for a cryptate (the oxygen bridges are lying external to the cavity for example Figure 3.26a), Chem-X allows us to estimate the internal diameter of cavity. Figure 3.27 shows the atomic distances of the eight oxygen atoms with respect to each other.

Oxygen-Oxygen Distance (Å)*

1. O₁₃-O₂₆ = 2.52Å
2. O₁₆-O₂₃ = 2.46Å
3. O₃₃-O₄₆ = 2.84Å
4. O₂₆-O₄₃ = 2.12Å

Average = 2.435Å

Figure 3.27a Shows the Intercrown O-O Distances.
Figure 3.27b Shows the Intercrown O-O Distances. (* Free space Å between oxygen atoms in the polyether bridges of Fc[2.2]M (assuming Van der Waals radius for O of 1.5 Å)).

It is important to note that the cavity size estimations were carried out based on C-C contacts and that the distance between the crown's "best planes" being about 4.73Å. Using Chem-X, an imaginary bound ion was placed in the internal cavity and its diameter was varied. The calculations suggest that the internal diameter is approximately (after attempting to mainpulate the crown in order to achieve maximum binding) 3.3Å. The value suggested by Figure 3.27 (4.37Å) was estimated from the data collected on the Fc[2.2]D structure with the crown's "best planes" in their most uncomprimising binding position.

The above calculation suggests that an ion of radius of 1.65Å would fit well into this cavity (Table 0.2). Of the alkali metals rubidium has the
optimum dimensions was later verified using ion-extraction experiments.

Plates (3.5 and 3.6) were generated using Chem-X showing the full crystallographic structures of Fc[2.2]D.

3.7.3 Solid State $^{13}$C N.M.R. Study on Fc[2.2]D.

As already discussed in great detail in Section 3.3.3 solid state $^{13}$C n.m.r. gives a very useful indication of the conformations of molecules within the unit cell. Figure 3.28a shows the solid state spectrum for Fc[2.2]D whereas Figure 3.28b shows the equivalent $^{13}$C solution spectrum.

There are several notable features which from this information (Table 3.34) may suggest an expected conformation for Fc[2.2]D: (i) there is only one carbonyl signal, suggesting that the carbonyl groups sit in a single conformation, (ii) there is only one C-N signal at 49.38ppm, suggesting that the amide planes sit in only conformation, and finally (iii) that the three signals shown in the solid state spectrum are a mixture of C-O and ferrocenyl C-C signals. The ipso carbons in the ferrocene moiety may be found at 78.93ppm using nonquaternary suppression experiments.
Figure 3.28a  Solid State $^{13}$C N.M.R. spectrum of Fc[2.2]D.

Figure 3.28b  Solution State $^{13}$C N.M.R. Spectrum of Fc[2.2]D (62.5 MHz, CDCl$_3$).
Table 3.34 Comparison of $^{13}$C Chemical Shifts in Solution and in the Solid State.

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>$\delta(23^\circ C)$ ppm</th>
<th>Solid State ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-C</td>
<td>47.3</td>
<td></td>
</tr>
<tr>
<td>N-C</td>
<td>49.3</td>
<td>49.375</td>
</tr>
<tr>
<td>O-C</td>
<td>67.7 br</td>
<td></td>
</tr>
<tr>
<td>Ferrocene C-3'/4'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-C</td>
<td>70.4 br</td>
<td>71.845</td>
</tr>
<tr>
<td>O-C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrocene C-3'/4'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-C</td>
<td>72.0</td>
<td></td>
</tr>
<tr>
<td>Ferrocene C-2'/5'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-C</td>
<td>73.9 br</td>
<td>78.931</td>
</tr>
<tr>
<td>Ferrocene C-2'/5'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrocene C(Ipso)</td>
<td>79.6</td>
<td>78.931</td>
</tr>
<tr>
<td>C=0</td>
<td>170.1</td>
<td>169.031</td>
</tr>
</tbody>
</table>

(* Number scheme refer to Figure 3.25).

From the solid state information listed in Table 3.34 there appears to be good agreement with the X-ray crystallographic data. The presence of one carbonyl resonance and one C-N resonance is consistent with the conformation of Fc[2.2]D found by crystallography. However, in order to verify this completely variable temperature solid state n.m.r. experiments should be carried out.
3.7.4 Discussion of the Solid State Features of Fc[2.2]D.

With a completed solid state structural analysis of Fc[2.2]D, attention was focussed (as in the case of Fc[2.2]M) on its cryptate (Figure 3.29). As with Fc[2.2]M, we were interested in exploring whether the iron atom of the ferrocene moiety becomes involved with the binding of a cation. In the Fc[2.2]D system the possibility of electron transfer processes between a ferrocene unit — reducible metal ion — ferrocene unit offers an interesting and exciting redoxable system. Therefore in order to discover the effect of a bound cation in the Fc[2.2]D, a similar chain of experiments, to those which proved so successful with the Fc[2.2]M cryptates, were also carried out.

Figure 3.29 Fc[2.2]D Cryptate.
3.8 PHYSICAL PROPERTIES OF Fc[2.2]D.

3.8.1 Cation Binding Properties.

Even though Bell and Hall had carried out extraction experiments of Fc[2.2]M, no extraction experiments had ever been attempted on the dimeric material. Therefore due to the success of using oxonol dyes as extracting agents (Section 3.4.2), the ion binding ability of Fc[2.2]D was monitored by the same procedure as used for Fc[2.2]M.

The results of the extraction experiments attempted on the Fc[2.2]D macrocycle are shown in Table 3.35. These show clearly that the Rb⁺ ion is most successfully extracted by Fc[2.2]D which is in good agreement with the crystallographic information in Section 3.7.1.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>3.29%</td>
</tr>
<tr>
<td>K⁺</td>
<td>4.13%</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>6.89%</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>5.67%</td>
</tr>
</tbody>
</table>

Unfortunately to our knowledge there is no analogous structure with which to compare the extraction ability of Fc[2.2]D currently in the literature. It is impossible to say at this stage whether the encapsulated cation sits internal or
external to the cryptand cavity. In order to assess the structural conformations of a Fc[2.2]D cryptate a series of complexation reactions were carried out.

3.9 SYNTHESIS OF Fc[2.2]D CRYPTATES.

The complexes prepared with the Fc[2.2]D macrocycle are present in Table 3.36. The reason for preparing the rubidium triflate complex was in an attempt to grow decent single crystals for an X-ray structural study. Whereas the purpose of preparing a Fc[2.2]D/rubidium TCNQ complex was in order to carry out electrical measurements (Chapter 4).

Table 3.3.6 Complexes Prepared from Fc[2.2]D.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Stiochiometry</th>
<th>Element Analysis</th>
<th>Yields</th>
<th>Mol.Weight</th>
<th>Found (Calc)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc[2.2]D/RbCF₃SO₃</td>
<td>1:1</td>
<td></td>
<td>47.23</td>
<td>5.11</td>
<td>4.42</td>
</tr>
<tr>
<td></td>
<td>1234</td>
<td></td>
<td>(47.65)</td>
<td>(5.19)</td>
<td>(4.54)</td>
</tr>
<tr>
<td>FC[2.2]D/RbTCNQ</td>
<td>1:1</td>
<td></td>
<td>55.39</td>
<td>5.17</td>
<td>8.47</td>
</tr>
<tr>
<td></td>
<td>1289</td>
<td></td>
<td>(55.86)</td>
<td>(5.27)</td>
<td>(8.69)</td>
</tr>
</tbody>
</table>

3.9.1 Spectroscopic Analysis of the Fc[2.2]D Cryptates.

Unfortunately time did not allow for a larger series of complexes to be prepared (compared with the Fc[2.2]M cryptates). However, the complexes which were isolated, have been characterised in the
following manner.

3.9.2 Mass Spectrometry.

Electron ionisation mass spectrometry was carried out on the \((\text{Fc}[2.2]D)(\text{RbTCNQ})\) complex and fragmentation patterns showed the presence of both \(\text{Fc}[2.2]\)M and TCNQ. However, and as shown in the case of the \(\text{Fc}[2.2]\)M cryptates, no complex formation of the \((\text{Fc}[2.2]D)\text{Rb}^+\) cryptate was observed.

As stated in Section 3.2.2 on the mass spectrometry of the \(\text{Fc}[2.2]\)M cryptates, f.a.b. mass spectrometry was successful at showing a \((\text{Fc}[2.2]\)M)\text{Li}^+\) complex. For this reason an \((\text{Fc}[2.2]\)D)(\text{RbTCNQ})\) complex has been submitted and the results are eagerly awaited.

3.9.3 Infra Red Spectroscopy.

As shown in the work on the \(\text{Fc}[2.2]\)M cryptates, infra red spectroscopy proved useful for establishing complex formation. In just the same manner adopted for the \(\text{Fc}[2.2]\)M cryptates, so infra red spectroscopy results were recorded for the \(\text{Fc}[2.2]\)D cryptates. These spectra may be seen in Figure 3.30a which shows the original \(\text{Fc}[2.2]\)D macrocycle and Figure 3.30b the \((\text{Fc}[2.2]\)D)(\text{RbSO}_3\text{CF}_3)\) cryptate. Again characteristic changes take place in the spectrum of the ligand all of which were discussed earlier (Section 3.23).
Figure 3.30a Infra Red Spectrum of Fc[2.2]D.

Figure 3.30b Infra Red Spectrum of Fc[2.2]D/RbCO_3CF_3.
3.9.4 **$^1$H N.M.R.**

As before another useful way of discovering more information about complexation is via chemical shift changes in $^1$H n.m.r. This was discussed in detail in Section 3.5.2 and following the previous experiments, the $^1$H n.m.r. spectrum of Fc[2.2]D and (Fc[2.2]D)(RbSO$_3$CF$_3$) were recorded in deuterochloroform (Table 3.3.7).

Table 3.3.7 $^1$H N.M.R. Chemical Shift Differences Between Fc[2.2]D and Fc[2.2]D RbCF$_3$SO$_3$ (@ 400 MHz CDCl$_3$).

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>Fc[2.2]D</th>
<th>Fc[2.2]D Rb</th>
<th>$\Delta\delta$,ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-CH$_2$</td>
<td>3.46-4</td>
<td>3.5-3.98</td>
<td>0.04/0.02</td>
</tr>
<tr>
<td>N-CH$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 /4-H</td>
<td>4.35</td>
<td>4.35</td>
<td>-</td>
</tr>
<tr>
<td>2 /5 -H</td>
<td>4.63</td>
<td>5.63</td>
<td>-</td>
</tr>
</tbody>
</table>

(* Number scheme refer to figure 3.29).

The large number of protons involved makes a complete assignment of the spectrum Fc[2.2]D very difficult. However, is clear from the table of results is that the complex's regions of -CH$_2$- chemical shifts are different from those of the original Fc[2.2]D molecule. In fact the region associated with the methylene bridge units appears to constrict in the complex compared with the uncomplexed molecule. To actually say what is
happening is difficult, all that is clear is that the bound Rb\(^+\) ion effects only the methylene bridge units and not the ferrocene bridging units. In order to gain more insight \(^{13}\)C n.m.r. spectroscopy was attempted.

### 3.9.5 \(^{13}\)C N.M.R.

As mentioned in the earlier section with the Fc[2.2]M cryptate, \(^{13}\)C n.m.r. is a much more sensitive technique for studying conformational changes. Table 3.38 below shows the \(^{13}\)C n.m.r. shift differences associated with the complexed and uncomplexed Fc[2.2]D cryptand.

#### Table 3.38 \(^{13}\)C N.M.R. Chemical Shift Differences Between Fc[2.2]D and (Fc[2.2]D)(RbCF\(_3\)SO\(_3\)) (\(@ 100\) MHz: CDCl\(_3\)) Room Temperature.

<table>
<thead>
<tr>
<th>Assignment*</th>
<th>Fc[2.2]D</th>
<th>Fc[2.2]D Rb</th>
<th>(\Delta S, \text{ppm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-C</td>
<td>47.188</td>
<td>47.209</td>
<td>0.021</td>
</tr>
<tr>
<td>N-C</td>
<td>49.213</td>
<td>49.231</td>
<td>0.018</td>
</tr>
<tr>
<td>C-3'/C-4'</td>
<td>67.618 br</td>
<td>67.562 br</td>
<td>0.056</td>
</tr>
<tr>
<td>C-4'/C-3'</td>
<td>70.389 br</td>
<td>70.102 br</td>
<td>0.287</td>
</tr>
<tr>
<td>C-2'/C-5'</td>
<td>72.641</td>
<td>72.645</td>
<td>0.004</td>
</tr>
<tr>
<td>C-2'/C-5'</td>
<td>73.719</td>
<td>73.715</td>
<td>0.004</td>
</tr>
<tr>
<td>C=O</td>
<td>79.439</td>
<td>79.430</td>
<td>0.009</td>
</tr>
<tr>
<td>C=O</td>
<td>169.811</td>
<td>169.939</td>
<td>0.128</td>
</tr>
</tbody>
</table>

(* Number scheme refer to Figure 3.29).
Clearly from the results presented about the large chemical shift difference is associated with C-O region of the ether linkages in the methylene bridges. However, because of the various dynamic processes (Section 3.67) and the large number of carbon atoms involved makes a complete structural assessment difficult.

3.9.6 Mössbauer Spectroscopy.

The effect of complexing a Rb+ ion with the Fc[2.2]D structure produced no significant changes in the Mössbauer spectrum. The spectrum of the (Fc[2.2]D)(RbSO3CF3) is shown in Figure 3.31a and is identical with that of Fc[2.2]D Figure 3.31b.

![Mössbauer Spectrum of (Fc[2.2]D)(RbSO3CF3)](image)

Figure 3.31a Mössbauer Spectrum of (Fc[2.2]D)(RbSO3CF3).

Attempts at trying to isolating single crystals of Fc[2.2]D/rubidium trifluoroacetate proved unsuccessful. Work is being continued to attempt to produce not only a good quality crystal but also to refine and solve a Fc[2.2]D cryptate crystal structure. Even though we did not succeed in producing a (Fc[2.2]D)Rb⁺ crystal structure, some of the Plates (3.7 and 3.8) give an indication of the possible orientation of the Rb⁺ ion with the macrocycle. These crystallographic structures were generated using Chem-X\textsuperscript{169}, when trying to assess the correct ion to bind with the Fc[2.2]D structure.
Plate 3.7

Plate 3.8
3.9.8 Discussion of Fc[2.2]D Cryptates.

Even though small progress has been made with the assessment of a Fc[2.2]D cryptate structure, it is obvious that there is considerably much more to investigate. The presence of the two diaza-[18]-crown-6 (7) units within the structure of the Fc[2.2]D offer an exciting prospect for ion-binding of not only alkali-metals, but also alkaline earth-metals and transition metals. Whether or not such a bound ion would be affected by the ferrocene moieties, in the light of this work, looks uncertain.
CHAPTER 4

RESULTS AND DISCUSSION II

The synthesis and properties
of some novel electrically active
crown ether/cryptate complexes

The resistance of a conductor is a property of
the whole conductor between its contact electrodes.
But if we want to compare, say copper with glass,
then a quantity which is independent of the amount of
material present must be defined.

Consider a conductor of length \( l \) and of
constant cross-sectional area \( A \). If the resistance
between its ends is \( R \), then the resistivity \( \rho \) of
the conducting material may be defined as follows:

\[
\rho = \frac{RA}{l}
\]
4. RESULTS AND DISCUSSION II

4.1 ELECTRICAL PROPERTIES OF SEMI-INSULATING AND SEMICONDUCTING MATERIALS.

4.1.1 Basic Classification.

The current flowing through a conductor is proportional to the potential difference between the ends of the conductor provided the physical conditions of the conductor (particularly the temperature) are held constant.

If $V$ is the potential difference across the conductor and if $I$ is the current flowing through it, Ohm's law tells us that:

$$\frac{V}{I} = \text{constant.}$$

It is one thing to know Ohm's law, it is another thing to know the circumstances in which Ohm's law is valid, hence resistance must be defined.

The resistance of a conductor is a property of the whole conductor between the contact electrodes but if we want to compare, say copper with glass, then a quantity which is independent of the amount of material present must be defined.

Consider a conductor of length ($L$) and of constant cross-section ($A$). If the resistance between its ends is $R$, then the resistivity ($\rho$) of the conducting material may be defined as follows:
Conductance \( (\sigma_0) \) may then be defined as the reciprocal of resistivity and from the equation above it is possible to derive an expression from which the d.c conductivity, at varying temperatures, can be deduced.

\[
\sigma_0 = \frac{1}{R} \cdot \frac{L}{A} \quad \text{(units S cm}^{-1} \text{ or } \Omega^{-1} \text{ cm}^{-1})
\]

Materials may be classified as metals, semiconductors\(^{201}\) or as insulators, depending on their conductivity, although the limits of conductivity which mark the boundaries between the three classes are somewhat arbitrary. At room temperature if the d.c conductivity lies in the range \(10^6-10^3 \text{ S cm}^{-1}\), the material is said to be a metal whereas insulators have conductivity ranges < \(10^{-12} \text{ S cm}^{-1}\). Typical semiconductors have a conductance range of \(10^{-3}-10^{-7} \text{ S cm}^{-1}\), although not all materials with conductivities within this range are semiconductors. Substances which fall into the range of \(10^{-7} < \sigma < 10^{-12} \text{ S cm}^{-1}\) may be regarded as "poor" or semi-insulators". 
4.1.2 Band Theory.

Band theory arises from a consideration of the consequence of atomic orbitals on individual atoms in a lattice combining together to form molecular orbitals. When two atoms are brought together the combination of atomic orbitals produces a bonding and an anti-bonding orbital (Figure 4.1). As a third atomic orbital is introduced the range of energies increases and a third molecular orbital is formed within the range (Figure 4.1). As more atoms are introduced into the system, the range of energies become effectively continuous and are known as a bandwidth. In fact, usually more than one band is available, for example when an atom has p-orbitals then another band will be formed (p-band), similar to that for the s-orbitals, but of higher energy (Figure 4.2).

Band filling can be thought of as analogous to the Aufbau principle for atoms. Electrons are placed in the lowest energy states and then successively higher energy states are filled. The highest occupied state is called the Fermi level. Only the states that are near in energy to the Fermi level are readily accessible and influence physical properties.
If the highest filled band (often called the valence band) is only partially full, empty states will exist infinitesimally close to the Fermi level, and those electrons nearby in energy can take part in electrical conduction. On the other hand, if the highest filled band is entirely full, and there is some band gap between it and the next lower band (conduction band), then a relatively large amount of energy (compared with the available thermal energy)
will be needed to put electrons into states where they will be available for conduction and where they may influence other properties. Representative energy band diagrams for a metal (a) and insulator (b) and a semiconductor (c) are shown in Figure 4.3.

(a) Metal    (b) Insulator    (c) Semiconductor
(FL = Fermi Level)

Figure 4.3 Energy Band Diagrams.

4.1.3 Metals.

Metals are characterised by an upper energy band which is approximately half filled. Such a band can originate for two reasons; (i) overlap can occur between the valence and conduction bands; or (ii) the atoms may have insufficient valence electrons to fill the available states in the valence band (e.g. in alkali metals).

Since vacant electron energy levels exist in close proximity to the levels which are occupied, electrons can be readily excited to higher levels
when an electric field is applied and current can flow. The high conductivity of metal arises because of the large number of electrons with energies in the topmost partially filled band (approximately one per atom).

One of the properties of a metal is that its conductivity decreases with increasing temperature. In a metal the mobile electrons are accelerated by electric forces until they collide inelastically with a lattice ion. They are then accelerated again until they collide with another ion. When this involves a large number of electrons, the macroscopic effect is that of a steady current flow. It can be seen that the electron gains drift velocity only between collisions. Hence, conduction can be related to the frequency of collisions with the lattice ions. If the temperature increases then the amplitude of vibrations of the lattice ions will increase, reducing the time between collisions. Consequently, the conductivity decreases with increasing temperature.

4.1.4 Insulators.

If a material has a full valence band and an empty conduction band, which is separated by a forbidden band gap, then it is either an insulator or a semiconductor. An insulator is characterised by a conduction band which is virtually empty, both under
conditions of thermal equilibrium and when an electric field is applied. This means that the forbidden gap separating the energy levels of the valence and conduction has to be so large that electrons cannot be thermally excited from the valence to the conduction band.

4.1.5 Intrinsic Semiconductors.

If the valence and conduction bands are separated by a narrow forbidden energy gap, then at all temperatures above absolute zero there may be some electrons in the conduction band and some holes in the valence band (i.e. even though no external exciting radiation or electric field is applied). Since the conduction band is then partially filled and the valence band is partially empty, further energy can be absorbed from an external electric field by the electrons in the conduction band and by the holes in the valence band. For such an "intrinsic" semiconductor the density, \( n_i \), of electrons in the conduction band is equal to the density, \( p_i \), of holes in the valence band and both classes of carrier will contribute to the current.

4.1.6 Extrinsic Semiconductors.

The usefulness of semiconductors in electronic devices is ultimately bound up, not with the pure or "intrinsic" type of semiconductor referred to above, but with the modifications brought about in such
materials by incorporating relatively small percentages of selected impurities in the host crystal. The resulting material is known as an impurity or "extrinsic" semiconductor. The basic features of extrinsic semiconduction can be simply demonstrated with reference to germanium, which in pure form is an intrinsic semiconductor.

Germanium is tetravalent. In single crystal form each germanium atom is surrounded by four nearest neighbours at the corners of the regular tetrahedron. Each of the four valence electrons

\[ \begin{align*}
\text{Ge} & \quad \text{Ge} \quad \text{Ge} \\
\text{Ge} & \quad \text{Ge} \quad \text{Ge}
\end{align*} \]

Figure 4.4(a)

combines with a similar electron belonging to one of the near-neighbour atoms to form a covalent bond. This arrangement is shown diagrammatically in two dimensions in Figure 4.4(a). Each pair of lines represents a covalent bond. In Figure 4.4(b) the modification of this diagram is shown when one of the germanium atoms is replaced by a pentavalent atom such as arsenic. Only four of the five valence electrons of the arsenic atom can form covalent
bonds, the fifth remains associated with the arsenic nucleus. The microscopic energy band picture in the vicinity of the arsenic atom is illustrated in Figure 4.5. A potential well has been shown at the site of the arsenic atom, in which there is a localised electron energy level just below the bottom of the conduction band. At very low temperatures the fifth valence electron will occupy this level. Since the level is very near the bottom of the conduction band, only a small amount of thermal energy is required to excite this electron into the conduction band. The arsenic atom is then positively ionised and the liberated electron is free to move through the crystal.

![Figure 4.5. Energy Band Diagram in the Vicinity of an Arsenic Atom Embedded in a Germanium Lattice.](image)

A pentavalent atom like arsenic in the germanium lattice is called a donor impurity, since it has in effect donated a conduction electron. When the
concentration of free electrons in the conduction band exceeds the concentration of positive holes in the valence band, the conductivity is termed "n-type".

Trivalent atoms such as indium replacing germanium atoms produce a concentration of holes in the valence band which exceeds the concentration of electrons in the conduction band. The resulting conductivity is termed "p-type" (holes have positive charge). Such impurities are called "acceptors" since they accept an electron from the valence band in their ionised state. The mechanism is illustrated in Figure 4.6.

![Figure 4.6. Energy Band Diagram in the Vicinity of an Indium Atom Embedded in a Germanium Lattice.](image)

In any practical semiconductor both donor and acceptor impurities will be present although, by design, one impurity type is usually dominant. Since in thermal equilibrium the general tendency is for electrons to occupy the lowest levels, one finds that
the acceptors are ionised as far as possible by the extra electrons available from donor atoms. In consequence, as far as impurity carrier density is concerned, this is of a type equivalent to the dominant impurity present. If the densities of donors and acceptors are \( N_d \) and \( N_a \) respectively then materials for which \( N_d > N_a \) are n-type, and if \( N_a > N_d \) they are p-type. If \( N_a = N_d \) the material is said to be "compensated" and as far as free carrier densities are concerned it will behave like intrinsic material. Its conduction properties will differ from intrinsic material, however, because of the extra scattering of free charges introduced by the ionised donor and acceptor atoms.

Foreign atoms in a perfect crystal are referred to as chemical impurities. From the viewpoint of making semiconductor devices, however, impurities is perhaps not a good word, since foreign atoms are deliberately introduced in controlled concentrations to produce desired electrical properties. This act of deliberately introducing impurities into a crystal is called "doping".

### 4.2 ORGANIC CONDUCTING MATERIALS.

Until 1900 organic compounds were thought to be electrical insulators with a room temperature conductance of \( \sigma \) (298 K) \( 10^{-9} - 10^{-14} \) S cm\(^{-1} \). However, in the early part of the 20th century it was
suggested that organic compounds might show significant electrical conductivity\textsuperscript{204,205}. Despite this it was not until the early 1960's that a semiconducting organic compound was synthesised. Melby\textsuperscript{206} produced a new good electron acceptor, 7,7,8,8-tetracyanoquinodimethane (TCNO) which readily forms radical anions on reduction (Equation 4.1).

\begin{equation}
\begin{array}{c}
\text{CN} = y = \text{CN} - e^- \\
\text{CN} = y = \text{CN} - e^-
\end{array}
\end{equation}

Equation 4.1.

At about this time Little\textsuperscript{207} proposed a mechanism whereby superconductivity could arise in organic compounds even at room temperature. Little's model structure consisted of a conjugated carbon chain (Figure 4.7) which acted as a conduction path for electrons with polarisable side groups, for example cyanine dyes.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{conjugated-chain.png}
\caption{Little's Proposed Model for an Organic Superconductor.}
\end{figure}

Little suggested that an electron moving through the conduction band, along the conjugated chain,
would repel the polarisable valence electrons in the side groups. This would create a region of high positive charge density centred around the chain which would attract a second electron. By this means it would be possible to form a Cooper pair in which the electrons, would oscillate back and forth as if attached by a spring (analogous to a metallic superconductor). Little's theory was very controversial but has led to a great increase in interest in potential organic metals, though an organic molecule approaching this model has yet to be synthesised.

In 1970 a new good electron donor was synthesised tetrathiofulvalene (TTF)\textsuperscript{208}. This forms a stable charge transfer complex and will undergo one-electron oxidation to give a stable radical cation (Equation 4.2).

\[
\begin{align*}
\text{SSS} & \rightleftharpoons \text{SSS}^+ \\
\text{-e}^- & \rightleftharpoons \text{+e}^-
\end{align*}
\]

Equation 4.2.

Organic metals are charge-transfer complexes which consist of donor (D) and acceptor (A) molecules. These organic crystals are of two forms; (i) Both donor and acceptor molecules are organic and are either neutral or charged radicals in the
crystals. The molecules tend to be planar and form segregated stacks of donor and acceptor molecules, e.g. TTF-TCNQ (Figure 4.8)\(^{209}\).

(ii) The donor (or acceptor) is organic and is a radical cation (anion) within the crystal. It forms segregated stacks with closed-shell negative (positive) counter ions in the crystal, e.g. \((\text{TMTSF})_2\text{ClO}_4\) (Figure 4.9).

Charge-transfer compounds have considerably higher conductivities, as shown in Table 4.1. even in some cases approaching those of metals.
Figure 4.9. Crystal Structure of \((\text{TMTSF})_2\text{ClO}_4\)

Table 4.1 Conductivity of Charge-Transfer Compounds.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\sigma)</th>
<th>(n)</th>
<th>(\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>(6.6 \times 10^5)</td>
<td>(5.8 \times 10^{22})</td>
<td>70</td>
</tr>
<tr>
<td>Cu</td>
<td>(6.4 \times 10^5)</td>
<td>(8.5 \times 10^{22})</td>
<td>47</td>
</tr>
<tr>
<td>Hg</td>
<td>(4.4 \times 10^4)</td>
<td>(4.2 \times 10^{22})</td>
<td>6.6</td>
</tr>
<tr>
<td>InSb</td>
<td>(3.5 \times 10^2)</td>
<td>(6.5 \times 10^4)</td>
<td></td>
</tr>
<tr>
<td>Si (n-type)</td>
<td>(4 \times 10^1)</td>
<td>(1 \times 10^{18})</td>
<td>240</td>
</tr>
<tr>
<td>TCNQ salts</td>
<td>(1 - 1000)</td>
<td>(\approx 10^{21})</td>
<td>4</td>
</tr>
<tr>
<td>Perylene.I3</td>
<td>(2 \times 10^1)</td>
<td>(1.3 \times 10^{20})</td>
<td>(\approx 1)</td>
</tr>
<tr>
<td>Anthracene</td>
<td>(\ll 10^{-14})</td>
<td>(\ll 10^5)</td>
<td>(\approx 1)</td>
</tr>
<tr>
<td>Teflon</td>
<td>(\ll 10^{-14})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(All values at room temperature, \(\sigma\) = conductivity in \(\Omega^{-1}\) cm\(^{-1}\), \(n\) = density of carriers in cm\(^{-3}\), and \(\mu\) = mobility in cm\(^2\) V\(^{-1}\) s\(^{-1}\)).
In many of the radical salts, the donors and acceptors are arranged in separate stacks, as shown in Figure 4.10.

\[
\begin{array}{cccc}
D & A & D & A \\
D & A & D & A \\
D & A & D & A \\
\end{array}
\]

Figure 4.10 Arrangement of the Donor/Acceptor Molecules.

In a crystal of TTF-TCNQ, the "molecules" in each stack are also tilted with respect to the axis of the stack; adjacent columns being arranged to form a herringbone pattern (Figure 4.11). A common feature of all radical ion salts and complexes is the planarity of the individual component "molecules".
The metallic conductivities referred to in Table 4.1 appear only in those compounds in which D and A are in separate stacks. This gives rise to the term "segregated stacking". The direction of high conductivity is along these stacks. The short interplanar distances between adjacent molecules (3.17Å for TCNQ and 3.47Å for TTF) allow significant interaction between π-molecular orbitals of neighbours, leading to formation of a band (that is, a restricted range of allowed energies for the electrons) in the solid. The tight-binding theory usually employed to describe the bands is analogous to simple Hückel molecular orbital theory for an infinite linear polyene. The highest occupied π-molecular orbital (π-HOMO), for a donor, or lowest unoccupied π-molecular orbital (π-LUMO) for an acceptor, plays the role of π-atomic orbitals in Hückel theory. The formation of the donor is an oxidation process. Electrons are removed, leaving the π-HOMO partially occupied and electrical conduction becomes possible. With the formation of the acceptor, reduction takes place. Electrons are added, leaving the π-LUMO partially occupied and making electrical conduction possible.

The anisotropy that is observed in the electrical conductivity and other properties of TTF-TCNQ is a general characteristic of organic charge-transfer
salts with segregated stacks. In fact such anisotropy is usually so pronounced that the materials are often treated as one-dimensional structures, that dimension being the direction of high conductivity. The anisotropy arises from the much greater π-overlap in the stacking directions. The nearest neighbours in the stacking direction are 3 to 4 Å away, whereas nonstacking neighbours often may be separated by as much as 10 to 15 Å. In addition the π-orbitals are much better orientated for interaction along the stacking direction. The

![Diagram showing electronic states mix to form energy bands.](image)

Figure 4.12 Electronic States Mix to Form Energy Bands P-Orbitals.
term "quasi-one-dimensional" is commonly used to describe the nearly uniaxial nature of the physical properties of such organic charge-transfer salts.

The temperature dependence of the electrical conductivity of TTF-TCNQ is also prototypical for the class of organic metals. Conductivity reaches a maximum at some temperature, usually less than ambient temperature. Above this point, the temperature dependence is metallic, that is, conductivity increases as temperature decreases. Below it the temperature dependence is that of a semiconductor. The temperature dependence of the conductivity (\(\sigma\)) or resistivity (\(\rho\)) of a semiconductor and metal are characterised by the following expressions. The electrical conductivity

\[
\text{Semiconductor } \sigma(T) = \sigma_0 e^{-E_0/RT}
\]
\[
\text{Metal } \sigma(T) = 1/\rho
\]

of a metal decreases with increased temperature whereas a semiconductor conductivity increases with increased temperature.

4.2.1 Superconductors.

Superconductivity is one of the striking discoveries of 20th century science. When certain metals are cooled past a critical temperature, \(T_c\), which is characteristic of the material, their
electrical resistance abruptly vanishes and they cannot be penetrated by an applied magnetic field. This magnetic flux exclusion is called the Meissner effect. A sufficiently large magnetic field will overcome the Meissner effect and restore the normally conducting state.

In 1911, Onnes\textsuperscript{211} of the University of Leiden first observed superconductivity in mercury metal at liquid helium temperatures. Soon afterwards superconductivity was observed in many metal oxides and metal alloys. An explanation for the unusual phenomena occurring in superconductors had to wait until 1957, when Baren, Cooper and Schrieffer (i.e. BCS theory), at the University of Illinois, developed the theory that is currently accepted. Superconductivity is anomalous in comparison with the mechanisms so far mentioned and cannot be explained in terms of band theory. It is thought to arise when electrons in a conductor form loosely bound pairs, called "Cooper pairs". At low temperature these "Cooper pairs" form as a result of an interaction between conduction electrons and phonons (lattice vibrations). The electrons in the "Cooper pair" move at the same speed but in opposite directions. A negatively charged electron travelling through a lattice of fixed positive ions will attract these ions to itself. Another electron in the lattice will
be attracted to this area of high positive charge density and hence can become correlated to the motion of the first electron. At this stage, the restoration force will act on the positive ions. These will overshoot their equilibrium positions momentarily giving rise to a region of low positive charge density. So the electrons in the "Cooper pair" will vibrate back and forth as a result of the changing charge densities set up in the lattice due to their motion. These "Cooper pair" are sufficiently different from electrons to be treated as a separate species and it is the highly co-ordinated motion of these "Cooper pairs" that is thought to produce superconductivity.

Resistance in metals arises from the scattering of electrons by thermal vibrations of the lattice. Each inelastic collision with a lattice ion results in a decrease in the electrical current accompanied by an increase in the vibrational energy stored in the lattice. This suggests that resistance will be zero at absolute zero as there will be no thermal vibrations of the lattice atoms.

Superconductivity, however, can be observed at finite temperatures. This is because the "Cooper pairs" gain a net momentum from an applied field and the result is that the energy required to scatter a "Cooper pair" is less than the binding energy between
the electrons. However, the binding energy is still very low so superconductivity remains a low temperature phenomenon, specifically below the critical temperature for the particular metal. Above these temperatures, vibrational energy of the lattice is enough to separate the "Cooper pair" electrons and the resistance will jump to a finite value (Figure 4.13).

![Graph Illustrating the Critical Temperature of Superconductivity](image)

**Figure 4.13** Graph Illustrating the Critical Temperature of Superconductivity.

### 4.2.2 Organic Superconductors

Over the years, a number of superconducting organic compounds have been reported. In 1980, Bechgaard and Jerome found that (TMTSF)$_2$PF$_6$ under a pressure of 12 kilobars behaves as a superconductor.
below about 1 K. Soon after this discovery, a number of other salts containing TMTSF and inorganic ions with a stoichiometry of (TMTSF)$_2$X joined (TMTSF)$_2$PF$_6$ among the ranks of organic superconductors$^{212}$. Although not all the salts of the formula (TMTSF)$_2$X become superconductors, the PF$_6^-$, AsF$_6^-$, TaF$_6^-$, SbF$_6^-$, ReO$_4^-$ and ClO$_4^-$ salts are among those that do.

More recently, some salts of the molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have been reported to become superconducting at low temperatures and high pressure. Like the TMTSF salts, BEDT-TTF salts are also grown electrochemically, but in this case, many phases form simultaneously. The existence of multiple phases initially caused some confusion and certainly poses experimental challenges. (BEDT-TTF)$_2$I$_3$ has been reported by Soviet and Japanese groups to become superconducting at 8 K under pressure, a new record for the highest Tc of an organic superconductor. In addition to the quasi-one-dimensional organic charge-transfer salts, some organic polymers have shown unusually high conductivity. This will be discussed in more detail in Chapter 5.

In the last two years there has of course been a revolution in superconductivity technology; arising from the discovery of superconductivity behaviour at above liquid nitrogen temperatures, in mixed metal
oxides\textsuperscript{213}. Early work centered around materials containing lanthanides\textsuperscript{214}, but critical temperatures as high as 120-130 K have now been attained using thallium based materials\textsuperscript{215}. Such discoveries would seem to make the TTFTCNQ superconductor technology irrelevant, however, exploitation of these new materials is currently hampered by problems of fabrication and long term stability. It is not clear whether or not the mechanisms of the superconductors in high critical temperature structures are similar to those in more traditional materials. Consequently, the organic superconductors still remain of great interest from the theoretical point of view, and have the virtue of relatively easy structural manipulation and control. It would therefore seem that research into these compounds will continue for sometime to come.

4.2.3 Properties of Anion-Radical Derivatives and Complexes of 7,7,8,8-Tetracyanoquinodimethane.

The ability of quinones to form stable solid complexes with aromatic amines has been known for many decades\textsuperscript{216}, and in modern terms such complex formation is ascribed to interaction of the electron poor $\pi$-orbital system of the quinone ($\pi$-acid or acceptor) with the electron-rich $\pi$-orbitals of the amine ($\pi$-base or donor). Some of the solid complexes formed between aromatic diamines and relatively
strong π-acids, such as polyhalo quinones exhibit electron paramagnetic resonance (ESR) absorption indicating unpairing of electron spins. Some complexes of this type are classed as semiconductors because of exponential variation of their electrical resistivities with temperature. For example, there has been considerable interest in the semiconductor character of chloranil/p-phenylene-diamine-type complexes, whose resistivities are of the order of $10^4$ to $10^8 \Omega\text{cm}$ at room temperature. The unique character of TCNQ as a π-acid derives partly from the high electron affinity of the polyene system conferred by the powerful electron-withdrawing effect of the four cyano groups and partly from the planarity and high symmetry of the TCNQ structure.

Tetracyanoquinodimethane forms three types of electrically conducting compounds. The first, in keeping with its quinoid character, are crystalline π-complexes (charge-transfer complexes) with aromatic hydrocarbons, amines and polyhydric phenols. These complexes are characterised by intermediate to high resistivity ($10^3$ to $10^4 \Omega\text{cm}$) and very weak E.S.R. absorption. It is the second and third types of electrically conducting compounds which are of interest to the current line of research. These include two series of stable TCNQ salt-like derivatives, each involving complete transfer of an
electron to TCNQ with the formation of the anion-radical TCNQ\(^-\) represented by the resonance of the (55).

Typical of the first series is a simple salt formula \(M^+(TCNQ)_n\) in which \(M^+\) may be a metallic or organic cation. These materials are characterised by intermediate to high resistivity (\(10^4\) to \(10^{12}\) \(\Omega\)cm) and weak e.s.r. absorption in the solid state\(^4\).

Members of the second salt-like series, the complex salts represented by the formula \(M^{n+}(TCNQ)_n\) (TCNQ) contain a molecule of formally neutral TCNQ in addition to each TCNQ\(^-\); this series is characterised by exceptionally low electrical resistivity (\(10^{-2}\) to \(10^3\) \(\Omega\)cm) and variable e.s.r. absorption, both of which properties are anisotropic as determined by measurements on single crystals\(^219\).

4.2.4 Simple Salts of the TCNQ\(^-\), Anion Radical Synthesis.

TCNQ undergoes facile one-electron reduction when treated with metal iodides or with certain
metals\(^{206,220}\). For example, TCNQ in acetonitrile will react at room temperature with metallic copper or silver to form metal salts of the anion-radical TCNQ\(^-\). In the iodide reaction, the TCNQ oxidises iodide ion to free iodine and takes up the electron to form TCNQ\(^-\). With the free metal, direct oxidation/reduction occurs and, in the case of copper, for example, the cuprous salt of TCNQ is formed.

\[
\text{CuI + TCNQ} \rightarrow \text{CuTCNQ + HI}_2
\]

\[
\text{Cu + TCNQ} \rightarrow \text{CuTCNQ}
\]

The iodide reaction is the more convenient for direct preparation of simple metal TCNQ\(^-\) salts and proceeds with facility when hot solutions of the iodide and TCNQ in acetonitrile or acetone are mixed. In this way the lithium, sodium and potassium salts of TCNQ\(^-\) have been prepared. The TCNQ\(^-\) salts precipitate as red or purple crystalline solids with a metallic sheen, the by-products remaining in solution. In practice, an excess of metal iodide is used so that the iodine by-product can be scavenged as I\(_3^+\), e.g.

\[
\text{CH}_3\text{CN}
\]

\[
3\text{LiI + 2TCNQ} \rightarrow 2\text{LiTCNQ + Li}^+ + \text{I}_3^-
\]
With this stoichiometry, high yields are realised since the oxidative reverse reaction $\text{HI}_2 + \text{TCNQ}^- \rightarrow \text{TCNQ} + \text{I}^-$ is largely obviated. The occurrence of this oxidation has been established since free TCNQ can be isolated by oxidation of TCNQ salts with a large excess of iodine.

The solubility of $\text{Li}^+ + \text{TCNQ}^-$ in water or ethanol at room temperature is about 1% by weight in contrast to other metal-TCNQ salts which are virtually insoluble in water and organic solvents. This feature makes $\text{Li}^+\text{TCNQ}^-$ a convenient intermediate, since metatheses in these media provide a wide variety of TCNQ- derivatives containing metallic, organometallic and onium cations.

4.3 NOVEL CROWN ETHER COMPLEXES.

As already discussed in the introduction (Chapter 1), many inorganic salts have been known to complex with crown ethers. However, there have been very few reports which appeared with the aims of studying electrical, magnetic and optical properties of these. Part of our work has been concerned with the investigation of the electrical properties of a number of cation/crown ether complexes. Two particular types of compound have been studied: (1) Crown ether/TCNQ salts and (2) Crown ether/Oxonol dye salts. These two areas allow us to compare the effect of crown ether encapsulation on the properties
of an organic semiconductor and a semi-insulator.

4.3.1 Crown Ether/TCNQ Salts.

Since the original report of the synthesis of TCNQ\textsuperscript{220} much attention has been paid to the high electrical conductivities and characteristic magnetic, optical, and structural properties of TCNQ salts\textsuperscript{221}. As already discussed, the segregated nature of the TCNQ stacks within a crystal lattice leads to high conductivity. A modification of the crystal structure might, therefore, induce interesting changes in its electrical properties. In order to explore this, Nogami and others studied, alkali-metal\textsuperscript{113,222}, ammonium\textsuperscript{223}, alkaline-earth metals\textsuperscript{224} and transition metal\textsuperscript{225} TCNQ salts incorporating a variety of crown ethers\textsuperscript{223}. They expected that surrounding the cation with a crown ether would weaken the interaction between the cation and TCNQ anion radicals, and lead to a change in the physical properties.

Even though Nogami and co-workers have carried out an extensive survey of the various crown ether/TCNQ complexes, the results are of questionable value. For all the crown ether/TCNQ complexes the d.c. measurements were recorded at room temperature only. Such measurements do not give any indication of how the material is really behaving, and it is important to support the d.c. characteristics with
a.c. measurements. Our intention was to repeat these results taking variable temperature d.c. measurements and then comparing this data with a.c. measurements over a large range of frequencies. From this work we hope to try to understand some of the conduction mechanisms present within the crown ether/TCNQ complexes.

4.4. SYNTHESIS OF CROWN ETHER/TCNQ COMPLEXES.

Using the procedures outlined by Nogami and co-workers a whole series of crown ether/TCNQ complexes have been prepared and fully characterised.

4.4.1 Crown Ether/Alkali Metal TCNQ Complexes.

(Crown Ether)\(m\)(M\(^+\)TCNQ)\(_n\).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Combustion Analysis</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>Found (calc)(%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>(12C4)(LiTCNQ)</td>
<td>61.55</td>
<td>5.23</td>
</tr>
<tr>
<td>387</td>
<td>(62.02)</td>
<td>(5.20)</td>
</tr>
<tr>
<td>(12C4)(NaTCNQ)</td>
<td>59.09</td>
<td>4.89</td>
</tr>
<tr>
<td>403</td>
<td>(59.55)</td>
<td>(4.96)</td>
</tr>
<tr>
<td>(12C4)(_2)(NaTCNQ)</td>
<td>57.81</td>
<td>6.29</td>
</tr>
<tr>
<td>579</td>
<td>(58.03)</td>
<td>(6.22)</td>
</tr>
<tr>
<td>(15C5)(NaTCNQ)</td>
<td>58.85</td>
<td>5.30</td>
</tr>
<tr>
<td>447</td>
<td>(59.06)</td>
<td>(5.37)</td>
</tr>
</tbody>
</table>

Cont. ...
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Combustion Analysis</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(15C5)(KTCNQ)</td>
<td>57.25</td>
<td>5.16</td>
<td>12.00</td>
</tr>
<tr>
<td>465</td>
<td>(57.02)</td>
<td>(5.18)</td>
<td>(12.09)</td>
</tr>
<tr>
<td>(15C5)₂(KTCNQ)</td>
<td>55.95</td>
<td>6.36</td>
<td>8.28</td>
</tr>
<tr>
<td>683</td>
<td>(56.22)</td>
<td>(6.44)</td>
<td>(8.19)</td>
</tr>
<tr>
<td>(18C6)(NaTCNQ)</td>
<td>58.37</td>
<td>5.67</td>
<td>11.22</td>
</tr>
<tr>
<td>491</td>
<td>(58.65)</td>
<td>(5.7)</td>
<td>(11.4)</td>
</tr>
<tr>
<td>(18C6)(KTCNQ)</td>
<td>56.61</td>
<td>5.41</td>
<td>11.27</td>
</tr>
<tr>
<td>507</td>
<td>(56.8)</td>
<td>(5.52)</td>
<td>(11.04)</td>
</tr>
<tr>
<td>(18C6)(NH₄TCNQ)</td>
<td>59.52</td>
<td>6.35</td>
<td>14.8</td>
</tr>
<tr>
<td>486</td>
<td>(59.26)</td>
<td>(6.58)</td>
<td>(14.4)</td>
</tr>
<tr>
<td>(DB18C6)(KTCNQ)</td>
<td>63.69</td>
<td>4.79</td>
<td>9.06</td>
</tr>
<tr>
<td></td>
<td>(63.68)</td>
<td>(4.64)</td>
<td>(9.29)</td>
</tr>
<tr>
<td>(DDB18C6)(NH₄TCNQ)</td>
<td>65.80</td>
<td>4.72</td>
<td>9.51</td>
</tr>
<tr>
<td>582</td>
<td>(65.98)</td>
<td>(4.81)</td>
<td>(9.62)</td>
</tr>
<tr>
<td>(DDA18C6)(LiTCNQ)</td>
<td>69.52</td>
<td>6.31</td>
<td>12.64</td>
</tr>
<tr>
<td>653</td>
<td>(69.83)</td>
<td>(6.43)</td>
<td>(12.86)</td>
</tr>
<tr>
<td>(DDA18C6)(NaTCNQ)</td>
<td>67.98</td>
<td>6.19</td>
<td>12.32</td>
</tr>
<tr>
<td>669</td>
<td>(68.16)</td>
<td>(6.28)</td>
<td>(12.55)</td>
</tr>
<tr>
<td>(DDA18C6)(KTCNQ)</td>
<td>66.21</td>
<td>6.07</td>
<td>12.14</td>
</tr>
<tr>
<td>685</td>
<td>(66.57)</td>
<td>(6.13)</td>
<td>(12.26)</td>
</tr>
<tr>
<td>(DDA18C6)(NH₄TCNQ)</td>
<td>67.25</td>
<td>6.80</td>
<td>14.47</td>
</tr>
<tr>
<td>664</td>
<td>(68.67)</td>
<td>(6.93)</td>
<td>(14.76)</td>
</tr>
</tbody>
</table>

Cont. ...
### Complexes Combustion Analysis Yield

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Found (calc)%</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
</tbody>
</table>

| (Fc[2.2]M)(LiTCNQ) | 60.59 | 4.89 | 11.68 | 48% | Green |
| 711               | (60.76) | (5.06) | (11.81) | 711 (60.76) | (5.06) | (11.81) | Green |
| (Fc[2.2]M)(NaTCNQ) | 59.24 | 4.9 | 11.41 | 32% | Green |
| 727               | (59.42) | (4.95) | (11.55) | 727 (59.42) | (4.95) | (11.55) | Green |
| (Fc[2.2]D)(RbTCNQ) | 55.86 | 5.27 | 8.69 | 39% | Violet |
| 1289              | (55.39) | (5.17) | (8.49) |

#### 4.4.2 Crown Ether/Alkali Metal TCNQ/TCNQ Complexes.

(Crown Ether)$_m$(M$^+$TCNQ)$_n$(TCNQ)$_i$.

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Found (calc)%</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
</tbody>
</table>

| (12C4)(LiTCNQ)(TCNQ) | 64.67 | 3.96 | 18.90 | 34% | Black |
| 591               | 64.97 | (4.06) | (18.85) | 591 (64.97) | (4.06) | (18.85) | Black |
| (12C4)(LiTCNQ)(TCNQ)$_2$ | 66.22 | 3.47 | 21.00 | 100% | Black |
| (12C4)$_2$(NaTCNQ)(TCNQ) | 61.01 | 5.09 | 14.21 | 49% | Black |
| 783               | (61.30) | (5.11) | (14.32) | 783 (61.30) | (5.11) | (14.32) | Black |

Cont. ...
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Molecular Weight</th>
<th>Combustion Analysis</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>(15C5)(NaTCNQ)(TCNQ)</td>
<td>62.99</td>
<td>3.79</td>
<td>18.11</td>
<td>30%</td>
</tr>
<tr>
<td>607</td>
<td>(63.26)</td>
<td>(3.95)</td>
<td>(18.45)</td>
<td>Black</td>
</tr>
<tr>
<td>(15C5)(NaTCNQ)(TCNQ)$_2$</td>
<td>64.34</td>
<td>3.69</td>
<td>19.47</td>
<td>100%</td>
</tr>
<tr>
<td>855</td>
<td>(64.56)</td>
<td>(3.74)</td>
<td>(19.65)</td>
<td>Black</td>
</tr>
<tr>
<td>(15C5)$_2$(KTCNQ)(TCNQ)</td>
<td>59.62</td>
<td>5.16</td>
<td>13.07</td>
<td>48%</td>
</tr>
<tr>
<td>843</td>
<td>(59.78)</td>
<td>(5.22)</td>
<td>(13.28)</td>
<td>Black</td>
</tr>
<tr>
<td>(18C6)(KTCNQ)(TCNQ)</td>
<td>61.10</td>
<td>4.45</td>
<td>15.63</td>
<td>40%</td>
</tr>
<tr>
<td>711</td>
<td>(60.76)</td>
<td>(4.5)</td>
<td>(15.75)</td>
<td>Black</td>
</tr>
<tr>
<td>(18C6)(NH$_4$TCNQ)(TCNQ)</td>
<td>62.47</td>
<td>5.09</td>
<td>18.11</td>
<td>30%</td>
</tr>
<tr>
<td>690</td>
<td>(62.61)</td>
<td>(5.22)</td>
<td>(18.26)</td>
<td>Black</td>
</tr>
<tr>
<td>(DB18C6)(KTCNQ)(TCNQ)</td>
<td>65.19</td>
<td>3.84</td>
<td>13.69</td>
<td>32%</td>
</tr>
<tr>
<td>807</td>
<td>(65.43)</td>
<td>(3.96)</td>
<td>(13.87)</td>
<td>Black</td>
</tr>
<tr>
<td>(DDA18C6)(KTCNQ)(TCNQ)</td>
<td>67.23</td>
<td>5.03</td>
<td>15.60</td>
<td>30%</td>
</tr>
<tr>
<td>889</td>
<td>(67.49)</td>
<td>(5.17)</td>
<td>(15.75)</td>
<td>Black</td>
</tr>
</tbody>
</table>
4.4.3 Crown Ether/Alkaline-Earth Metal TCNQ Complexes.

\[(\text{Crown Ether})_m (M^{2+}(\text{TCNQ}^-)_2)_n\]

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Combustion Analysis</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>Found (calc)%</td>
<td>Remarks</td>
</tr>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>(12C4)(Ca(TCNQ)_2)</td>
<td>61.29</td>
<td>3.78</td>
</tr>
<tr>
<td>624</td>
<td>(61.54)</td>
<td>(3.85)</td>
</tr>
<tr>
<td>(12C4)_2(Ca(TCNQ)_2)</td>
<td>59.76</td>
<td>4.91</td>
</tr>
<tr>
<td>800</td>
<td>(60.00)</td>
<td>(5.00)</td>
</tr>
<tr>
<td>(15C5)(Ca(TCNQ)_2)</td>
<td>60.84</td>
<td>4.10</td>
</tr>
<tr>
<td>668</td>
<td>(61.07)</td>
<td>(4.19)</td>
</tr>
<tr>
<td>(15C5)_2(Ba(TCNQ)_2)</td>
<td>53.37</td>
<td>4.81</td>
</tr>
<tr>
<td>985</td>
<td>(53.60)</td>
<td>(4.87)</td>
</tr>
<tr>
<td>(18C6)(Ca(TCNQ)_2)</td>
<td>60.43</td>
<td>4.35</td>
</tr>
<tr>
<td>712</td>
<td>(60.67)</td>
<td>(4.49)</td>
</tr>
<tr>
<td>(18C6)(Ba(TCNQ)_2)</td>
<td>53.11</td>
<td>3.87</td>
</tr>
<tr>
<td>809</td>
<td>(53.34)</td>
<td>(3.95)</td>
</tr>
<tr>
<td>(DB18C6)(Ca(TCNQ)_2)</td>
<td>65.17</td>
<td>3.89</td>
</tr>
<tr>
<td>808</td>
<td>(65.35)</td>
<td>(3.96)</td>
</tr>
<tr>
<td>(DB18C6)(Ba(TCNQ)_2)</td>
<td>58.12</td>
<td>3.45</td>
</tr>
<tr>
<td>905</td>
<td>(58.34)</td>
<td>(3.54)</td>
</tr>
<tr>
<td>(DDA18C6)(Ba(TCNQ)_2)</td>
<td>60.56</td>
<td>4.58</td>
</tr>
<tr>
<td>987</td>
<td>(60.79)</td>
<td>(4.66)</td>
</tr>
</tbody>
</table>

Cont. ...
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Molecular Weight</th>
<th>Combustion Analysis</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>*(CYCLAM)(Fe(TCNQ\textsuperscript{-})\textsubscript{2})</td>
<td>61.17</td>
<td>4.74 25.09</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td>664 (61.44)</td>
<td>(4.82) (25.3)</td>
<td>Green</td>
</tr>
<tr>
<td>*(CYCLAM)(Cu(TCNQ\textsuperscript{-})\textsubscript{2})</td>
<td>60.52</td>
<td>4.70 24.88</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>671.5 (60.76)</td>
<td>(4.76) (25.02)</td>
<td>Green</td>
</tr>
</tbody>
</table>

* Transition metals included in these results.

### 4.4.4 Crown Ether/Alkaline Earth Metal TCNQ/TCNQ Complexes.

(Crown Ether)\textsubscript{m} (M\textsuperscript{2+}(TCNQ\textsuperscript{-})\textsubscript{2})\textsubscript{n} (TCNQ)\textsubscript{j}.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Molecular Weight</th>
<th>Combustion Analysis</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Found (calc)%</td>
<td>Remarks</td>
</tr>
<tr>
<td>*(12C4)\textsubscript{2})(Ca(TCNQ\textsubscript{2})(TCNQ)</td>
<td>62.01</td>
<td>4.31 16.73</td>
<td>29%</td>
</tr>
<tr>
<td></td>
<td>1189 (62.15)</td>
<td>(4.41) (16.89)</td>
<td>Black</td>
</tr>
<tr>
<td>*(15C5)(Ca(TCNQ\textsubscript{2})(TCNQ)</td>
<td>63.11</td>
<td>3.58 19.07</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td>916 (63.30)</td>
<td>(3.67) (19.27)</td>
<td>Black</td>
</tr>
<tr>
<td>*(15C5)\textsubscript{2}(Ba(TCNQ\textsubscript{2})(TCNQ)</td>
<td>56.27</td>
<td>4.30 14.00</td>
<td>53%</td>
</tr>
<tr>
<td></td>
<td>872 (56.52)</td>
<td>(4.37) (14.13)</td>
<td>Black</td>
</tr>
<tr>
<td>*(18C6)(Ba(TCNQ\textsubscript{2})(TCNQ)</td>
<td>62.61</td>
<td>3.98 18.12</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td>1004 (62.88)</td>
<td>(3.93) (18.34)</td>
<td>Black</td>
</tr>
</tbody>
</table>

Cont. ...
Complexes | Combustion Analysis | Yield |
---|---|---
Molecular Weight | Found (calc)% | Remarks |
---|---|---
(18C6)(Ca(TCNQ)_2)(TCNQ) | 56.47 3.62 16.43 65% |
1013 | (56.86) (3.55) (16.58) Black |
(DB18C6)(Ca(TCNQ)_2)(TCNQ) | 66.17 3.48 16.23 35% |
1012 | (66.40) (3.56) (16.60) Black |
(DB18C6)(Ba(TCNQ)_2)(TCNQ) | 60.27 3.17 15.03 29% |
1109 | (60.59) (3.25) (15.15) Black |

4.4.5 Spectroscopic Analysis of Crown Ether/TCNQ Complexes.

Even though Nogami and co-workers carried out extensive combustion analysis characterisations of the crown ether/TCNQ complexes, the use of other spectroscopic techniques for characterisation were very limited. Therefore, with the experience gained (Chapter 3) when studying the complexes of the ferrocene macrocycles, a variety of spectroscopic techniques were employed to further characterise the crown ether/TCNQ salts. In fact a few of the complexes made in this part of the project were used as reference compounds when characterising the ferrocene macrocycle complexes in more depth.
However, due to the volume of complexes made only selected typical examples will be detailed here in order to give an indication of the spectroscopic analysis of the crown ether/TCNQ salts.

4.4.6 Mass Spectrometry.

Even though complexation cannot be seen directly using electron ionisation mass spectrometry, detailed information could be gained. Table 4.2 shows the fragmentation patterns of the $K^+\text{TCNQ}^-$ and $[18]\text{-crown-6}$ before complexation. In both these mass spectra neither of the molecular ions were seen ($K^+\text{TCNQ}^- \text{m/e} = 243$) ($[18]\text{-crown-6 m/e} = 264$) however, the fragmentations which are seen clearly define the compound in question. For example, for $K^+\text{TCNQ}^-$ the major peak is at m/e 204 which is the mass of TCNQ, suggesting that $K^+$ is lost. As the TCNQ fragments, it loses the nitrile groups (loss of 26 for every $C=\text{N}$). Once the nitrile groups are removed then the residual fragmentation pattern shows the loss of two carbons leading to the final major peak at m/e 76 which is the benzene ring with only four hydrogens.

The fragmentation of the crown ether involves the removal of ethylene oxy groups. The first major peak seen is m/e 177 which in $[18]\text{-crown-6}$ represents the loss of two ethylene oxy groups. However, the base
Table 4.2 Mass Spectrometry (Electron Ionisation)*
Fragmentation Patterns of a Crown Ether/TCNQ Complex
Compared with the Uncomplexed Crown Ether and TCNQ Salt.

<table>
<thead>
<tr>
<th>KTCNQ Salt</th>
<th>[18]-crown-6</th>
<th>(18C6)(KTCNQ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M⁺ = 243)</td>
<td>(M⁺ = 264)</td>
<td>(M⁺ = 507)</td>
</tr>
<tr>
<td>204.07 (100%)</td>
<td>176.99</td>
<td>204.06</td>
</tr>
<tr>
<td>177.98</td>
<td>132.02 (100%)</td>
<td>133.06</td>
</tr>
<tr>
<td>152.05</td>
<td>100.04</td>
<td>88.04</td>
</tr>
<tr>
<td>126.06</td>
<td>88.06</td>
<td>76.07</td>
</tr>
<tr>
<td>99.94</td>
<td>44.04</td>
<td>44.15 (100%)</td>
</tr>
<tr>
<td>88.02</td>
<td>39.84</td>
<td></td>
</tr>
<tr>
<td>76.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* All spectra were recorded at (70eV).

peak for [18]-crown-6 is at m/e 132 which is the crown ether completely split into two halves. The fragmentations below this arise from successive loss of ethylene oxy groups from the crown ether structure. In the case of this complex (and for all the other samples), it was possible, by matching the TCNQ salt fragmentation pattern with the crown ether
fragmentation pattern, to show the presence of both structures. This is clearly seen in the example shown in Table 4.2, which shows the presence of K\textsuperscript{+}TCNQ\textsuperscript{-} and [18]-crown-6. However, in order to demonstrate that crown ether/TCNQ complexation had taken place, Fast Atom Bombardment (f.a.b.) mass spectrometry was attempted (Chapter 3 Section 3.5.2). A typical example of the type of spectrum recorded for a crown ether/TCNQ complex is shown in Figure 4.14 which is of (12C4)(LiTCNQ).

All the f.a.b. mass spectra recorded for the crown ether/TCNQ complexes showed a large peak corresponding to the crown ether and the encapsulated cation. F.a.b. spectra also showed the presence of (12C4)\textsubscript{2}Na\textsuperscript{+} ions in the (12C4)\textsubscript{2}NaTCNQ complex. Therefore this technique proved to be an invaluable diagnostic technique for revealing crown ether/TCNQ complexation.

![Figure 4.14 F.A.B. Mass Spectrometry Spectrum of (12C4)(LiTCNQ).](image)
4.4.7 Infra-Red Spectroscopy.

Infra red spectroscopy has also been widely used to study the complexation of macrocyclic ligands for example, Popov and Mosier-Boss have shown that [18]-crown-6 will complex with many solvents using infra red spectroscopy. For the reasons above and the reasons stated in Chapter 3 (Section 3.5.3), Fourier Transform infra red spectroscopy (F.T.I.R.) was carried out on the crown ether/TCNQ salts. From this it was hoped to show that the complexation of crown ether with metal TCNQ salts had taken place.

In order to prevent solvent interaction proposed by Popov et al, all the infra red spectroscopy was carried out in the solid state using KBr discs. Initial studies with TCNQ clearly showed the changes which occur when it is reduced to an $\mathrm{MN}^+$ salt. The common features of the spectra are listed in Table 4.3.

From the table of infra red frequencies, there are certain characteristics which highlight the reduction of TCNQ to TCNQ$^-$. These include; (a) the splitting of the nitrile (\(-\mathrm{C=\text{N}}\)) frequencies (b) conversion of a conjugated system into an aromatic system. The splitting of nitrile in TCNQ$^-$ when
Table 4.3 Comparison of the FTIR Spectra of TCNQ and KTCNQ.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ (cm$^{-1}$)</td>
<td>C-H Stretching</td>
<td>Cis Alkene (-CH=CH-)</td>
</tr>
<tr>
<td>3050.0 (m)</td>
<td>-C=O Stretching</td>
<td>Nitriles</td>
</tr>
<tr>
<td>2224.0 (s)</td>
<td>-C=C- Stretching</td>
<td>$\alpha,\beta$ Conjugated Compounds</td>
</tr>
<tr>
<td>1543.0 (s)</td>
<td>C-H Deformations</td>
<td>Alkenes Saturated</td>
</tr>
<tr>
<td>1353.0 (m)</td>
<td>C-H Deformations</td>
<td>C-H Deformation out of Plane</td>
</tr>
<tr>
<td>1285.0 (m)</td>
<td>C-H Deformations</td>
<td>C-H Deformation of Plane</td>
</tr>
</tbody>
</table>

K$^+$/TCNQ$^-$

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ (cm$^{-1}$)</td>
<td>C-H Stretching</td>
<td>Aromatic Characteristic 2 or 3 Bands</td>
</tr>
<tr>
<td>1578.0 (m)</td>
<td>C-H Deformations</td>
<td>Characteristic Para-Substituted Aromatic</td>
</tr>
<tr>
<td>1508.0 (m)</td>
<td>C-H Deformations</td>
<td>Characteristic Para-Substituted Aromatic</td>
</tr>
<tr>
<td>1366.0 (m)</td>
<td>C-H Deformations</td>
<td>Characteristic Para-Substituted Aromatic</td>
</tr>
<tr>
<td>1335.0 (m)</td>
<td>C-H Deformations</td>
<td>Characteristic Para-Substituted Aromatic</td>
</tr>
<tr>
<td>1182.0 (m)</td>
<td>C-H Deformations</td>
<td>Characteristic Para-Substituted Aromatic</td>
</tr>
<tr>
<td>824.0 (s)</td>
<td>C-H Deformations</td>
<td>Characteristic Para-Substituted Aromatic</td>
</tr>
<tr>
<td>720.0 (m)</td>
<td>C-H Deformations</td>
<td>Aromatics</td>
</tr>
</tbody>
</table>
compared with TCNQ is probably a result of a change in environment of the nitrile group. In TCNQ the nitriles are all equivalent and give a sharp stretching frequency at 2240 cm⁻¹. However, in TCNQ⁻ the molecule loses its symmetry giving rise to two cyanide environments and hence a multiple signal. The conversion of TCNQ from an alkene to an aromatic system TCNQ⁻, is also highlighted by -C=C- stretching which is at 1543 cm⁻¹ in TCNQ, while in the TCNQ⁻ this -C=C- stretching forms the characteristic 1500 cm⁻¹ and 1580 cm⁻¹ present in an aromatic ring. One final feature which highlights the aromatic system is the strong band at 824 cm⁻¹ which reflects a characteristic C-H deformation in a para-disubstituted benzene.

After the complete characterisation of K⁺TCNQ⁻, attention focussed on the crown ether ([18]-crown-6) and the crown ether/TCNQ complex ((18C6)(KTCNQ)). The infra red spectra of these are shown in Figure 4.15a and 4.15b, with the characteristic features outlined in Table 4.4.

Comparing the features of the infra red spectra of K⁺TCNQ⁻ and the [18]-crown-6 it is clear to see that both are reflected in the (18C6)(KTCNQ) complex. The strong nitrile (C≡N) splitting is prevalent showing a shift of about 10 cm⁻¹ in the complex. However, the most important and dramatic
Figure 4.15a  F.T.IR Spectrum of [18]-crown-6.

Figure 4.15b  F.T.IR Spectrum of (18C6)(KTCNQ).
Table 4.4 Comparison of [18]-crown-6 with [18]-crown-6/K⁺TCNQ⁻ F.T.IR.

<table>
<thead>
<tr>
<th>[18]-crown-6</th>
<th>Assignment</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2863.0 (vs)</td>
<td>-CH₂-</td>
<td>Stretching</td>
<td>Characteristic Alkane.</td>
</tr>
<tr>
<td>1470.0 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1451.0 (m)</td>
<td></td>
<td></td>
<td>Characteristic</td>
</tr>
<tr>
<td>1356.0 (m)</td>
<td>C-H-</td>
<td>Deformation</td>
<td></td>
</tr>
<tr>
<td>1294.0 (m)</td>
<td></td>
<td>Alkane</td>
<td></td>
</tr>
<tr>
<td>1252.0 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1131.0 (vs)</td>
<td>C-O</td>
<td>Stretch</td>
<td>Cyclic Ethers/Saturated Aliphatic Ethers</td>
</tr>
<tr>
<td>1043.0 (vs)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[18]-Crown-6/K⁺TCNQ⁻</th>
<th>Assignment</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2889.0 (s)</td>
<td>-CH₂-</td>
<td>Stretching</td>
<td>Alkane of Ether</td>
</tr>
<tr>
<td>2187.0 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2177.0 (s)</td>
<td>-CN</td>
<td>Stretching</td>
<td>Nitriles of TCNQ⁻</td>
</tr>
<tr>
<td>2156.0 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1585.0 (m)</td>
<td>-C=C-</td>
<td>Stretching</td>
<td>Aromatic Ring</td>
</tr>
<tr>
<td>1504.0 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cont. ...
<table>
<thead>
<tr>
<th>Assignment</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (cm$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1473.0 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1455.0 (m)</td>
<td></td>
<td>Alkane C-H Stretches</td>
</tr>
<tr>
<td>1355.0 (m)</td>
<td>C-H Deformations</td>
<td></td>
</tr>
<tr>
<td>1285.0 (m)</td>
<td></td>
<td>and Aromatic C-H</td>
</tr>
<tr>
<td>1249.0 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1180.0 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1139.0 (vs)</td>
<td>C-O Stretches</td>
<td>Aliphatic Cyclic</td>
</tr>
<tr>
<td>1107.0 (vs)</td>
<td></td>
<td>Ether</td>
</tr>
<tr>
<td>964.0 (s)</td>
<td>C-H Deformation</td>
<td>Aromatic</td>
</tr>
<tr>
<td>833.0 (s)</td>
<td>C-H Deformation</td>
<td>Para Substituted Benzene</td>
</tr>
</tbody>
</table>

Change in the complex is the stretching frequencies of the C-O. When $K^+$ is bound to the ether ligand a frequency shift ($\sim 25$ cm$^{-1}$) is seen to take place, accompanied by a change in the shape of the C-O signal. These features are in agreement with those observed by Pedersen in the early work on crown ether complexes.

Infra red spectroscopy was also useful for studying complexes comprising of a crown ether, a $M^{n+}(TCNQ^-)_n$ salt and neutral TCNQ. Even though the spectra obtained were complex a few outstanding features can be extracted from the data. Table 4.5 below shows some of the characteristic signals.
monitored for a 1:1:1 complex salt.

Table 4.5 Characteristic Frequencies of [18]-crown-6/K\(^+\)TCNQ\(^-\)/TCNQ F.T. IR Spectrum.

<table>
<thead>
<tr>
<th>Frequency (\nu(\text{cm}^{-1}))</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>3040.0 (m) C-H Stretching</td>
<td></td>
<td>Cis Alkene ((\text{-C=C-}))</td>
</tr>
<tr>
<td>2899.0 (s) -CH(_2)- Stretching</td>
<td>Alkane. Crown Ether</td>
<td></td>
</tr>
<tr>
<td>2223.0 (s) -C(_2)N Stretching</td>
<td>Nitrile TCNQ neutral</td>
<td></td>
</tr>
<tr>
<td>2209.0 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2195.0 (s) -C(_3)N Stretching</td>
<td>Nitrile TCNQ(^-)</td>
<td></td>
</tr>
<tr>
<td>2177.0 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1566.0 (m) C-C Stretch</td>
<td>Aromatic TCNQ(^-)</td>
<td></td>
</tr>
<tr>
<td>1542.0 (m) C=C Stretch</td>
<td>Alkene TCNQ</td>
<td></td>
</tr>
<tr>
<td>1505.0 (m) C=C Stretch</td>
<td>Aromatic TCNQ(^-)</td>
<td></td>
</tr>
<tr>
<td>1472.0 (m) C-H Deformations</td>
<td>Alkane Crown Ether</td>
<td></td>
</tr>
<tr>
<td>1454.0 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1353.0 (m)</td>
<td>Mixture of Alkenes</td>
<td></td>
</tr>
<tr>
<td>1286.0 (m) C-H Deformation</td>
<td>Aromatic &amp; Alkanes</td>
<td></td>
</tr>
<tr>
<td>1180.0 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1136.0 (Vs) C-O Stretches</td>
<td>M(^+)/Crown Ether</td>
<td></td>
</tr>
<tr>
<td>1105.0 (Vs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>962.0 (s) C-H Deformation</td>
<td>Aromatic</td>
<td></td>
</tr>
<tr>
<td>840.0 (s) C-H Deformation</td>
<td>Para Substituted Benzene</td>
<td></td>
</tr>
</tbody>
</table>
Notable characteristics of these spectra include the presence of the nitrile (-C≡N) bands, that at 2223 cm⁻¹ corresponding to the neutral TCNQ and the other three to the TCNQ⁻. From the infra red data it is easy to pick out the three structures; the alkanes of the cyclic ether, the aromatics of the TCNQ⁻ and the conjugated alkene of the neutral TCNQ.

4.4.8 ¹H N.M.R.

As already discussed in detail in Chapter 3 (Section 3.5.4) proton and carbon n.m.r. have been used to characterise crown ethers and their interactions with metal ions. By using ¹³C and ¹H n.m.r. we hoped to show that the metal ion was bound into the crown ether by looking at chemical shift changes. This technique would hopefully reveal that the crown ether/TCNQ salt arises as a direct result of the metal ion encapsulation within the crown.

Due to the paramagnetic nature of TCNQ⁻ (radical anion) simple ¹H spectra in which the integration of the protons of TCNQ⁻ could be directly related to the integration of the protons of the crown ether is not impossible. Figure 4.16 shows how the paramagnetic nature of the TCNQ⁻ distorts the ¹H spectrum of a simple crown ether. Rather than trying to relate integration values to TCNQ and crown ether the only information which could be gained from the ¹H n.m.r. spectra related to chemical shift changes of the
Crown ether. Free crown ether had a different chemical shift to crown ether/metal ion (Table 4.9). Therefore, even though information could not be gained about the stoichiometric composition of the crown ether/TCNQ, the fact that a complex had formed is self evident.

Table 4.6 1H n.m.r. data on crown ethers complexed with Mn⁺(TCNQ⁻)ₙ salts [90 MHz; CDCl₂.]

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ 1H N.M.R. ppm</th>
<th>Δδ±0.003ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]-crown-4</td>
<td>3.687</td>
<td></td>
</tr>
<tr>
<td>(12C4)(LiTCNQ)</td>
<td>3.692</td>
<td>0.005</td>
</tr>
<tr>
<td>(12C4)₂(NaTCNQ)</td>
<td>3.711</td>
<td>0.024</td>
</tr>
<tr>
<td>[15]-crown-5</td>
<td>3.687</td>
<td></td>
</tr>
<tr>
<td>(15C5)(NaTCNQ)</td>
<td>3.722</td>
<td>0.035</td>
</tr>
<tr>
<td>(15C5)(KTCNQ)</td>
<td>3.700</td>
<td>0.013</td>
</tr>
<tr>
<td>(15C5)₂(KTCNQ)</td>
<td>3.725</td>
<td>0.038</td>
</tr>
<tr>
<td>(15C5)(Ca(TCNQ)₂)</td>
<td>3.714</td>
<td>0.027</td>
</tr>
<tr>
<td>[18]-crown-6</td>
<td>3.6810</td>
<td></td>
</tr>
<tr>
<td>(18C6)(NaTCNQ)</td>
<td>3.6919</td>
<td>0.010</td>
</tr>
<tr>
<td>(18C6)(KTCNQ)</td>
<td>3.7882</td>
<td>0.107</td>
</tr>
<tr>
<td>(18C6)(NH₄TCNQ)</td>
<td>3.779</td>
<td>0.098</td>
</tr>
<tr>
<td>(18C6)(Ca(TCNQ)₂)</td>
<td>3.687</td>
<td>0.006</td>
</tr>
<tr>
<td>(18C6)(Ba(TCNQ)₂)</td>
<td>3.759</td>
<td>0.078</td>
</tr>
</tbody>
</table>
Figure 4.16 $^1$H N.M.R. of Various Crown Ether/TCNQ Complexes.
All the samples were run at 90 MHz using CDC13 as solvent. The chemical shifts given in Table 4.6 give a rough idea of the stability of some of the TCNQ complexes. For example, large changes in chemical shifts are seen when two [15]-crown-5 encapsulate a K⁺ ion, while smaller shifts are seen when [12]-crown-4 binds to lithium. The ¹H n.m.r. experiments do clearly show the interaction of a crown ether with a metal ion does change the chemical shifts.

4.4.9 ¹³C N.M.R.

Also mentioned in Chapter 3 (Section 3.5.5) is the fact that ¹³C chemical shifts are known to be sensitive to conformation and relatively less sensitive to perturbations than are proton chemical shifts. Therefore, as well as looking at shift changes by ¹H n.m.r., ¹³C n.m.r. spectra were also investigated. Even though the paramagnetic nature of the TCNQ⁻ effects the n.m.r. experiment it is possible, given a long enough accumulation time, to collect a ¹³C n.m.r. spectra on TCNQ. However, attempting to do so took a whole weekend at 22.5 MHz before a reasonable spectrum was recorded. Therefore rather than look for the TCNQ signals, in these experiments the chemical shift changes of the crown ether ¹³C n.m.r. resonances were monitored. By considering the shift changes it was hoped to make an
assessment of the stability of some of the crown ether/TCNQ complexes. Table 4.7 shows the chemical shifts ($^{13}$C) of many of the complexes with respect to those of their simple crown ether compounds.

These results are in good agreement with those expected by work reported in the literature and with the results recorded for the $^1$H n.m.r. spectra. From these results it is clear that the complexes of [18]-crown-6/K$^+$TCNQ$^-$ and [15]-crown-5/Na$^+$TCNQ$^-$ show the largest chemical shift changes. It is interesting to note that the 2:1 complexes also show greater chemical shift differences (and hence stability) compared with their simple 1:1 salts. The spectra and interpretation of the more complex Dibenzo-[18]-crown-6 complexes are interpreted and discussed in Chapter 5.

Table 4.7 $^{13}$C N.M.R. Data Comparing Crown Ether/TCNQ Salts with Crown Ether (22.5 MHz; CDCl$_3$).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^{13}$C N.M.R. ppm</th>
<th>$\Delta$S $\pm$ 0.03 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]-crown-4</td>
<td>70.5507</td>
<td></td>
</tr>
<tr>
<td>(12C4)(LiTCNQ)</td>
<td>70.8666</td>
<td>0.3159</td>
</tr>
<tr>
<td>(12C4)$_2$(NaTCNQ)</td>
<td>70.9969</td>
<td>0.4462</td>
</tr>
<tr>
<td>[15]-crown-5</td>
<td>71.2049</td>
<td></td>
</tr>
<tr>
<td>(15C5)(NaTCNQ)</td>
<td>70.6383</td>
<td>0.5666</td>
</tr>
</tbody>
</table>

Cont. ...
**Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{13}$C N.M.R. ppm</th>
<th>Δ$\delta$ ± 0.03 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(15C5)(KTCNQ)$</td>
<td>70.8257</td>
<td>0.3792</td>
</tr>
<tr>
<td>$(15C5)_{2}(KTCNQ)$</td>
<td>70.8041</td>
<td>0.4008</td>
</tr>
<tr>
<td>$(15C5)<em>{2}(Ba(TCNQ)</em>{2})$</td>
<td>71.3132</td>
<td>0.1083</td>
</tr>
<tr>
<td>[18]-crown-6</td>
<td>70.9882</td>
<td></td>
</tr>
<tr>
<td>$(18C6)(NaTCNQ)$</td>
<td>71.2049</td>
<td>0.2167</td>
</tr>
<tr>
<td>$(18C6)(KTCNQ)$</td>
<td>70.4464</td>
<td>0.5418</td>
</tr>
<tr>
<td>$(18C6)(NH_{4}TCNQ)$</td>
<td>70.7173</td>
<td>0.2709</td>
</tr>
<tr>
<td>$(18C6)(Ca(TCNQ)_{2})$</td>
<td>71.0423</td>
<td>0.0541</td>
</tr>
<tr>
<td>$(18C6)(Ba(TCNQ)_{2})$</td>
<td>70.5548</td>
<td>0.4334</td>
</tr>
</tbody>
</table>

**4.5 SOLID STATE STUDIES.**

**4.5.1 Electrical Spectroscopy.**

**4.5.1.1 D.C. Measurements.**

The conductance of an electronically conducting sample is assumed to behave as:

$$\sigma = A \exp^{-\Delta E_{act}/2kT}$$

Where $\sigma_T$ is the conductivity (S cm$^{-1}$) at a temperature $T$.

From this expression $\Delta E$, referred to as the "activation energy" or "band gap energy", may be calculated for each sample by plotting $\ln \sigma_T$ vs. $1/T$. The conductivity depends on $\Delta E_{act}$ and can be thought of as a measure of the number of available electrons in the conduction band compared to the...
valence band. A low value of $\Delta E_{\text{act}}$ indicates (at a high temperature), that many electrons are available for carrying current. While a high value of $\Delta E_{\text{act}}$ means most of the electrons are trapped or are in the valence band. Another major factor that will control conductivity will be the density of the fractile units (i.e. the conducting units).

As already stated in earlier sections, the literature reports on the d.c. measurements of the crown ether/TCNQ salts are of questionable value since those measurements were carried out at only one temperature. It was for this reason that the uncomplexed TCNQ salts were amongst the first samples to be investigated in this work. A considerable body of literature is available on the d.c. conductivity of the TCNQ salts and this proved a good reference point with which to compare our experimental results. The experimental details for obtaining the d.c. measurements are outlined in Appendix III.

Table 4.11 below shows the room temperature conductivity of the TCNQ (with $\Delta E_{\text{act}}$ values) salts as compared with those reported in the literature. Figure 4.17a shows the behaviour of a typical d.c. conductor, e.g. potassium TCNQ.

It is clear from Table 4.8 that the conductivity data for the TCNQ salts are in good agreement with results already quoted in the literature. The
differences which arise may be accounted for by the temperatures at which the results were recorded, our results having been measured at $20^\circ C$, whereas the literature values are quoted at room temperature.

Attention was then focussed onto the crown ether/alkali-metal TCNQ complexes. The results of our findings are presented in Table 4.9 and Figure 4.17b shows a typical d.c. plot for a crown ether/TCNQ complex.

Figure 4.17a Typical $\ln \sigma$ vs $1/T$ Plot of a TCNQ Salt.
Figure 4.17b  Typical lnσ vs 1/T Plot of a Crown Ether/Alkali-Metal TCNQ Salt.

Table 4.8  D.C. Conductivity Results of the TCNQ Salts Compared with those Cited in the Literature.

<table>
<thead>
<tr>
<th>TCNQ Salts</th>
<th>σ20</th>
<th>Δσac</th>
<th>σRT</th>
<th>Δσac</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTCNQ</td>
<td>3.4 x 10^-6</td>
<td>0.87</td>
<td>5 x 10^-6</td>
<td>0.5</td>
</tr>
<tr>
<td>NaTCNQ</td>
<td>1.04 x 10^-5</td>
<td>0.51</td>
<td>3.34 x 10^-5</td>
<td>0.55</td>
</tr>
<tr>
<td>KTCNQ</td>
<td>2.5 x 10^-5</td>
<td>0.65</td>
<td>2 x 10^-4</td>
<td>0.45</td>
</tr>
<tr>
<td>RbTCNQ</td>
<td>1.04 x 10^-4</td>
<td>0.47</td>
<td>3.57 x 10^-4</td>
<td>0.44</td>
</tr>
<tr>
<td>NH4TCNQ</td>
<td>2.57 x 10^-5</td>
<td>0.54</td>
<td>3.34 x 10^-5</td>
<td>-</td>
</tr>
<tr>
<td>Ca(TCNQ)_2</td>
<td>1.23 x 10^-5</td>
<td>0.65</td>
<td>1 x 10^-4</td>
<td>-</td>
</tr>
<tr>
<td>Ba(TCNQ)_2</td>
<td>3.11 x 10^-7</td>
<td>0.81</td>
<td>1.25 x 10^-6</td>
<td>-</td>
</tr>
<tr>
<td>Fe(TCNQ)_2</td>
<td>8.08 x 10^-5</td>
<td>0.55</td>
<td>2 x 10^-5</td>
<td>-</td>
</tr>
<tr>
<td>Cu(TCNQ)_2</td>
<td>8.6 x 10^-2</td>
<td>0.13</td>
<td>2 x 10^-2</td>
<td>0.12</td>
</tr>
</tbody>
</table>
In general this data suggest the following:

(a) Addition of a crown ether to the TCNQ salt decreases the conductivity and increases the activation energy.

(b) Crown ethers which bind specific ions well (e.g. [18]-crown-6 and K⁺) exhibit lower conductivities and higher activation energies. In the case of the 2:1 complexes (crown ether:TCNQ) this is highlighted even more dramatically.

Table 4.12a D.C. Conductivity Results for the Crown Ether/Alkali-Metal TCNQ Complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>σ₂₀ (Ω⁻¹ cm⁻¹)</th>
<th>ΔE(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12C₄)(LiTCNQ)</td>
<td>2.97 x 10⁻⁴</td>
<td>0.29</td>
</tr>
<tr>
<td>(12C₄)(NaTCNQ)</td>
<td>9.06 x 10⁻⁵</td>
<td>0.64</td>
</tr>
<tr>
<td>(12C₄)₂(NaTCNQ)</td>
<td>3.30 x 10⁻⁶</td>
<td>1.25</td>
</tr>
<tr>
<td>(15C₅)(NaTCNQ)</td>
<td>6.44 x 10⁻⁵</td>
<td>0.85</td>
</tr>
<tr>
<td>(15C₅)(KTCNQ)</td>
<td>4.17 x 10⁻⁵</td>
<td>0.69</td>
</tr>
<tr>
<td>(15C₅)₂(KTCNQ)</td>
<td>1.85 x 10⁻⁶</td>
<td>1.14</td>
</tr>
<tr>
<td>(18C₆)(NaTCNQ)</td>
<td>1.68 x 10⁻³</td>
<td>0.49</td>
</tr>
<tr>
<td>(18C₆)(KTCNQ)</td>
<td>1.86 x 10⁻⁸</td>
<td>1.92</td>
</tr>
<tr>
<td>(18C₆)(NH₄TCNQ)</td>
<td>8.84 x 10⁻⁵</td>
<td>1.31</td>
</tr>
<tr>
<td>(DB18C₆)(KTCNQ)</td>
<td>1.85 x 10⁻¹¹</td>
<td>1.92</td>
</tr>
<tr>
<td>(DB18C₆)(NH₄TCNQ)</td>
<td>8.82 x 10⁻⁸</td>
<td>1.40</td>
</tr>
<tr>
<td>(DDA18C₆)(LiTCNQ)</td>
<td>1.27 x 10⁻⁸</td>
<td>2.48</td>
</tr>
<tr>
<td>Complexes</td>
<td>$\sigma_0$ $\Omega^{-1}$ cm$^{-1}$</td>
<td>$\Delta E$ (eV)</td>
</tr>
<tr>
<td>------------------------------------</td>
<td>------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>(DDA18C6)(NaTCNQ)</td>
<td>$8.58 \times 10^{-7}$</td>
<td>1.35</td>
</tr>
<tr>
<td>(DDA18C6)(KTCNQ)</td>
<td>$1.85 \times 10^{-11}$</td>
<td>1.92</td>
</tr>
<tr>
<td>(Fc[2.2]M)(LiTCNQ)</td>
<td>$9.72 \times 10^{-8}$</td>
<td>0.90</td>
</tr>
<tr>
<td>(Fc[2.2]M)(NaTCNQ)</td>
<td>$1.18 \times 10^{-10}$</td>
<td>2.03</td>
</tr>
<tr>
<td>(Fc[2.2]D)(RbTCNQ)</td>
<td>$2.58 \times 10^{-13}$</td>
<td>3.53</td>
</tr>
</tbody>
</table>

(c) The aliphatic crown ethers show higher conductivities and lower activation energies than the aromatic crown ethers. The "redoxable" cryptands Fc[2.2]M and Fc[2.2]D showed no difference in conductivities in comparison with the analogous open chain dibenzyl diaza-[18]-crown-6/TCNQ complexes.

(d) Finally, the larger aliphatic crown ethers (i.e. when going from [12]-crown-4 to [18]-crown-6) both showed a dramatic increase in both activation energy with a decrease in conductivity. The crown ethers obviously "bulk out" the solid, reducing the freedom of conduction within the TCNQ stacks.

When comparing these results with those for the complexes in which neutral TCNQ has been added (crown ether)$_m$ (M$^+$TCNQ)$_n$ (TCNQ)$_i$ dramatic changes are seen. Table 4.10 shows the d.c. conductivity measurements recorded for these complexes.

In general the results clearly show an extremely large increase in conductivity and a dramatic lowering of the associated activation energy.
example, \((15C5)(NaTCNQ)(TCNQ)_2\) is extremely conductive when compared with the \((12C4)_2(NaTCNQ)(TCNQ)\). In the latter case, two molecules of crown ether exist within the complex and it clearly shows that the function of the ligand is to "bulk" out the system rather than to contribute to any conduction mechanism. The crown ether may be thought of as providing the framework into which TCNQ may be added providing a long TCNQ stacking arrangement (Figure 4.18a). In the case of the 2:1:1 complex, further addition of neutral TCNQ would help to retain the stacking arrangement of the TCNQ, thus allowing conduction to proceed unhindered (Figure 4.18b). In order to support these conclusions X-ray crystallographic studies on these materials are now underway.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(\sigma_20 \ \Omega^{-1} \text{cm}^{-1})</th>
<th>(\Delta E (eV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((12C4)(LiTCNQ)(TCNQ))</td>
<td>(4.08 \times 10^{-4})</td>
<td>0.22</td>
</tr>
<tr>
<td>((12C4)_2(NaTCNQ)(TCNQ))</td>
<td>(1.39 \times 10^{-6})</td>
<td>0.73</td>
</tr>
<tr>
<td>((15C5)(NaTCNQ)(TCNQ))</td>
<td>(0.06 \times 10^{-5})</td>
<td>0.50</td>
</tr>
<tr>
<td>((15C5)(KTCNQ)(TCNQ)_2)</td>
<td>(1.88 \times 10^{-3})</td>
<td>0.081</td>
</tr>
<tr>
<td>((19C6)(KTCNQ)(TCNQ))</td>
<td>(3.67 \times 10^{-6})</td>
<td>0.81</td>
</tr>
<tr>
<td>((DB18C6)(KTCNQ)(TCNQ))</td>
<td>(6.67 \times 10^{-9})</td>
<td>0.772</td>
</tr>
</tbody>
</table>
It is clear from Figure 4.18a and b that the intermolecular spacing between the TCNQ molecules is very important in the conduction processes. This is evident from the activation energies observed for some of these complexes. Hence in the case of the 1:1:2 complex an extremely low activation energy is seen whereas in a 2:1:1 complex the reverse is observed.

D.c. measurements were carried out on the crown ether/alkaline-earth metal and transition metal TCNQ complexes, in a similar manner to that adopted for the crown ether/alkali-metal TCNQ salts. The results of these findings are tabulated in Table 4.11.

![Diagram](image)

Figure 4.18a Showing How the Crown Ether May Provide a Backbone with which the TCNQ could Stack.
Figure 4.18b  Showing How the Crown ether In 2:1:1 Complex Bulks Out the TCNQ⁻/TCNQ Stacks.

Table 4.11  D.C. Measurement of Crown Ether/Alkaline-Earth Metal and Transition Metal TCNQ Complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\sigma_0 \ \Omega^{-1} \ cm^{-1}$</th>
<th>$\Delta E \ (eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12C4)(Ca(TCNQ)₂)</td>
<td>$9.047 \times 10^{-7}$</td>
<td>0.648</td>
</tr>
<tr>
<td>(12C4)₂(Ca(TCNQ)₂)</td>
<td>$3.323 \times 10^{-7}$</td>
<td>0.707</td>
</tr>
<tr>
<td>(15C5)(Ca(TCNQ)₂)</td>
<td>$5.642 \times 10^{-7}$</td>
<td>0.582</td>
</tr>
<tr>
<td>(15C5)₂(Ba(TCNQ)₂)</td>
<td>$5.769 \times 10^{-10}$</td>
<td>1.338</td>
</tr>
<tr>
<td>(18C6)(Ca(TCNQ)₂)</td>
<td>$1.33 \times 10^{-7}$</td>
<td>0.569</td>
</tr>
<tr>
<td>(18C6)(Ba(TCNQ)₂)</td>
<td>$1.088 \times 10^{-7}$</td>
<td>0.945</td>
</tr>
<tr>
<td>(DB18C6)(Ca(TCNQ)₂)</td>
<td>$3.223 \times 10^{-7}$</td>
<td>0.706</td>
</tr>
<tr>
<td>(DB19C6)(Ba(TCNQ)₂)</td>
<td>$1.759 \times 10^{-8}$</td>
<td>0.737</td>
</tr>
<tr>
<td>(DDA18C6)(Ba(TCNQ)₂)</td>
<td>$1.00 \times 10^{-9}$</td>
<td>1.34</td>
</tr>
<tr>
<td>(Cyclam(Fe(TCNQ)₂)</td>
<td>$1.47 \times 10^{-7}$</td>
<td>0.667</td>
</tr>
<tr>
<td>(Cyclam)(Cu(TCNQ)₂)</td>
<td>$3.66 \times 10^{-5}$</td>
<td>0.245</td>
</tr>
</tbody>
</table>
The general trends of results for this series of crown ether/TCNQ salts are similar to those observed for the alkali metals. The more encapsulated the cation (i.e. the stronger the complex) the higher the activation energy. Even though this series of compounds follow the same pattern as those of the alkali metals, what is obvious from the table of results is that the activation energies are all much lower. This may be explained by the fact that there are twice as many TCNQ anions per cation here, and the ease with which conduction takes place is greatly facilitated.

A comparison of these results with those for the complex (1:1:1) salts (crown ether/\textit{M}^+\textit{TCNQ}^-/\textit{TCNQ}) reveals some dramatic changes. The conductivities of the (1:1:1) salts are detailed in Table 4.12 below. These again show similar trends to those for the (1:1:1) alkali metal TCNQ complexes. In this case, however, the conductivities are extremely high with low activation energies.
Table 4.12  D.C. Conductivities Results for the Crown Ether/Alkaline-Earth Metal TCNQ/Neutral TCNQ Complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\sigma_0$ $\Omega^{-1}$ cm$^{-1}$</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(12C4)_2(Ca(TCNQ)_2)(TCNQ)$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>0.09</td>
</tr>
<tr>
<td>$(15C5)(Ca(TCNQ)_2)(TCNQ)$</td>
<td>$2.45 \times 10^{-3}$</td>
<td>0.05</td>
</tr>
<tr>
<td>$(15C5)(Ba(TCNQ)_2)(TCNQ)$</td>
<td>$2.76 \times 10^{-3}$</td>
<td>0.10</td>
</tr>
<tr>
<td>$(18C6)(Ca(TCNQ)_2)(TCNQ)$</td>
<td>$2.6 \times 10^{-5}$</td>
<td>0.37</td>
</tr>
<tr>
<td>$(18C6)(Ba(TCNQ)_2)(TCNQ)$</td>
<td>$1.33 \times 10^{-5}$</td>
<td>0.50</td>
</tr>
<tr>
<td>$(DB18C6)(Ca(TCNQ)_2)(TCNQ)$</td>
<td>$1.98 \times 10^{-5}$</td>
<td>0.26</td>
</tr>
<tr>
<td>$(DB18C6)(Ba(TCNQ)_2)(TCNQ)$</td>
<td>$1.77 \times 10^{-5}$</td>
<td>0.3</td>
</tr>
</tbody>
</table>

4.5.1.2 A.C. Dielectric Response Spectroscopy.

In order to understand the possible conduction mechanism occurring in particular materials it is important to carry out a.c. dielectric loss measurements\textsuperscript{227,228}. The use of these measurements allow bulk properties of materials to be investigated. Low frequency measurements allow the study of the individual fractile units which make up the bulk of material under investigation. From the spectral information a mathematical modelling technique is used to fit the acquired spectrum to a theoretical curve. This curve fitting technique allows the user to establish what kind of conduction processes are involved within the system\textsuperscript{228}. Figure 4.19 shows a typical dielectric loss spectrum.
ether/TCNQ complexes show some very interesting trends. The 1:1:1 and 1:1:2 complexes use an electronic mechanism as the main form of conduction throughout the system. When the 2:1:1 and 1:1 complexes are examined, the a.c. measurements suggest that both electronic and ionic conductivity are taking place. However, in these cases the electronic conductivity dominates over the ionic conduction mechanism. In the case of the 2:1 complex quasi d.c. conductivity is observed and now conduction is not electronic but ionic in nature.

Some of the conclusions drawn from the d.c. measurements are verified clearly by the a.c. measurements. The 1:1:1 and 1:1:2 complexes are highly conducting and a.c. measurements show that a large electronic conduction process is taking place. In the 2:1:1 and 1:1 complexes which are intrinsically less conducting, both ionic conduction and electronic conduction mechanism are seen to be taking place. The 2:1 complex, which is the least conducting, shows quasi d.c. conductivity behaviour and the mechanism of conduction is now ionic. Obviously the bulking out of the system by the crown ether inhibits any electronic conduction along TCNQ stacks and so conduction must be taking place via the cation bound within the crown ether. These conclusions contrast with the work of Newman et al.111
and later Nogami et all112, who suggested that conduction processes taking place in crown ether/metal halides complexes involve anion transport. Clearly the electrical work in this section of work has thrown a different light onto conduction processes within crown ether complexes.

4.5.2 Electron Spin Resonance.

In the final stages of this study, preliminary electron spin resonance measurements were carried out.
on a few of these complexes. The eventual aim of this work was to attempt to calculate the electron density within the complexes and to relate this to the conductivity. Obviously the electron density of the complexes will give an indication of the availability of electrons and hence the ability of that complex to conduct. However, because only a few measurements have as yet been made we do not feel confident at this stage to say any more about the findings of such work.

4.5.3 X-Ray Crystallographic Studies.

As stated earlier, the verification of many of the points raised in the discussion of the structure of crown ether/TCNQ complexes would be provided by X-ray crystallography. Considerable time and effort was spent on attempting to grow crystals suitable for such work. Even though Nogami and co-workers reported that crown ether/TCNQ complexes were isolated as pure crystals, we have found that crystallographically, such materials were of extremely poor quality. Scanning electron microscopy was used to give an indication of both size (Plate 4.1) and crystal shape, and revealed that the crystals obtained were simply too small and of too low quality for a single crystal investigation.

Nakayama and Ishii\textsuperscript{229} suggest that the crystal structure of a crown ether/TCNQ complex does exist
but Dr. K. Ishii has not yet responded to a request for information. However, up until now no information has been published on this crystal structure and attempts to gain access to the reference cited by Ishii et al have proved unsuccessful.

In the last few months, however, using another variation on the crystal growing techniques already attempted, a successor has resulted in the isolation of high quality crystals. Hopefully, it will not be long before an X-ray structural study of a crown ether/TCNQ complex will be completed.

Plate 4.1 Electron Microscopy gives an Indication of Size and Shape of the Crown Ether/TCNQ Complexes.
4.6 INTRODUCTION TO PHOTOGRAPHIC DYSES.

Dyes are used in photography for a number of distinct purposes, the most important of which are (1) as spectral sensitizers (sensitizing dyes), (2) as colour images in colour photography, (3) in antihalation, filter layers and in colour filters and (4) as densitizers. The "dyes" were discovered in 1856 by Greville Williams, while characterising quinoline obtained by the distillation of alkaloids with caustic alkali. After quaternisation with alkyl iodides, these samples of quinoline gave reddish blue dyes by treatment with silver oxide. Although the dyes attracted little attention as fabric dyes, a small firm in Paris manufactured small quantities of these compounds (Figure 4.20) naming them "cyanine" which means blue. Spectral sensitisation was discovered in 1873 by Vogel during a study of the spectral sensitivity of silver halide dry collodion plates. Certain plates gave spectral sensitivity maxima in the green. This spectral sensitivity was removed by washing the plate prior to exposure and regained by addition of other dyes, including Williams' original cyanine.
By the early 20th century spectral sensitivity had been extended throughout the visible region with isocyanine dyes erythrosin and hundreds of other dyes. Pope and Mills prepared and carefully evaluated a great many dyes. However, one of the most important structural discoveries was published by Mills and Hamer. Up until this time the majority of dyes were believed to consist of a monomethine link between two heterocyclic nuclei. However, it was Mills and Hamer that suggested "Pinacyanol" consisted of two quinoline rings linked not by one but by three methine carbons. The structure of the benzothiazole dye which had until this time also been thought to be monomethine, was
also found to be a trimethine dye. As a result of showing that the monomethine dye absorbed light at a different wavelength to the trimethine dye, an important relationship between dye colour and structure was developed. The term carbocyanine was suggested for the trimethine dye, the term simple cyanine being used to describe the monomethine dye.

After the development of the colour-structure relation, enormous synthetic efforts brought generalised synthetic procedures, new intermediates and a new class of dyes (merocyanines). Koenig used orthoester and vinylogues of these compounds \((\text{EtO-}(\text{CH=CH})_n-\text{CH(OEt)})_2, n=0,1\) to prepare symmetrical dyes. Variations of such reagents led to powerful sensitisers and to extended-chain dyes with seven methine carbons. Piggott and Rod developed unsymmetrical dyes which are known as "ICI intermediates". The development of the merocyanines proved not only useful as sensitisers but also served as intermediates for complex dyes. Finally, extended-chain quaternary salts provided an important synthetic entry into infra red sensitisers.

In addition to the developments above, structural modification of the linked heterocycles also took place. The replacement of the nitrogen (cyanines) by other heteroatoms, for example oxygen, led to the
oxonol dyes. Many of these novel chromophores were developed along with ferrocene and phosphorus containing dyes.

Sensitising dyes are characterised by high extinction transitions in the visible or infrared regions of the spectrum. The primary types of chromophores for these molecules are the amidinium-ion system (A), the carboxyl-ion system (B) and the dipolar amidic system (C) (Figure 4.21). For each system two extreme resonance structures are shown, where any of the formal changes are located at the ends of the chromophore. Intermediate resonance structures, with the charges nearer the centre of the chromophore or with additional dipoles, were considered less important in the resonance picture of dyes. However, structural changes which favoured intermediate forms had significant effects on the colour of symmetrical dyes (A)\textsuperscript{237}. For the amidic dyes (C) structural features stabilising both neutral and dipolar extreme resonance forms gave longer wavelengths absorbing dyes\textsuperscript{238}.

The important characteristics that influence the absorption wavelengths for these dyes are the length of the conjugated chain and the nature of the terminal group. Many of the early cyanine dyes comprised of a chain with an odd number of methine carbon atoms (C-H) and two heterocyclic rings like
quinoline or benzothiazole. Historically\textsuperscript{239}, the
terms simple cyanine, carbocyanine and
dicarbocyanine, were used to designate both the
specific dyes derived from quinoline and also generic
dye structures (Figure 4.22) from other heterocycles
with one, three, five etc, methine carbon atoms. For
the dyes from quinoline, the ring position attached
to the methine chain and the N-substituent are
usually specified (e.g. 1,1-diethyl-2,2-cyanine is a
dye where $X = (CH=CH)$ and $n = 0$).

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{cyanine_dyes}
\caption{Cyanine Dyes.}
\end{figure}

\begin{align*}
(A) & \quad \text{N} = \text{CH} - (\text{CH} = \text{CH})_n - \text{N} \\
(B) & \quad \text{O} = \text{C} - \text{CH} = \text{C} - \text{O}^- \\
(C) & \quad \text{N} - (\text{CH} = \text{CH})_n - \text{C} = \text{O} \\
\end{align*}
Dyes derived from the primary chromophores $B + (C)$ (Figure 4.21) were subsequently designated oxonols and merocyanines, although the term neutrocyanine has been used for $(C)$. For certain cyanine dyes and for merocyanines the "simple" designation refers to a dye with the shortest possible linkage that retains the chromophore between the terminal groups.

Table 4.13  Absorptions of Vinylogous Dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$n=0$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Diagram 1]</td>
<td>423nm</td>
<td>557nm</td>
<td>650nm</td>
<td>758nm</td>
</tr>
<tr>
<td>![Diagram 2]</td>
<td>542nm</td>
<td>613nm</td>
<td>714nm</td>
<td>--</td>
</tr>
<tr>
<td>![Diagram 3]</td>
<td>432nm</td>
<td>528nm</td>
<td>605nm</td>
<td>635nm</td>
</tr>
<tr>
<td>![Diagram 4]</td>
<td>396nm</td>
<td>458nm</td>
<td>490nm</td>
<td>510nm</td>
</tr>
<tr>
<td>$\text{Ph}-(\text{CH}_2)_m\text{Ph}$</td>
<td>--</td>
<td>328nm</td>
<td>357nm</td>
<td>383nm</td>
</tr>
</tbody>
</table>
Dyes that differ only by the number of vinyl groups (CH=CH) in the conjugated chain are termed a vinylogous series. Absorption maxima for vinylogous series of dyes like 2-5 in Table I shift to longer wavelengths as the methine chain length increases (Table 4.13).

4.6.1 Application of Dyes.

A photographic dye may be defined as a component of photographic assembly (film, paper etc.) which is not present in the final version of that assembly. The dye is removed during one of the processing states and is shown below in a simplified picture of a typical photographic assembly.

A - Non-stress and U.V. Absorber
B - Blue-Sensitive Emulsion
C - Yellow Filter Layer
D - Green-Sensitive Emulsion
E - Magenta Filter Layer
F - Red-Sensitive Emulsion
G - Underlayer
H - Base
I - Backing Layer

(I) is usually not present in a colour negative film but has been included for the sake of completeness. (A) is a mechanically protective
coating and may contain a U.V. light absorber. The silver halide crystals are activated by U.V. light therefore a U.V. absorber is incorporated to prevent incorrect colour rendition (for example, it is essential that the red-sensitive region is excited by red light only). (B) is an emulsion sensitive to blue light $\lambda = 400-500\text{nm}$ and is absorbed by layer (C). (C) is a yellow filter and will absorb blue light, blue and yellow being complementary colours. Below this is a green-sensitive emulsion (D) ($\lambda = 500-600\text{nm}$) and an associated green absorbing layer (E), followed by a red-sensitive emulsion (F) ($\lambda = 600-700\text{nm}$) and an underlayer (G). The latter absorbs all the light that negotiates regions (A) to (F) without absorption. Layer (I) is only present in certain fibres (microfibres and X-ray fibres) and performs the same function as layer (G). It may also serve to balance the load of gelatin on either side of the base, thus keeping the film flat (a particular problem in X-ray films).

Dyes are used in underlayers and backing layers as antihalation agents (Figure 4.23). In (B) a bleachable dye underlayer prevents all reflections and a sharper image is obtained.
4.6.2 Bleachable Dyes.

It is possible to eliminate halation by uniformly distributing a dye (known as an acutance dye) throughout the emulsion layer. A disadvantage of this is that light which would normally have reached a silver halide crystal may be absorbed before it finds its target, with the result that a longer exposure is needed. However, acutance dyes do increase the definition of an image by eliminating the light scattered by the individual silver halide crystals.

It is not possible however, to select a dye and insert it into a photographic assembly and expect perfect performance. Dyes must be compatible with all the other components and should not sensitize or desensitize an emulsion. This rules out many cationic dyes. Strictly speaking, an acutance dye has a densitizing effect on the film as a whole, but not specifically on the halide crystals. Dyes should
be removable at some point between the end of exposure and the end of processing, that is the dyes should be "bleachable". Theoretically any water-soluble dye may be washed out during processing, but complete removal is difficult, and the image remained delicately stained and the processing solutions highly coloured.

In the majority of cases it is the sulphite of the developer which destroys the bleachable dye. Bleachable dyes on the whole, contain an α,β-unsaturated carbonyl centre (Scheme 4.1) and will be available for Michael-type addition. The consequence of this type of addition is that the chromophore is broken making the dye more water soluble. As well as the sulphite being present, hydroxylamine, ethylenediamine, hydrazine, thiols and thiosulphate are all nucleophiles found in the processing solutions. These will also undergo Michael addition.

\[
\begin{align*}
\text{Scheme 4.1 Michael Addition of Sulphite.}
\end{align*}
\]

A bleachable dye must also be substantive, that is the dye must be layer specific. The acutance dye is everywhere in the film and a gelatin-soluble
(water soluble) dye can be used, assisting also the bleaching phase of processing. As for a filter or antihalation dye the requirements of layer specificity are more severe. The problem of layer specificity is to treat the gelatin as a 3-D array of inert strands and to design a dye which is bulky enough to be caught in this "fishing net" type array. This works well unless the dye is too bulky for it then becomes difficult to remove when processing takes place. It is difficult to obtain dyes of exactly the right bulk to be not only layer specific but also to bleach completely.

The type of bleachable dyes used today are shown below:

1. Oxonols

\[ n = 0-2 \]
\[ Z, X = \text{Heterocyclic rings} \]

2. Benzylidenes and Cinnamylidenes

\[ n = 0,1 \]
\[ \text{Ar} = \text{-Ph-NR}_2, \text{or} \]
\[ \text{nitrogen containing heterocycle for example 3-Indolyl.} \]
3. Merocyanines

\[ \begin{align*}
Z, X &= \text{Heterocyclic rings} \\
n &= 0, 1
\end{align*} \]

4. Azamethines

\[ \begin{align*}
Z, X &= \text{Heterocyclic rings} \\
\text{Azamethine} &\quad \text{Azamethinenol}
\end{align*} \]

4.6.3 Electrical Properties of the Dyes.

In 1945 Sheppard and co-workers\(^{242}\) recognised the importance of the electrical properties of the cyanine dyes. The relationship between structure and electrochemical properties became important in the structure-property study of sensitising dyes. The chemistry and self-aggregating properties of cyanine dyes have been studied extensively because of their role as silver halide sensitizers. More recently cyanines have shown potential as low-dimensional organic conductors. Increasing methine chain lengths lead to decreased thermal activation energies and increased d.c. conductivities (Table 4.14).
Table 4.14 Increase in Methine Bridge Length Increases Conductivity.

<table>
<thead>
<tr>
<th>n</th>
<th>N</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\Delta\varepsilon$ /eV</th>
<th>$\sigma/\Omega^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>605</td>
<td>1.8</td>
<td>$2 \times 10^{-13}$</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>710</td>
<td>1.3</td>
<td>$1 \times 10^{11}$</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>817</td>
<td>0.69</td>
<td>$1.3 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

$N$ is the number of $\pi$ electrons

Grossel and Edwards\textsuperscript{115} thoroughly investigated the solid state properties of the oxonol dyes. The work showed that the oxonol dyes had semi-insulating properties. They found evidence that structural changes in the oxonol dye and the introduction of a variety of counter-ions induce changes in the conduction processes in these materials. Using X-ray crystallography and solid state n.m.r. techniques they attempted to elucidate a general relationship between crystal packing and conductivity within the series of oxonol dyes.
4.6.4 Synthesis of Symmetrical Hydroxypyridone Methine Bridged Oxonol Dyes.

4.6.4.1 Preparation of Cyanoacetamides.

Cyanoacetamides may be prepared by the basic procedure of Carson, Scott and Vose. This involves the treatment of an ester, of a cyanoacetic acid, with an amine (Scheme 4.2).

\[
\text{NCCH}_2\text{CO}_2\text{R} + \text{R NH}_2 \rightarrow \text{NCCH}_2\text{CONHR} \quad (\text{R} = \text{H, Me, Et})
\]

Scheme 4.2 Preparation of Cyanoacetamides.

4.6.4.2 Conversion of Cyanoacetamides to Hydroxypyridones.

The procedure followed for the preparation of simple hydroxypyridones (where R = H, Me, Et) was that of Bobbitt and Scola who had investigated the preparation and reactions of 4-methyl-3-substituted pyridines. This involved condensation of the cyanoacetamides with ethyl acetoacetate (Scheme 4.3).

\[
\text{NCCH}_2\text{CONHR} + \text{CH}_3\text{COCCH}_2\text{COEt} \xrightarrow{\text{Base}} \text{R}
\]

Scheme 4.3 Preparation of Hydroxypyridones.
4.6.4.3 Preparation of the Dye.

The general synthetic route to these materials involves the condensation of two moles of hydroxypyridine with one mole of coupling agent in the presence of a base or salt (usually an acetate or halide). For monomethine bridge oxonol salts triethylorthoforraate is the coupling agent. For the trimethine analogues 1,1',3,3'-tetramethoxypropane is used (Scheme 4.4).

\[
\begin{align*}
\text{Scheme 4.4 Preparation of Oxonol Dyes.}
\end{align*}
\]

4.7 NOVEL CROWN ETHER/OXONOL DYE COMPLEXES.

After the initial work of Grossel and Edwards, when relating conductivity to oxonol dye structure, it was our intention to investigate the effect on adding a crown ether to a photographic dye salt. As shown in the work on the crown ether/TCNQ complexes, we were interested to know how the presence of a crown ether would effect the conductivity of a semi-
insulating oxonol dye. The crown ether/oxonol dye complexes would also provide an excellent system with which to compare the crown ether/TCNQ complexes. A longer term aim of this work was to see whether the incorporation of a photographic dye into an electrochemically active molecular stack would induce any unusual photoelectric and electro-optical properties.  

4.7.1 Crown Ether/Alkali-Metal Oxonol Dye Complexes.

To our knowledge crown ether/oxonol dyes complexes are unknown. However as already stated earlier (Section 3.4.2) they proved very useful as extraction agents. The synthesis of the crown ether/oxonol dyes followed that adopted for the crown ether/TCNQ complexes.

\[(\text{Crown Ether})_m(M^{+}Ox^-)_n\]  

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Combustion Analysis</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. Weight</td>
<td>Found (calc.)%</td>
<td>Remarks</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>(12C4)(LiOx)</td>
<td>60.21</td>
<td>5.95</td>
<td>9.49</td>
</tr>
<tr>
<td>574</td>
<td>(60.63)</td>
<td>(6.01)</td>
<td>(9.76)</td>
</tr>
<tr>
<td>(12C4)2(NaOx)</td>
<td>57.72</td>
<td>6.58</td>
<td>7.24</td>
</tr>
<tr>
<td>766</td>
<td>(57.96)</td>
<td>(6.66)</td>
<td>(7.31)</td>
</tr>
<tr>
<td>(15C5)(NaOx)</td>
<td>58.42</td>
<td>6.10</td>
<td>8.00</td>
</tr>
<tr>
<td>634</td>
<td>(58.67)</td>
<td>(6.15)</td>
<td>(8.83)</td>
</tr>
</tbody>
</table>

Cont. ...
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Combustion Analysis</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. Weight</td>
<td>Found (calc.)%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(15C5)_2(KOx)</td>
<td>C 6.23 H 6.69 N 6.31</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>870</td>
<td>(56.55) (6.78) (6.44)</td>
<td>Violet</td>
<td></td>
</tr>
<tr>
<td>(18C6)(NaOx)</td>
<td>C 58.11 H 6.26 N 8.05</td>
<td>42%</td>
<td>Lt Blue</td>
</tr>
<tr>
<td>678</td>
<td>(58.40) (6.34) (8.25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18C6)(KOx)</td>
<td>C 56.89 H 6.10 N 8.23</td>
<td>58%</td>
<td>Green</td>
</tr>
<tr>
<td>694</td>
<td>(57.06) (6.19) (8.07)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18C6)(NH₄Ox)</td>
<td>C 58.60 H 6.88 N 10.19</td>
<td>22%</td>
<td>Violet</td>
</tr>
<tr>
<td>673</td>
<td>(58.84) (6.98) (10.40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(DB18C6)(KOx)</td>
<td>C 62.01 H 5.29 N 7.00</td>
<td>60%</td>
<td>Purple</td>
</tr>
<tr>
<td>790</td>
<td>(62.28) (5.4) (7.09)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(DB18C6)(NH₄Ox)</td>
<td>C 63.59 H 6.01 N 8.89</td>
<td>17%</td>
<td>Blue</td>
</tr>
<tr>
<td>769</td>
<td>(63.98) (6.11) (9.10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2.2.2)(NaOx)</td>
<td>C 58.97 H 6.79 N 10.38</td>
<td>59%</td>
<td></td>
</tr>
<tr>
<td>790</td>
<td>(59.24) (6.96) (10.63)</td>
<td></td>
<td>Green</td>
</tr>
<tr>
<td>(2.2.2)(KOx)</td>
<td>C 57.83 H 6.7 N 10.27</td>
<td>62%</td>
<td></td>
</tr>
<tr>
<td>806</td>
<td>(58.07) (6.82) (10.42)</td>
<td></td>
<td>Green</td>
</tr>
</tbody>
</table>

Many of the complexes had water of crystallisation associated with them. They were therefore dried prior to combustion analysis.
Crown Ether/Alkaline Earth (and Transition) Metal Oxonol Dye Complexes.

$$(\text{Crown Ether})_m(M^{2+}(Ox^-))_{2n}$$

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Mol. Weight</th>
<th>Found (calc.)%</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>(12C4)(Mg(Ox^-)2)</td>
<td>60.89</td>
<td>5.37</td>
<td>11.30</td>
<td>19%</td>
</tr>
<tr>
<td>982</td>
<td>(61.09)</td>
<td>(5.49)</td>
<td>(11.41)</td>
<td>Blue</td>
</tr>
<tr>
<td>(12C4)2(Ca(Ox^-)2)</td>
<td>58.98</td>
<td>5.87</td>
<td>9.28</td>
<td>54%</td>
</tr>
<tr>
<td>1174</td>
<td>(59.28)</td>
<td>(5.96)</td>
<td>(9.54)</td>
<td>Blue</td>
</tr>
<tr>
<td>(15C5)(Mg(Ox^-)2)</td>
<td>61.02</td>
<td>5.58</td>
<td>10.77</td>
<td>43%</td>
</tr>
<tr>
<td>1026</td>
<td>(60.82)</td>
<td>(5.65)</td>
<td>(10.42)</td>
<td>Violet</td>
</tr>
<tr>
<td>(15C5)(Ca(Ox^-)2)</td>
<td>59.66</td>
<td>5.48</td>
<td>10.62</td>
<td>31%</td>
</tr>
<tr>
<td>1042</td>
<td>(59.88)</td>
<td>(5.56)</td>
<td>(10.75)</td>
<td>Purple</td>
</tr>
<tr>
<td>(15C5)2(Ba(Ox^-)2)</td>
<td>59.78</td>
<td>5.65</td>
<td>10.39</td>
<td>40%</td>
</tr>
<tr>
<td>1086</td>
<td>(59.67)</td>
<td>(5.71)</td>
<td>(10.31)</td>
<td>Purple</td>
</tr>
<tr>
<td>(18C6)(Ca(Ox^-)2)</td>
<td>54.58</td>
<td>5.62</td>
<td>8.11</td>
<td>39%</td>
</tr>
<tr>
<td>1359</td>
<td>(54.75)</td>
<td>(5.74)</td>
<td>(8.24)</td>
<td>Blue</td>
</tr>
<tr>
<td>(18C6)(Ba(Ox^-)2)</td>
<td>54.56</td>
<td>5.17</td>
<td>9.58</td>
<td>33%</td>
</tr>
<tr>
<td>1183</td>
<td>(54.77)</td>
<td>(5.24)</td>
<td>(9.47)</td>
<td>Blue</td>
</tr>
<tr>
<td>(DB18C6)(Ba(Ox^-)2)</td>
<td>58.01</td>
<td>4.78</td>
<td>8.64</td>
<td>63%</td>
</tr>
<tr>
<td>1279</td>
<td>(58.17)</td>
<td>(4.85)</td>
<td>(8.76)</td>
<td>Purple</td>
</tr>
<tr>
<td>(Cyclam)(Cu(Ox^-)2)</td>
<td>59.29</td>
<td>5.66</td>
<td>15.84</td>
<td>21%</td>
</tr>
<tr>
<td>1045.5</td>
<td>(59.29)</td>
<td>(5.55)</td>
<td>(16.07)</td>
<td>Purple</td>
</tr>
<tr>
<td>(Cyclam)(Fe(Ox^-)2)</td>
<td>Pending results</td>
<td></td>
<td></td>
<td>16%</td>
</tr>
</tbody>
</table>

Blue

Cont. ...
Complexes Combustion Analysis
Mol. Weight Found (calc.)% Yield

(Cyclam)(Fe(Ox−)3) Pending results 18%

(Cyclam)(Co(Ox−)2) 59.54 5.39 15.99 23%
1042 (59.86) (5.56) (16.12) Purple

MR+(Ox−)n = Oxonol Dye (Table 0.2).

4.7.2 Spectroscopic Analysis of Crown Ether/Oxonol Dyes.

The same pattern of spectroscopic analysis carried out through this project was adopted for the characterisation of the crown ether/oxonol dyes.

4.7.3 Mass Spectrometry.

Many of the complexes made were studied by electron ionisation and f.a.b. mass spectrometry. The f.a.b. experiments clearly showed the crown ether/oxonol dye complexation in just the same manner as that observed in the crown ether/TCNQ complexes. However, electron ionisation fragmentation patterns gave an indication of the structures present in the crown ether/oxonol dye complexes. A good representative example of this is seen in Table 4.15 of (DB18C6)(NH4Ox).
Table 4.15 - A Typical Fragmentation Pattern* Seen in the Crown Ether/Oxonol Dye Complexes.

<table>
<thead>
<tr>
<th></th>
<th>NH$_4$Ox</th>
<th>Dibenzo[18]-crown-6</th>
<th>(DB18C6)(NH$_4$Ox)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$^+$ = 409</td>
<td>M$^+$ = 360</td>
<td>M$^+$ = 769</td>
<td></td>
</tr>
<tr>
<td>391.01</td>
<td>180.10</td>
<td>361.78</td>
<td></td>
</tr>
<tr>
<td>362.12</td>
<td>164.07</td>
<td>333.10</td>
<td></td>
</tr>
<tr>
<td>332.89</td>
<td>136.03(100%)</td>
<td>200.09</td>
<td></td>
</tr>
<tr>
<td>200.17</td>
<td>75.98</td>
<td>180.04</td>
<td></td>
</tr>
<tr>
<td>101.09(100%)</td>
<td></td>
<td>136.85</td>
<td></td>
</tr>
<tr>
<td>86.04</td>
<td></td>
<td>101.11(100%)</td>
<td></td>
</tr>
<tr>
<td>60.17</td>
<td></td>
<td>86.02</td>
<td></td>
</tr>
<tr>
<td>54.03</td>
<td></td>
<td>76.04</td>
<td></td>
</tr>
</tbody>
</table>

* All spectra were recorded at 70 eV.

4.7.4 Infra Red Spectroscopy.

As already stated infra red spectroscopy was extremely useful at showing the complexation of a crown ether with a salt (M$^+$X$^-$). In the same way as employed for crown ether/TCNQ salts (Section 4.4.7), it was possible to gain evidence for the complexation between the crown ethers and oxonol dyes. Figure 4.24b compares the infra red spectrum of a representative example of a crown ether/oxonol dye complex, with the oxonol dye precursor (Figure 4.24a).
Figure 4.24a  Infra Red Spectrum of Sodium Oxonol.

Figure 4.24b  Infra Red Spectrum of (15C5)(NaOx).
4.7.5 \textbf{\textsuperscript{1}H N.M.R.}

As stated earlier the paramagnetic nature of the TCNQ salts makes it difficult to record n.m.r. spectra of such materials. However, in the case of the oxonol dyes it is possible to record a \textsuperscript{1}H n.m.r. spectrum\textsuperscript{115} (Figure 4.25a). Figure 4.25b shows a typical crown ether oxonol dye spectrum for (DB18C6)(KOx). From the integration of such a spectrum it is possible to work out the stoichiometric composition of the crown ether with respect to the oxonol dyes. It was therefore useful to run \textsuperscript{1}H n.m.r. spectrum in order to check that the proposed composition was in fact accurate.

![Figure 4.25a \textsuperscript{1}H N.M.R. Spectrum of Potassium Oxonol Dye [400 MHz: d\textsuperscript{6}-DMSO].]
As was pointed out for the crown ether/TCNQ complexes, the crown ether has a different chemical shift when complexed than when uncomplexed. A series of shift patterns similar to those seen in the crown ether/TCNQ complexes were also recorded for the crown ether/oxonol dye complexes.

Figure 4.25b  \(^1\text{H N.M.R. Spectrum of (DB18C6)(KOx)}\) [400 MHz:CDCl\(_3\)].

4.7.6  \(^{13}\text{C N.M.R.}\)

After studying the crown ether/oxonol dye complexes using \(^1\text{H n.m.r.,}^{13}\text{C n.m.r. was employed. Figure 4.26a shows a representative example of a metallic cation oxonol dye spectrum, and a complete assignment of this spectrum is presented in Table 4.16. Figure 4.26b shows the spectrum of a crown ether/oxonol dye complex.}
Table 4.16  

$^{13}$C N.M.R. Assignment of Sodium Oxonol Dye.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\delta$(d$^6$-DMSO)</th>
<th>Assignment</th>
<th>$\delta$(d$^6$-DMSO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1),C(20)</td>
<td>13.08</td>
<td>C(11)</td>
<td>120.92</td>
</tr>
<tr>
<td>C(7),C(15)</td>
<td>18.53</td>
<td>C(10),C(12)</td>
<td>157.38</td>
</tr>
<tr>
<td>C(2),C(19)</td>
<td>33.80</td>
<td>C(4),C(16)</td>
<td>158.81</td>
</tr>
<tr>
<td>C(6),C(14)</td>
<td>92.26</td>
<td>C(3),C(9)</td>
<td>161.38</td>
</tr>
<tr>
<td>C(8),C(13)</td>
<td>110.41</td>
<td>C(18),C(21)</td>
<td>161.98</td>
</tr>
<tr>
<td>C(5),C(17)</td>
<td>117.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.26a  

$^{13}$C N.M.R. Spectra of Oxonol Dye

(* 62.9 MHz in d$^6$-DMSO).
As shown for the crown ether/TCNQ complexes the stability of the crown ether/oxonol dye was reflected by the chemical shift changes in the crown ether ring. The chemical shift changes for the crown ether/oxonol dyes are tabulated in Table 4.17.

Figure 4.26b $^{13}$C N.M.R. Spectra of Crown Ether/Oxonol Dye Complex (at 250 MHz; CDCl$_3$).

Table 4.17 $^{13}$C N.M.R. Chemical Shift Changes for Complexed and Uncomplexed Crown Ethers [22.5 MHz; CDCl$_3$].

<table>
<thead>
<tr>
<th></th>
<th>$^{13}$C N.M.R.</th>
<th>$\Delta\delta$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]-crown-4</td>
<td>70.5507</td>
<td></td>
</tr>
<tr>
<td>([12]-crown-4)(LiOx)</td>
<td>70.7791</td>
<td>0.228</td>
</tr>
<tr>
<td>([12]-crown-4)(NaOx)</td>
<td>70.8772</td>
<td>0.326</td>
</tr>
</tbody>
</table>

Cont. ...
<table>
<thead>
<tr>
<th>[12]-crown-4)(Mg(Ox)$_2$</th>
<th>70.6651</th>
<th>0.114</th>
</tr>
</thead>
<tbody>
<tr>
<td>[12]-crown-4)(Ca(Ox)$_2$</td>
<td>70.7502</td>
<td>0.199</td>
</tr>
<tr>
<td>[15]-crown-5</td>
<td>71.2049</td>
<td></td>
</tr>
<tr>
<td>[15]-crown-5)(NaOx)</td>
<td>70.4299</td>
<td>0.775</td>
</tr>
<tr>
<td>[15]-crown-5)(KOx)</td>
<td>70.3371</td>
<td>0.868</td>
</tr>
<tr>
<td>[15]-crown-5)(Ca(Ox)$_2$</td>
<td>70.983</td>
<td>0.322</td>
</tr>
<tr>
<td>[15]-crown-5)(Ba(Ox)$_2$</td>
<td>71.0996</td>
<td>0.105</td>
</tr>
<tr>
<td>[18]-crown-6</td>
<td>70.9882</td>
<td></td>
</tr>
<tr>
<td>[18]-crown-6)(NaOx)</td>
<td>70.7715</td>
<td>0.217</td>
</tr>
<tr>
<td>[18]-crown-6)(KOx)</td>
<td>70.103</td>
<td>0.885</td>
</tr>
<tr>
<td>[18]-crown-6)(Ba(Ox)$_2$</td>
<td>71.404</td>
<td>0.416</td>
</tr>
</tbody>
</table>

4.8 SOLID STATE STUDIES

4.8.1 Electrical Spectroscopy.

4.8.1.1 D.C. Measurements.

Using the same method adopted for determining the d.c. conductivity of the crown ether/TCNQ complexes (Appendix III), the d.c. electrical properties of the crown ether/oxonol dyes were investigated. Table 4.18 shows the room temperature d.c. conductivity measurements and thermal activation energies for all the oxonol dyes used in this study.
Table 4.18  D.C. Conductivity Measurements of the Oxonol Dyes.

<table>
<thead>
<tr>
<th>Oxonol Dyes</th>
<th>$\sigma_{20}(\Omega^{-1} \text{ cm}^{-1})$</th>
<th>$\Delta \varepsilon_{ac}(\text{eV})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOx</td>
<td>$5.53 \times 10^{-13}$</td>
<td>1.46</td>
</tr>
<tr>
<td>NaOx</td>
<td>$1.52 \times 10^{-13}$</td>
<td>1.03</td>
</tr>
<tr>
<td>KOx</td>
<td>$3.58 \times 10^{-13}$</td>
<td>1.11</td>
</tr>
<tr>
<td>NH$_4$Ox</td>
<td>$2.34 \times 10^{-13}$</td>
<td>1.31</td>
</tr>
<tr>
<td>Mg(Ox)$_2$</td>
<td>$1.02 \times 10^{-13}$</td>
<td>1.26</td>
</tr>
<tr>
<td>Ca(Ox)$_2$</td>
<td>$7.5 \times 10^{-13}$</td>
<td>1.04</td>
</tr>
<tr>
<td>Ba(Ox)$_2$</td>
<td>$1.2 \times 10^{-13}$</td>
<td>1.28</td>
</tr>
<tr>
<td>Fe(Ox)$_2$</td>
<td>$3.56 \times 10^{-11}$</td>
<td>1.32</td>
</tr>
<tr>
<td>Fe(Ox)$_3$</td>
<td>$2.63 \times 10^{-9}$</td>
<td>1.17</td>
</tr>
<tr>
<td>Cu(Ox)$_2$</td>
<td>$1.27 \times 10^{-7}$</td>
<td>1.07</td>
</tr>
<tr>
<td>Co(Ox)$_2^*$</td>
<td>$1.07 \times 10^{-15}$</td>
<td>$= 1.00$</td>
</tr>
</tbody>
</table>

* Poor result ($\sigma \sim 10^{-13}$ are in noise).

From the results presented above it is clear that the oxonol dyes of both the alkali and alkaline-earth metal groups, have a similar room temperature conductivity. The activation energy for this process within this series of dyes is approximately 1 eV. From an examination of the transition element oxonol dyes, it is clear that these show considerably higher room temperature conductivity.

On complexation with the crown ethers (Table 4.19) the oxonol dye conductivities change considerably. However, rather than reflecting the
trends seen in the crown ether/TCNQ complexes, the crown ether/oxonol dye series show different general behaviour:

(a) The addition of a crown ether to an oxonol dye generally improves the conductivity by $10^2$ to $10^3$ in the alkali metals. For the alkaline-earth metals the effect is not so dramatic with improved conductivities being about improved by $10^1$ to $10^2$. The addition of the tetra-aza cyma crown ether to the transition element oxonol dyes reduces the conductivity by $10^{-1}$ to $10^{-2}$.

(b) The largest changes in conductivity are seen in the 2:1 complexes of the crown ether/oxonol dyes.

Table 4.19 D.C. Measurements of the Crown Ether/Oxonol Dyes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\sigma_{20}$ (Ω$^{-1}$ cm$^{-1}$)</th>
<th>$\Delta E_{ac}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12C4)(LiOx)</td>
<td>$1.57 \times 10^{-12}$</td>
<td>1.21</td>
</tr>
<tr>
<td>(12C4)$_2$(NaOx)</td>
<td>$1.47 \times 10^{-10}$</td>
<td>1.51</td>
</tr>
<tr>
<td>(15C5)(NaOx)</td>
<td>$6.29 \times 10^{-11}$</td>
<td>1.47</td>
</tr>
<tr>
<td>(15C5)$_2$(K0x)</td>
<td>$4.31 \times 10^{-8}$</td>
<td>1.22</td>
</tr>
<tr>
<td>(18C6)(NaOx)</td>
<td>$3.20 \times 10^{-10}$</td>
<td>1.38</td>
</tr>
<tr>
<td>(19C6)(K0x)</td>
<td>$5.50 \times 10^{-9}$</td>
<td>1.84</td>
</tr>
<tr>
<td>(18C6)(NH$_4$Ox)</td>
<td>$7.50 \times 10^{-10}$</td>
<td>2.13</td>
</tr>
<tr>
<td>(DB18C6)(K0x)</td>
<td>$5.84 \times 10^{-13}$</td>
<td>2.81</td>
</tr>
<tr>
<td>(DB18C6)(NH$_4$Ox)</td>
<td>$4.22 \times 10^{-13}$</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Cont. ...
Before attempting to draw any definite conclusions from these results, it was important to try to understand the conduction processes within these materials. For this reason it was necessary to carry out a.c. dielectric response measurements on them.

### 4.8.1.2 A.C. Measurements.

As stated earlier, the use of a.c. dielectric response spectroscopy provides greater insight into the electrical properties of a material. A typical a.c. spectrum recorded for the crown ether/oxonol dye

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\sigma_{20} (\Omega^{-1} \text{ cm}^{-1})$</th>
<th>$\Delta E_{ac} (\text{eV})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.2.2)(NaOx)</td>
<td>$1.43 \times 10^{-13}$</td>
<td>3.62</td>
</tr>
<tr>
<td>(2.2.2)(K0x)</td>
<td>$2.27 \times 10^{-13}$</td>
<td>3.79</td>
</tr>
<tr>
<td>(12C4)(Mg(Ox)$_2$)</td>
<td>$5.03 \times 10^{-13}$</td>
<td>1.28</td>
</tr>
<tr>
<td>(12C5)$_2$(Ca(Ox)$_2$)</td>
<td>$1.16 \times 10^{-10}$</td>
<td>0.86</td>
</tr>
<tr>
<td>(15C5)(Mg(Ox))</td>
<td>$4.50 \times 10^{-12}$</td>
<td>0.96</td>
</tr>
<tr>
<td>(15C5)(Ca(Ox)$_2$)</td>
<td>$2.79 \times 10^{-11}$</td>
<td>1.16</td>
</tr>
<tr>
<td>(15C5)$_2$(Ba(Ox)$_2$)</td>
<td>$1.66 \times 10^{-9}$</td>
<td>0.82</td>
</tr>
<tr>
<td>(18C6)(Ca(Ox)$_2$)</td>
<td>$1.17 \times 10^{-11}$</td>
<td>1.18</td>
</tr>
<tr>
<td>(18C6)(Ba(Ox)$_2$)</td>
<td>$4.59 \times 10^{-11}$</td>
<td>1.03</td>
</tr>
<tr>
<td>(DB18C6)(Ba(Ox)$_2$)</td>
<td>$9.81 \times 10^{-13}$</td>
<td>0.90</td>
</tr>
<tr>
<td>(Cyclam)(Cu(Ox)$_2$)</td>
<td>$6.4 \times 10^{-8}$</td>
<td>1.08</td>
</tr>
<tr>
<td>(Cyclam)(Fe(Ox)$_2$)</td>
<td>$1.47 \times 10^{-13}$</td>
<td>2.85</td>
</tr>
<tr>
<td>(Cyclam)(Fe(Ox)$_3$)</td>
<td>$2.13 \times 10^{-9}$</td>
<td>2.37</td>
</tr>
<tr>
<td>(Cyclam)(Co(Ox)$_2$)</td>
<td>$1.72 \times 10^{-15}$</td>
<td>1.07</td>
</tr>
</tbody>
</table>
complex is shown in Figure 4.27.

This study showed reveals that the conduction process involved with the crown ether/oxonol dye appears to be ionic in nature. In the light of the work carried out on the crown ether/TCNQ complexes, it seems reasonable that the cationic conduction processes are again involved in the crown ether/oxonol dye salts. The large and immobile anionic dye seems to be involved to a much lesser extent than the cations. This result is at variance
with the conclusions made by Newman et al. and later by Nogami et al., who suggest that a crown ether/metal halide complex shows anionic conduction. This is not altogether surprising since the small halide anions are more mobile than the corresponding anionic dyes. However, in both sets of work by these authors they failed to vary the crown ether sizes and simply looked at a series of metal halides with [18]-crown-6. In this study we have demonstrated that the crown ether size does affect the conductivity. Consequently, the stronger the ability of the crown ether to screen the cation from the anion the greater the conductivity observed. This is clearly supported by the data on the 2:1 complexes, in which the cation is allowed to sit in a crown ether "duct" (Figure 4.18). This network of "ducts" allow the cations to vibrate rapidly and hence interact with other cations, thus facilitating quasi d.c. conductivity. The only exception to the general trends seen in these materials is in the case of the [2.2.2] cryptand/oxonol dye complexes. It is apparent in these complexes that the cation is held so well that it is not allowed to interact as in the case of a two dimensional cryptand. Obviously, the three dimensional cryptand inhibits the quasi d.c. conductivity.

At this stage many of the conclusions drawn from
these electrical conductivity measurements are somewhat speculative. In order to verify the theories, it will be important to carry out X-ray crystallographic studies and to back these up with solid state n.m.r. data.

4.8.2 X-Ray Crystallography.

At the present time considerable effort is being made to isolate decent crown ether/oxonol dye crystals in order to carry out an X-ray diffraction study. There has been some success with this effort and a [2.2.2] cryptand/oxonol complex data set is currently being solved.

4.8.3 Solid State N.M.R.

As stated earlier (Section 3.3.7) solid state $^{13}$C n.m.r. spectra have been recorded for some macrocyclic polyether ligands and their complexes formed with salts of alkali and alkaline earth metals, by Belton et al. These compounds were chosen because their crystal structures have been well characterised, enabling a direct comparison to be made between spectra and structures. We hoped to make a similar comparison for crown ether/oxonol dyes. $(18C6)(0x)$ was chosen as the candidate for this solid state study since an X-ray data collection on this material is also underway.

In order to gain experience and to attempt to measure the solid state chemical shift of a typical
[18]-crown-6 complex, crystals of ([18]-crown-6)(KI) were prepared using the method suggested by Pedersen. Figure 4.29a shows the solid state spectrum of the ([18]-crown-6)(KI) with an individual peak recorded at $\delta$ 70.58 ppm. When this is compared with the (18C6)(K0x) Figure 4.28b the crown ether shift may be clearly seen at $\delta$70.698 ppm. The complete assignment of anionic dye spectrum is shown in Table 4.20.

![Diagram of [18]-crown-6 complex with K⁺ and I⁻ ions]

Figure 4.28a  $^{13}C$ CPMAS Spectrum of (18C6)(KI).
Table 4.23 Solid State and Solution State $^{13}\text{C}$ N.M.R. Data for Potassium Oxonol Dye.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Solid State ppm</th>
<th>Solution State [62.5 MHz; d$_6$-DMSO] ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C(1), C(20)$</td>
<td>14.537</td>
<td>13.08</td>
</tr>
<tr>
<td>$C(7), C(15)$</td>
<td>16.040</td>
<td>18.53</td>
</tr>
<tr>
<td></td>
<td>17.965</td>
<td>Cont.</td>
</tr>
<tr>
<td>Assignment</td>
<td>Solid State ppm</td>
<td>Solution State ppm [62.5 MHz; d6-DMSO]</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>C(2), C(19)</td>
<td>33.734</td>
<td>33.80</td>
</tr>
<tr>
<td></td>
<td>90.714</td>
<td></td>
</tr>
<tr>
<td>C(6), C(14)</td>
<td>93.619</td>
<td>92.26</td>
</tr>
<tr>
<td></td>
<td>94.891</td>
<td></td>
</tr>
<tr>
<td>C(8), C(13)</td>
<td>110.691</td>
<td>110.41</td>
</tr>
<tr>
<td>C(5), C(17)</td>
<td>111.379</td>
<td>117.67</td>
</tr>
<tr>
<td>C(11)</td>
<td>122.420</td>
<td>120.92</td>
</tr>
<tr>
<td>C(10), C(12)</td>
<td>155.986</td>
<td>157.38</td>
</tr>
<tr>
<td>C(4), C(16)</td>
<td>158.613</td>
<td>158.81</td>
</tr>
<tr>
<td>C(3), C(9)</td>
<td>161.034</td>
<td>161.38</td>
</tr>
<tr>
<td>C(18), C(21)</td>
<td>161.956</td>
<td>161.98</td>
</tr>
</tbody>
</table>

Even though time prevented a larger collection of data, Table 4.21 shows the chemical shift changes which take place on complexation of a crown ether with an oxonol dye. The shift changes seen in the crown ether resonances are in good agreement with those reported by Belton et al.174. Hopefully in the near future X-ray structural studies will aid the interpretation of the solid state n.m.r. data, giving detailed insight into the effects of crystal packing on electrical properties.
Table 4.21 Solid State $^{13}$C N.M.R. Shift Changes in Crown Ether/Oxonol Complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\Delta \delta$ ppm</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(15C5)$</td>
<td>71.20</td>
<td>Solution</td>
</tr>
<tr>
<td>$(15C5)(NaOx)$</td>
<td>70.80</td>
<td>Solid</td>
</tr>
<tr>
<td>$(15C5)_{2}(K0x)$</td>
<td>70.79</td>
<td>Solid</td>
</tr>
<tr>
<td>$(18C6)$</td>
<td>70.98</td>
<td>Solution</td>
</tr>
<tr>
<td>$(18C6)(K0x)$</td>
<td>70.68</td>
<td>Solid</td>
</tr>
<tr>
<td>$(18C6)(BaOx)$</td>
<td>70.77</td>
<td>Solid</td>
</tr>
</tbody>
</table>
Results and Discussion III

Chapter 5

5. RESULTS AND DISCUSSION III

5.1 CONDUCTING ORGANIC POLYMERS.

In addition to the quasi-one-dimensional organic charge-transfer salts discussed in Chapter 4, some organic polymers have shown unusually high electrical conductivity\textsuperscript{245,246}; polyacetylene being the first organic polymer reported to show this. MacDiarmid and Heeger\textsuperscript{247} first showed that electrical conductivity could be induced by exposing this material to an oxidising agent. When polyacetylene is oxidised (by an electron acceptor such as iodine or arsenic pentafluoride) or reduced (by donors such as lithium) its electrical conductivity increases by orders of magnitude, up to a maximum of about 500 S cm\textsuperscript{-1}. The disadvantage with polyacetylene lies in its handling and fabrication (arising from its high insolubility and ease of oxidation in air). Alternative synthetic routes and handling techniques are being widely researched today.

Beside polyacetylene, high conductivity has been reported for chemically treated samples of poly-p-phenylene, poly(phenylene sulphide), polypyrrole, poly(1,6-heptadiyne), poly(phenylene vinylene), polyaniline, polythiophene and a family of polyphthalocyanines. Some of these polymers have advantage over polyacetylene. For example, poly(phenylene sulphide) is commercially available.
and polypyrrole, polyaniline and polythiophene are easily synthesized by electrochemical oxidation.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Typical method of doping</th>
<th>Typical conductivity (ohm-cm)^−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene</td>
<td><img src="image" alt="structure" /></td>
<td>Electrochemical, chemical (AsF₅, Li,K)</td>
<td>500 (2000 for highly oriented films)</td>
</tr>
<tr>
<td>Polyphenylene</td>
<td><img src="image" alt="structure" /></td>
<td>Chemical (AsF₅, Li,K)</td>
<td>500</td>
</tr>
<tr>
<td>Poly(phenylene sulfide)</td>
<td><img src="image" alt="structure" /></td>
<td>Chemical (AsF₅)</td>
<td>1</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td><img src="image" alt="structure" /></td>
<td>Electrochemical</td>
<td>600</td>
</tr>
<tr>
<td>Polythiophene</td>
<td><img src="image" alt="structure" /></td>
<td>Electrochemical</td>
<td>100</td>
</tr>
<tr>
<td>Poly(phenyl-quinoline)</td>
<td><img src="image" alt="structure" /></td>
<td>Electrochemical, chemical (sodium naphthalide)</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 5.1 Doped Organic Polymers can be Electrical Conductors.

The process by which high conductivity is attained in these normally insulating polymers is called "doping", by analogy with the doping of semiconductors (Section 4.16). The electronic properties of pure semiconductors are altered by addition of small, controlled amounts of other elements, for example boron or phosphorus is added to silicon. However, the mole fraction of added material needed for the polymers is much larger,
approximately $10^{-2}$ to $10^{-1}$, based on monomer units, rather than $10^{-5}$ to $10^{-8}$ in the case of inorganic semiconductors. Polymer doping involves introduction of a different chemical species and also oxidation or reduction of the polymer itself. Furthermore, the process of doping in some cases leads to a structural modifications of the polymer itself.

The simple picture of a one-dimensional band structure previously described for segregated-stack charge-transfer salts can also be used for polymers. In polyacetylenes for example, the carbon $p_z$ orbitals play the same role as $\pi$-HOMO's in the salts. Because the highest occupied band in polyacetylene is filled, the polymer will be a semiconductor.

In the process of oxidation, electrons are removed from the band. Therefore, the band is only partially occupied and electrical conduction becomes possible. Likewise reduction places electrons into the lowest unoccupied band thereby facilitating conduction. The bandwidths of these polymers in general are much wider than those of the organic metals, approximately 8eV compared with about 1.5eV, because the monomer units of polymer are chemically bonded together, thereby increasing the transfer integral.

5.1.1 Spinless Conductivity.

This band picture fails to explain a phenomenon
called spinless conductivity that has been observed in polyacetylene and other polymers. The total number of free spins (measured by electron spin resonance) i.e. number of unpaired electrons, is too low to account for the electrical conductivity in polyacetylene and certain other polymers.

Schrieffer and Heeger\textsuperscript{248} have advanced an explanation based on solitons, which in polyacetylene takes the form of a reversal of phase in the sequence of single and double bonds along the polymer chain (Figure 5.2). For oxidatively doped polyacetylene, the soliton is in essence a carbocation, that necessitates a reversal of phase in the double-bond sequence in the polymer chain. Propagation of this plate kink under the influence of an electric field may give rise to the electrical conductivity observed in doped polyacetylene.

However, most other conducting polymers do not have the proper topology to allow soliton formation. Consequently Bredas and Chance\textsuperscript{249} have proposed that polarons (radical ions) and bipolarons (di-ions) are formed upon doping of conjugated polymers that do not have degenerate ground states (Figure 5.3).

A polaron in the usual solid-state sense is an electron or hole localised in a deformed region of the crystal lattice. For example, the oxidation of polypyrrole is likely to first produce a polaron (two
localised states in the band gap) and then further oxidation takes place by removing an electron from the polaron level to form a bipolaron, a doubly charged spinless species. In the formation of both the polaron and bipolaron, the so-called valence band remains full and the conduction band remains empty. Therefore, the relatively high conductivity of these polymers probably results from a diffusive motion of the bipolarons.

Figure 5.2 Solitons may Facilitate Conduction* in Oxidised Polyacetylene.

* Removal of two electrons from neutral \textit{trans}-polyacetylene forms two polarons (radical and cation pairs). Combination of the radicals results in two cations that cause phase kinks or domain walls in the double-bond alternation (solitons). Each cation is shown as being localized in this drawing, but it can be delocalized over several sites. The two cations can behave independently. The band diagram shows that oxidation of the polymer does not simply remove electrons from the full valence band but places carbocation or soliton (HC\textsuperscript{+}) states at mid-gap between the conduction and valence bands. Conduction in oxidized polyacetylene has been proposed to occur by means of these spinless solitons.
However, because defects of various kinds such as cross links between chains, chain ends, bends and kinks are common in polymer chains, the question of the origin of conductivity in the polymers remains open and the exact role of the counterion (dopant) still remains unknown. In fact doping is not even assured to be uniform for all samples. Consequently, much work remains before the basic conduction process in organic polymers is understood.

![Diagram of polymer conduction bands](image)

**Figure 5.3** Bipolarons may Play a Role in Oxidised Polyphenylene.
5.2 FUNCTIONALISED CROWN ETHERS.

Only a few derivatives of crown ethers were prepared in the early days because there was little call for them. However, it has become more and more desirable to introduce polyether rings into other structures for specific purposes, such as dyes, products for agriculture, drugs, polypeptides and polymers useful for conversion into fibres and films. Substituted crown ethers have been studied as phase transfer catalysts and it has been asserted that the more lipophilic ligands were superior catalysts. Work by Bradshaw et al. has shown that both metal-ligand complex stability and lipophilicity have an effect on the performance of crown ethers in extractive processes. However, they found that the common crown ethers are already sufficiently lipophilic that further increase in their hydrophobic bulk provides little, if any, improvement in their performance.

One application of these lipophilic crown ethers which we wish to examine is the use of substituted crown ether TCNQ salts in multi-component Langmir-Blodgett films (Appendix IV). Such a film occurs when the molecules stack in such a way as to form a monolayer on a surface. Such a monolayer should have properties similar to those of molecular stacks in crystals and hopefully display conducting
behaviour.

Even though Bradshaw et al.\textsuperscript{121} showed that the alkyl benzo crown ethers showed no satisfactory accomplishment as phase transfer catalysts, he went on to synthesise the acyl- and α-hydroxyalkylbenzo-crown ethers. The addition of a carbonyl group or hydroxy group would he hoped affect the phase transfer behaviour of the crown ethers more substantially than that of the simple alkyl crown ethers. To date there has been no literature dealing with the phase transfer behaviour of these acyl and dihydroxyl crown ethers.

Using the Bradshaw's et al synthetic strategy it was planned to make a series of substituted crown ethers and to study their electrical conductivity when complexed with TCNQ salts. Following our early work (Appendix IV) on long alkyl derivatives of cyanine dyes, it was planned to attempt to study the acylbenzo crown/TCNQ complexes using a Langmuir-Blodgett trough\textsuperscript{123}. The experiments on the cyanine dyes using a demonstration model from Cambridge instruments, showed the successful deposition of successive layers of these long alkyl chained cyanine dyes. Electromicroscopy experiments clearly showed the multilayers of cyanine dyes deposited on the microscope slides.

Bradshaw's method of producing acyl benzo crown
ethers involves aromatic acylation using carboxylic acids and Eaton's reagent (phosphorus pentoxide in methanesulphonic acid)\textsuperscript{251}. Using this procedure good yields have been obtained of acylated crown ethers. Table 5.1 details together the acylated benzo crown ethers prepared in this work with their respective yields. The experimental procedures may be found in Chapter 7 along with analytical and spectroscopic data which are in accordance with literature reports\textsuperscript{121}.

Table 5.1: Acylated Benzo Crown Ethers Preparative Yields.

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Yield</th>
<th>Melting Point</th>
<th>Literature Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R=\text{CH}_3^-$</td>
<td>84</td>
<td>198-206°</td>
<td>86 200-208°</td>
</tr>
<tr>
<td>$=\text{CH}_3(\text{CH}_2)_4^-$</td>
<td>73</td>
<td>144-146°</td>
<td>78 144-147°</td>
</tr>
<tr>
<td>$=\text{CH}_3(\text{CH}_2)_6^-$</td>
<td>78</td>
<td>114-117°</td>
<td>85 -</td>
</tr>
<tr>
<td>$=\text{CH}_3(\text{CH}_2)_8^-$</td>
<td>72</td>
<td>115-119°</td>
<td>75 117-129°</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{C}^-$</td>
<td>75</td>
<td>142-147°</td>
<td>85 146-152°</td>
</tr>
</tbody>
</table>

5.2.1 Polymeric Crown Ethers.

The incorporation of crown ethers into polymers is a useful extension of the applicability of crown
ethers as selective cation-complexing agents. Immobilisation prevents the loss of crown ethers and avoids separation problems. Hitherto, polymer-bonded crown ethers have been used as phase-transfer catalysts, in the separation of alkali and alkaline earth metal salts, and in membrane transport\textsuperscript{252}. Crown ethers can either be incorporated in the backbone of the polymer by (co)polymerisation or can be attached as a pendant group.

With the recent interest in conducting polymers (Section 5.1) and as an extension of the work carried out on crown ether/TCNQ complexes, Nogami et al\textsuperscript{120} produced cation-TCNQ complexes with a polymerised crown ether. However, again the results they presented are of questionable value and it was our intention to attempt to examine more closely the electrical properties of the polymeric crown ether/TCNQ complexes.

5.3 SYNTHESIS OF A POLYMERIC CROWN ETHER.

(Model Reaction).

The work of Reinhoudt and coworkers\textsuperscript{253} gives a preparative route to vinyl benzo crown ethers which could subsequently be polymerised. This shows that the insolation of vinyl benzo crown ethers is most effectively achieved by the functionalisation of the crown ethers. In order to gain experience with handling and spectroscopic characterisation of the
functionised crown ether, a model reaction was attempted using benzo-[15]-crown-5 (Scheme 5.1).

**Method A**

\[ \text{Ac}_2\text{O}/\text{AcOH}/\text{PPA}/60^{\circ}\text{C} \]

**Method B**

\[ \text{AcOH}/\text{MeSO}_3\text{H}(\text{P}_2\text{O}_5)/\text{r.t} \]

Scheme 5.1  Preparative Route to Vinyl Benzo-[15]-crown-5.

Benzo-[15]-crown-5 was acylated by either of the two following methods.

**Method A:** involved taking a mixture of benzo-[15]-crown-5, with acetic anhydride,
polyphosphoric acid and stirring overnight at 60°C in a solvent of acetic acid. The acetyl benzo-[15]-crown-6 was purified by column chromatography to give an 80% yield.

Method B: involved taking a mixture of benzo-[15]-crown-5 and acylating with a carboxylic acid and Eaton's reagent as just discussed in Section 5.2. After purification, the product from this method was collected in 63% yield, however this method was preferred technically as the handling and usage of polyphosphoric acid proved fairly difficult.

The work of Bradshaw and co-workers has shown that many of the acyl benzo-crown ethers could be reduced to the corresponding alcohols by the action of sodium borohydride. 4'-Acetyl benzo-[15]-crown-5 was reduced by this method to yield the α-hydroxyethyl-benzo-[15]-crown-5 in 91% yield.

Dehydration of the α-hydroxyethyl crown ether was achieved using pyridinium tosylate. Early investigatory work had shown that the dehydration of hydroxyethyl crown ethers with p-toluenesulphonic acid in benzene had given rise to polymerisation. With the slightly acidic pyridinium tosylate, the 4'-vinyl benzo-[15]-crown-5 was isolated without polymerisation in 90% yield.

5.3.1 Synthesis of Polymeric Dibenzo-[18]-crown-6.

The model reaction just discussed provided a
useful model for the synthesis of $4',4''$-divinyl dibenzo-[18]-crown-6, and the isolation and purification of the various products proceeded without difficulty (Scheme 5.2). Acetylation and borohydride reduction proceeded smoothly to give $4',4''$ (or $5''$) dihydroxyethyl dibenzo-[18]-crown-6. Bradshaw et al.\textsuperscript{12} had shown that the alcohol could be separated into the two isomers by exploiting the solubility differences in the extraction solvent.

Scheme 5.2 Synthetic Preparative Routes to $4',4''$Divinyl Dibenzo-[18]-crown-6.
Hence, in order to obtain only one isomeric product of divinyl dibenzo-[18]-crown-6, the isomers were separated. There is as yet no simple way of establishing whether the isomer is 4',4" or 4 ,5" as they have identical spectra.

The dehydration of the 4',4"(or 5") \( \alpha \)-hydroxyethyl benzo-[18]-crown-6 was achieved using pyridinium tosylate as suggested earlier. The 4',4"(or 5") divinyl dibenzo-[18]-crown-6 was purified in a 77% yield. The subsequent polymerisation of the vinyl crown ether was achieved using a radical initiator (azodiisobutyronitritle AZBN). Polymeric dibenzo-[18]-crown was isolated by reprecipitation into a stirred solution of methanol\(^2\). Spectroscopic characterisation of polymeric material agreed with the proposed structure (Chapter 7).

5.4 SYNTHESIS OF FUNCTIONALISED AND POLYMERIC CROWN ETHER/TCNQ COMPLEXES.

The isolation of the functionalised and polymeric crown ether/TCNQ complexes was achieved using the general method of complexation throughout this project. All of the crown ethers shown in Figure 5.4 were complexed with both sodium and potassium TCNQ salts.
Functionalised Crown Ethers.

\[ R' = R'' = H \text{ (DB18C6)} \]
\[ R' = R'' = \text{COCH}_3 \text{ (DADB18C6)} \]
\[ R' = R'' = \text{CO(CH}_2)_4\text{CH}_3 \text{ (DHDB18C6)} \]
\[ R' = R'' = \text{CO(CH}_2)_6\text{CH}_3 \text{ (DODDB18C6)} \]
\[ R' = R'' = \text{CO(CH}_2)_8\text{CH}_3 \text{ (DDDB18C6)} \]
\[ R' = R'' = \text{COC(CH}_3)_3 \text{ (DTADB18C6)} \]

Polymeric Crown Ether

![Polymeric Crown Ether](PDB18C6)

Figure 5.4 Crown Ethers which were Complexed with Sodium and Potassium TCNQ.

5.4.1 Spectroscopic Analysis of the Substituted Crown Ether/TCNQ Complexes.

With the experience gained during the work on the simple crown ether/TCNQ complexes, it was possible to characterise the functionalised and polymeric dibenzo-[18]-crown-6/TCNQ complexes.

5.4.2 Mass Spectrometry and Combustion Analysis.

As with the simple crown ether/TCNQ complexes, mass spectrometry was used to show the presence of both the TCNQ salt and the parent crown ether.
Combustion analysis of all these complexes gave good agreement with the predicted composition (Chapter 7).

5.4.3 Infra Red Spectroscopy.

The complexation of the TCNQ salts with the substituted and polymeric crown ethers was monitored using infra red spectroscopy. The spectral features highlighted by the simple crown ether/TCNQ salt (Section 4.4.7), were again present and easy to pick out (Chapter 7).

5.4.4 $^1$H N.M.R.

Due to the paramagnetic nature of the TCNQ radical anion $^1$H n.m.r. spectrum were broad and distorted and no real information could be gained.

5.4.5 $^{13}$C N.M.R.

$R' = R'' = CO(CH_2)_4CH_3(DHDB18C6)$

Figure 5.5a $^{13}$C Spectrum of Substituted Crown ether.
$^{13}$C spectra were collected on a few of the substituted and polymeric dibenzo-[18]-crown-6/TCNQ complexes. As suggested by the work in Chapter 4, complexation of a metal ion within a crown ether lead to chemical shift changes. However, solubility problems with many of the complexes in this section of work meant that extremely long acquisition times were required. Therefore only a few representative example spectra were collected. One such example is shown in Figure 5.5b and may be compared with that of the original substituted crown ether shown in Figure 5.5a.

Diacetyl Dibenzo-[18]-crown-6/Potassium TCNQ.

Figure 5.5b  $^{13}$C Spectrum of Substituted Crown Ether/TCNQ Complex.
5.5 SOLID STATE STUDIES.

5.5.1 Electrical Spectroscopy.

5.5.1.1 D.C. Measurement.

The d.c. conductivity measurements of the functionalised and polymeric crown ether/TCNQ complexes are presented in Table 5.2. It is clear from this series of results that the general pattern of adding substituents shows a decrease in d.c. conductivity and an increase in the band gap, the exception to the rule being showed in both cases with the complexes of the simple dibenzo-[18]-crown-6 derivatives which show high activation energies and low conductivities. Obviously the packing arrangements within this material is not as favourable as in the case of the diacetyl derivative. Whether or not the carbonyl function is in someway involved in conduction remains an unanswered question at this stage.

The polymeric dibenzo-[18]-crown-6/TCNQ complexes prepared in the course of this study are a lot less conducting than those reported by Nogami et al (Figure 5.6)\textsuperscript{120}. The major difference between their systems and ours is that they have polymerised an amide function. Whether or not this amide function is involved with the conductivity remains a puzzle. However, it is also important to note that the electrical properties of the two systems were
measured in two different ways. Nogami et al investigated a homogenous film, while we have studied a compact powder. It is therefore perhaps naive to compare both systems. There still remains the question as to why the dibenzo-[18]-crown-6/TCNQ complexes were less conducting than the substituted dibenzo[18]-crown-6/TCNQ complexes?

In order to

Table 5.2 D.C. Conductivity Measurements of the Substituted and Polymeric Crown Ether/TCNQ Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\sigma_{20}(\Omega^{-1}\text{cm}^{-1})$</th>
<th>$\Delta E_{ac}(eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaTCNQ</td>
<td>$1.4 \times 10^{-5}$</td>
<td>0.51</td>
</tr>
<tr>
<td>(DB18C6)(NaTCNQ)</td>
<td>$2.18 \times 10^{-11}$</td>
<td>1.42</td>
</tr>
<tr>
<td>(DADB18C6)(NaTCNQ)</td>
<td>$5.04 \times 10^{-7}$</td>
<td>0.50</td>
</tr>
<tr>
<td>(DHDB18C6)(NaTCNQ)</td>
<td>$1.50 \times 10^{-7}$</td>
<td>0.51</td>
</tr>
<tr>
<td>(DODB18C6)(NaTCNQ)</td>
<td>$3.84 \times 10^{-8}$</td>
<td>0.70</td>
</tr>
<tr>
<td>(DDDB18C6)(NaTCNQ)</td>
<td>$2.44 \times 10^{-9}$</td>
<td>0.79</td>
</tr>
<tr>
<td>(DTADB18C6)(NaTCNQ)</td>
<td>$7.83 \times 10^{-10}$</td>
<td>0.83</td>
</tr>
<tr>
<td>(PDB18C6)(NaTCNQ)</td>
<td>$4 \times 10^{-10}$</td>
<td>1.23</td>
</tr>
<tr>
<td>KTCNQ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(DB18C6)(KTCNQ)</td>
<td>$1.85 \times 10^{-13}$</td>
<td>1.92</td>
</tr>
<tr>
<td>(DADB18C6)(KTCNQ)</td>
<td>$9.22 \times 10^{-9}$</td>
<td>0.49</td>
</tr>
<tr>
<td>(DHDB18C6)(KTCNQ)</td>
<td>$2.76 \times 10^{-9}$</td>
<td>0.55</td>
</tr>
<tr>
<td>(DODB18C6)(KTCNQ)</td>
<td>$1.53 \times 10^{-11}$</td>
<td>1.89</td>
</tr>
<tr>
<td>(DDDB18C6)(KTCNQ)</td>
<td>$4.96 \times 10^{-10}$</td>
<td>2.64</td>
</tr>
<tr>
<td>(PDB18C6)(KTCNQ)</td>
<td>$1.33 \times 10^{-10}$</td>
<td>0.98</td>
</tr>
</tbody>
</table>
answer this more fully it will be necessary carry out X-ray structural studies on a series of substituted crown ether/TCNQ complexes. At the present time more effort is being concentrated on answering the questions revealed during the course of the work in Chapter 4. However, clearly materials such as those presented in this chapter of work offer exciting possibilities as new electronic devices.

\[
\begin{align*}
M^+ &= \text{Na}^+\text{TCNQ}^- & 4.0 \times 10^{-10} \\
M^+ &= \text{K}^+\text{TCNQ}^- & 1.2 \times 10^{-7} \\
M^+ &= (\text{Na}^+\text{TCNQ}^-)(\text{TCNQ}) & 1.61 \times 10^{-10} \\
M^+ &= (\text{K}^+\text{TCNQ}^-)(\text{TCNQ}) & 6.25 \times 10^{-7}
\end{align*}
\]

Figure 5.6 Nogami et al's Polymeric Dibenzo-[18]-crown-6/TCNQ Complexes.

5.6 POLYMERISATION OF A FERROCENE MACROCYCLE.

As an extension to the work on polymeric crown ethers, an interesting and exciting development would be to synthesize a polymeric ferrocene macrocycle. Such a system could be attached to a conducting or
semiconducting electrode surface, with the incorporation of light sensitive moieties such as organic dyes. Such a multifunctional matrix might act not only as a sensor, but also as a photoelectrolytic system (Figure 5.7).

![Diagram of conducting or semi-conducting surface with dye or TTF, redox centre, and ion selector](image)

**Figure 5.7** Incorporation of a Redoxable Macrocycle into an Electrode Surface.

Before attempting to polymerise a ferrocene macrocycle it was important to thoroughly investigate the polymerisation of ferrocene itself. It was felt that once a reliable synthetic pathway had been developed for this latter process, the same procedure could be used for the polymerisation of the expensive ferrocene macrocycles.

**5.6.1 Polymerisation of Ferrocene.**

A preparation of vinyl ferrocene has been reported by Arimoto and Haven\(^2\)\(^5\)\(^7\) and this pathway was initially investigated (Scheme 5.3).
Ferrocene was reacted with phosphoric acid/acetic anhydride and at 100°C for 10 minutes. The crude product was purified on an alumina column eluting firstly with light petroleum to recover the ferrocene as a yellow band, and then with mixed petroleum (b.p. 40–60°C)/diethyl ether (1:1), to give acetylferrocene as an orange band. The solvent was removed and the pure acetyl ferrocene (58%, m.p. 85°C–87°C; Lit.258 m.p. 85°C–86°C) was recrystallised from n-heptane.

Although early reports suggested that sublimation of the crude product (100°C @ 1 mmHg) would be sufficient to purify the acetylferrocene obtained thus in 71% yield (Mpt = 81°C–83°C), 1H n.m.r. spectroscopy of such material showed that small
quantities of ferrocene were still present and thin layer chromatography also suggested the presence of ferrocenium derivatives. These impurities could be removed much more effectively by column chromatography.

There are many routes by which ferrocene may be acylated using a number of Friedel-Crafts reagents to give both mono- and 1,1'-disubstituted products\textsuperscript{259}. As stated earlier benzo crown ethers are conveniently acylated with carboxylic acids by the action of Eaton's reagent (freshly distilled methanesulphonic acid with phosphorius pentoxide)\textsuperscript{251}. Ferrocene may be acylated in the same fashion in 63\% yield. Unreacted ferrocene was removed by column chromatography.

Early synthetic routes\textsuperscript{257} to 1-hydroxyethyl-ferrocene have been by reduction of acetylferrocene using lithium aluminium hydride (89\%). During the course of this project sodium borohydride was found to be as effective a reducing agent, giving yields of 93\%. The reaction was found to be very clean and any unreacted acetylferrocene was removed by column chromatography.

According to Arimoto and Haven\textsuperscript{257} the 1-hydroxyethylferrocene (carbinol) may then be dehydrated by two methods.
Method A (Scheme 5.4).

A sample of the carbinol is distilled (@ 33 mmHg) under pressure into a tube packed with alumina and heated to 200°. After cooling, the tube packing is extracted with several portions of ether and the ether is concentrated under reduced pressure. The product from this procedure had b.p. 80-85° (0.2mm) and m.p. 48-49°. It was very soluble in ether, petroleum ether and methanol and possessed a camphor-like odour. The yield was only 1.93g (21%).

Method B (Scheme 5.4).

The carbinol ferrocene in pyridine is treated with acetic anhydride at 0°C and then allowed to stand overnight at room temperature. After the solution is concentrated in vacuo to dryness the residue is then purified by column chromatography. This gave a much cleaner separation than did sublimation with yields of 85%. The acetate was then
pyrolysed under similar conditions to those used for the alcohol. Method A proved not to be as effective as Method B, the latter affording vinyl ferrocene in 54% yield.

Scheme 5.4 Method A vs Method B.

Both the above methods are long and involve technically quite difficult procedures. However Nitz and Paquette have dehydrated the carbinol ferrocene using a catalytic amount of pyridinium tosylate. The dehydration was completed in 2 hours and the vinyl ferrocene was separated by column chromatography. Not only is this method technically much easier to execute it gives yields of 78%. The modified reaction pathway for the preparation of vinyl ferrocene now looks as suggested by Scheme 5.5
Arimoto and Haven proved that the vinyl ferrocene could be incorporated into several homo- and copolymers. The most successful homopolymerisation was achieved with the radical initiator (azodiisobutyronitrile AZBN). The method involved taking a small quantity of the vinyl ferrocene in dry benzene, adding a trace AZBN and heating for several hours. The insoluble polymeric material was removed and collected as an analytically pure sample with a 52% yield.

5.6.2 Functionalisation of a Piperazine Cryptand.

With the development of a relatively quick and easy synthetic pathway to polymeric ferrocene, attention focussed onto the polymerisation of a ferrocene macrocycle. However, because we were
unsure whether the Fc[2.2]M macrocycle would be stable enough to survive the polymerisation procedure, it was decided that a cheap synthetic analogue should initially be used. For this reason a ferrocene piperazine cryptand seemed to be a good choice (Scheme 5.6).

However, the preparation of the piperazine cryptand$^{106,107}$ proved more difficult than anticipated. The hydroscopic nature of the piperazine$^{260}$ meant that if it was not dried well before use, the other reactant, 1,1'-ferrocene dicarboxyl chloride was hydrolysed into its corresponding bis acid. The purification of the piperazine cryptand also proved difficult as it tended to decompose on an alumina column if left for too long. Nevertheless, after several attempts an orange/brown powder was isolated in a 32% yield.

The characterisation of the material by combustion analysis showed a good agreement between calculated and found. However, mass spectrometry (EI) showed no molecular ion and the fragmentation pattern was not typical of other ferrocene derivatives. Both $^{13}$C n.m.r. and $^1$H n.m.r. gave spectra as anticipated for such a structure with variable temperature n.m.r. showing the presence of a coalescence phenomena. The infra red spectrum of this material shows the presence of a strong amide
C=O signal (V 1610 cm⁻¹) together with other characteristic ferrocene stretches. Therefore the characterisation of the piperazine cryptand on the whole would seem to support the proposed structure. Whether this material exists as a monomer or a dimer still remains to be answered.

Even though we have not managed to functionalise and eventually polymerise a ferrocene macrocycle, the work in this section provides a good starting point with which to work from. The development of the pathway to polymeric ferrocene should provide a
viable route for functionalising a ferrocene macrocycle. Once the polymeric ferrocene macrocycle has been developed it is hoped that it will show not only interesting properties but also commercial uses.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

It is clear from the work achieved in Chapter 5 that we have successfully answered many of the questions proposed at the start of this study. A completed X-ray study on a ferrocene single crystal provided a useful model for comparison with the more complicated ferrocene macromolecular analogues. The solid-state studies of these materials have given equal insight into their behaviour, and have helped to assess their ability to bind nitrate. In the wake of this work we have thrown up many unanswered questions. In order to attempt to answer these in the future it will be necessary to investigate some of the following:

(i) A complete solid state analysis of the [2.1] and [2.3] ferrocene cryptates and a direct comparison with their ruthenocene analogues.


(iii) To investigate in more depth the ion binding potential of Fe[2.2]B and to study a larger range of cryptate structures.

(iv) To synthesise and observe the possibility of charge transfer complexes in the Fe[2.2]M and Fe[2.2]B structures. Following the work...
6. CONCLUSIONS AND FUTURE WORK.

6.1 RESULTS AND CONCLUSION (PART I).

It is clear from the work achieved in Chapter 3 that we have successfully answered many of the questions proposed at the start of this study. A completed X-ray study on a ferrocene amide provided a useful model for comparison with the more complicated ferrocene macrocyclic amides. The solid state studies of these materials have given useful insight into their behaviour, and have helped to assess their ability to bind cations. In the wake of this work we have thrown open many questions which still remain unanswered. In order to attempt to answer these in the future it will be necessary to investigate some of the following:

(i) A complete solid state analysis of the [2.1] and [3.3] ferrocene cryptands and a direct comparison with their ruthenocene analogues.


(iii) To investigate in more depth the ion binding potential of Fc[2.2]D and to study a larger range of cryptate structures.

(iv) To synthesize and observe the possibility of charge transfer complexes in the Fc[2.2]M and Fc[2.2]D structures. Following the work
of Miller et al\textsuperscript{261} there exists the exciting possibility of ferromagnetic molecular charge-transfer complexes similar to those in Figure 6.1.

Figure 6.1 Charge Transfer Complexes of Fc[2.2]M.

6.2 RESULTS AND DISCUSSION (PART II).

The investigation of the electrical properties of the crown ether/TCNQ salts and later the crown ether/oxonol dyes proved very successful. This study has thrown new light onto a relatively poorly investigated series of materials which show both electronic and ionic conduction mechanisms. From this work we have shown that the crown ether can act as a backbone from which a radical anion or anionic dye can be associated. Even though a considerable amount of work has been carried out on both these materials X-ray structural work would facilitate the interpretation of the conductivity data. However, it is clear from the data currently available that there
is a strong relationship between packing arrangements and conductivity in the solid state. Future work in this section could include:

(i) An investigation of the sulphur substituted crown ethers and more fully the nitrogen substituted crown ethers, and to see how these modify the conductivity in both TCNQ and oxonol dye salts.

(ii) To use this work for a basis for the development of ion-detectors in the case of the oxonol dyes ion-detectors might be developed which undergo chromophoric changes and hence colour changes on binding.

(iii) To study different crown ether/metal-anion complexes to observe whether a more mobile anion would affect conductivity.

6.3 RESULTS AND DISCUSSION (PART III).

Time has not permitted completion of the work in Chapter 5. There clearly is considerable scope for future study which includes the following:

(i) To continue to attempt to produce electrically active monolayers, using as a basis the work described in Chapter 4.

(ii) To investigate in more depth the effect of substituents in the crown ethers on
electrical conductivity.

(iii) To prepare a series of polymeric crown ethers and to investigate the electrical behaviour of these materials.

(iv) To use the polymerisation pathway developed for by the ferrocene model reaction to produce a polymeric ferrocene crown ether/cryptand.

(v) To attempt to attach a polymeric ferrocene crown ether/cryptand to an electrode surface with a view to endeavour to producing an electrically switched ion-selective electrode.

(vi) To develop hydrophobic host molecules with incorporated redox centres. Interest in these molecules stems from the idea of investigating the potential catalytic interaction between the redox-active moiety and an included organic guest substrate.

It is clear from this proposed work that the development of electrically active ionophores offers an exciting and interesting challenge for the future.
CHAPTER 7

EXPERIMENTAL

7. EXPERIMENTAL.

7.1 GENERAL EXPERIMENTAL.

7.1.1 Instrumentation.

(a) Melting points.

Melting points were determined in open capillary tubes (unless stated) using an Electrothermal melting point apparatus.

(b) Elemental analysis.

Elemental analyses were carried out by Mr. H. W. Martin, Sayes House and District College (Chemistry Department) using a Perkin-Elmer 240-B Elemental Analyser. All quantities quoted were obtained in the presence of oxygen.

(c) Mass Spectrometry.

Mass spectrometry analyses were carried out by Mr. R. Hurst, Chelsea College, London University, using a Varian MAT 112 spectrometer. Fast atom bombardment mass spectrometry was carried out at the School of Molecular Sciences, University of Sussex, by Dr. A. J. Kennedy, using a Kratos MS80 double focusing mass spectrometer.

(d) Nuclear Magnetic Resonance Spectra.

Both 1H and 13C n.m.r. were carried out with a range of spectrometers within the London University N.M.R. Services.

(e) Mass Spectrometry. 1H n.m.r. spectra were recorded at 400 MHz and 13C at 100 MHz by Mr. A. Caponec.
7. EXPERIMENTAL.

7.1 GENERAL EXPERIMENTAL.

7.1.1 Instrumentation.

(i) Melting-points.

Melting points were determined in open capillary tubes (unless stated) using an Electrothermal melting-point apparatus.

(ii) Elemental Analysis.

Elemental analyses were carried out by Mrs. E. Whitaker, Royal Holloway and Bedford New College (Chemistry Department), using a Perkin-Elmer 240-Elemental Analyser. All analytical samples were dried in the presence of $\text{P}_2\text{O}_5$ in vacuo.

(iii) Mass Spectrometry Service.

Mass spectrometry analyses were carried out by Mr. R. Harper, Chelsea College, London University, using a V.G. Micromass 16B spectrometer. Fast atom bombardment mass spectrometry was carried out at the School of Molecular Sciences (University of Sussex), by Dr. K. Seddon, using a Kratos MS80RF double focusing mass spectrometer.

(iv) Nuclear Magnetic Resonance Spectra.

Both $^1\text{H}$ n.m.r. and $^{13}\text{C}$ n.m.r. were carried out with a range of spectrometers within the London University N.M.R. Services:

(a) Queen Mary College: $^1\text{H}$ n.m.r. were recorded at 400 mHz and $^{13}\text{C}$ at 100 mHz by Mr. P. Haycock.
Spectra were recorded on a Bruker WH-400 MHz pulsed Fourier transform spectrometer.

(b) King's College:- $^1$H n.m.r. were recorded at 250 MHz and $^{13}$C at 62.5 MHz by Mrs. J. Hawkes and Mrs. F. Gallwey. Spectra were recorded on a Bruker WH 250 MHz pulsed Fourier transform spectrometer.

(c) Royal Holloway and Bedford New College:- $^1$H n.m.r. were recorded at 200 MHz, 90 MHz or 60 MHz by Dr. D. Parkinson and by Mr. M. Draper. The 200 MHz spectra were recorded on a Nicolet 293A spectrometer. The 90 MHz spectra were recorded on a Joel FX90Q spectrometer and 60 MHz spectra were recorded on a Hitachi Perkin Elmer R 24B. $^{13}$C n.m.r spectra were recorded at 22.5 MHz on a Joel FX90Q and at 50 MHz on a Nicolet 293A n.m.r. spectrometer, by Dr. D. Parkinson and Mr. M. Draper. All samples were treated with 1% tetramethylsilane (T.M.S.) to provide an internal reference and the chemical shifts are expressed in parts per million from this standard.

(v) Solid State $^{13}$C N.M.R. Spectra.

The $^{13}$C N.M.R. spectra for most samples were recorded at Royal Holloway and Bedford New College on a Bruker MSL 300 MHz with a 7mm double air bearing magic angle spinning probe.

(vi) Multi-Nuclear N.M.R. Spectra.

Multi-nuclear n.m.r. spectra for all samples were
recorded on a Joel FX90Q 90 MHz spectrometer.

(vii) Infra Red Spectroscopy.

Infra Red spectra were recorded on either a Perkin-Elmer 197 instrument or on a Perkin-Elmer 1710 Fourier transform spectrometer. Samples were run in KBr discs.

(viii) Ultra-violet Visible Spectroscopy.

Spectra were recorded on a Perkin-Elmer 551S Ultraviolet-Visible Spectrophotometer.

(ix) Mössbauer Spectroscopy.

Mössbauer spectra were recorded by Mr. W. Marshall of Birkbeck College, London University I.R. Service. Spectra were run on a Cryophysics MS103 machine using a $^{57}$Co source in a rhodium matrix.

(x) X-ray Crystallography.

Details given in Appendix II.

(xi) A.C. and D.C. Electrical Measurements.

Details given in Appendix III.

7.1.2 Solvent Purification$^{265}$.

(i) Acetic acid (Lit.$^{265}$ b.p. 117.7/760 mmHg) was purified by adding some acetic anhydride to react with the water present, heating for 1 hour to just below boiling in the presence of chromium VI oxide (20g/litre) and then by fractional distillation.

(ii) Acetone (Lit.$^{265}$ b.p. 56.2⁰/760 mmHg) was purified by drying with anhydrous $\text{K}_2\text{CO}_3$ overnight and
then fractional distillation of the product. The dried acetone was stored over 4Å molecular sieve.

(iii) Acetonitrile (Lit.265 b.p. 81.6°/760 mmHg) was purified by stirring with calcium hydride until no further hydrogen was evolved. This leaves only traces of water and removed the acetic acid. The acetonitrile was then fractionally distilled from the calcium hydride taking precautions to exclude moisture.

(iv) Azodiisobutynonitrile\textsuperscript{266} (AZBN) was purified by recrystallisation from methanol and drying over phosphorus pentoxide.

(v) Benzene (Lit.265 b.p. 80.1°/760 mmHg) was purified by stirring with lithium aluminium hydride followed by careful fractional distillation (b.p. 80°).

(vi) 1-Butanol (Lit.\textsuperscript{265} b.p. 117.7°/760 mmHg) was purified by careful fractional distillation, water passing over in the first fraction as a binary azeotrope.

(vii) Chloroform (Lit.\textsuperscript{265} b.p. 61.2°/760 mmHg) was purified by washing with water to remove the ethanol impurities used to stabilise commercial chloroform. Calcium chloride was added to dry the chloroform, with refluxing followed by fractional distillation.

(viii) Dichloromethane (Lit.\textsuperscript{265} b.p. 40°/760 mmHg) was purified by pre-drying with calcium chloride,
followed by distillation from phosphorus pentoxide. It was stored away from bright light over 4Å molecular sieve.

(xi) Ethanol (Lit. 265 b.p. 78.3°/760 mmHg) was purified from rectified spirit (95%) by refluxing with calcium oxide (250g/litre) for 6 hours, and leaving overnight before distilling with precautions to exclude moisture.

(x) Ether (Ethyl Ether) (Lit. 265 b.p. 34.6°/760 mmHg) was purified by shaking ether (1 litre) with 10% aqueous sodium sulphite (2 x 250 cm³). The ether was then washed with water, dried for 24 hours with calcium chloride, filtered and dried further by the addition of sodium wire until the metal remained bright. The ether was stored in the dark, in a cool place, until it is distilled (b.p. 36°) from sodium just before use.

(xi) n-Hexane (Lit. 265 b.p. 68.7°/760 mmHg) was purified by distillation from sodium hydride.

(xii) Methanol (Lit. 265 b.p. 65.4°/760 mmHg) was purified by warming clean dry magnesium turnings (5g) and iodine (0.5g) with "absolute" methanol (50-75 cm³) in a flask until the iodine colour disappeared and all of the magnesium was converted to the methoxide. Up to 1 litre of methanol was added and, after refluxing for 2-3 hours, it was distilled off, excluding moisture from the system.
(xiii) Pyridine (Lit. \textsuperscript{265} b.p. 115.6\(^\circ\)/760 mmHg) was purified by refluxing with solid potassium hydroxide, followed by fractional distillation. Pyridine was stored over potassium hydroxide pellets and distilled before use.

(xiv) Tetrahydrofuran (Lit. \textsuperscript{265} 65.4\(^\circ\)/760 mmHg) was purified in a 1-litre portion by stirring magnetically in a flask fitted with a condenser (calcium chloride guard tube), to which lithium aluminium hydride (2-4g) was added in small portions. Periodically the mixture was allowed to settle and a sample of clear liquid was withdrawn and added to a little water; if vigorous evolution of hydrogen occurred, additional lithium aluminium hydride (2.3g) was added. The tetrahydrofuran was then distilled at atmospheric pressure. (Since LiAlH\textsubscript{4} decomposes at temperatures above 150\(^\circ\), the distillation was stopped well short of dryness.) The purified tetrahydrofuran was stored under nitrogen.

7.2 EXPERIMENTAL PART I (Chapter 3)

FERROCENE DERIVATIVES

Ferrocene was obtained from the Aldrich Chemical Company\textsuperscript{267}, and recrystallised prior to use from dry acetonitrile.
1,1'-Diacetylferrrocene

Ferrrocene (3.0g, 16mmol), dissolved in dry dichloromethane (50 cm³), was added over a period of 15 minutes to a stirred mixture of aluminium chloride (5.3g, 40mmol) and acetyl chloride (3.14g, 40mmol) in dry dichloromethane (200 cm³). The reaction mixture was kept in an atmosphere of dry nitrogen to avoid oxidation of ferrrocene, which was attached readily at room temperature with immediate evolution of hydrogen chloride and the formation of an intensely violet solution.

The mixture was stirred at room temperature for 2 hours, then cooled, decomposed with ice, and filtered from aluminium hydroxide. The aluminium hydroxide was washed with chloroform until colourless. The separated aqueous phase is washed with chloroform (3 x 100 mls) and all the combined organic layers were washed until neutral. The pale blue colour of the aqueous solution suggest that only little oxidation of the ferrrocene has taken place. The deep red organic solution was dried with magnesium sulphate and the solvent removed from the filtered solution to
yield crude diacetylferrrocene. The product (3.14 g, 72%) was recrystallised from hexane-chloroform (50:50) to give an analytically pure sample, m.p. 129°-130° (Lit. 268 m.p. 130°-131°);

Found: C, 62.31%; H, 5.24%. C₁₄H₁₄O₂Fe requires C, 62.22%, 5.19%; m/e (70 eV) 270 (M⁺); 240 (M⁺-(CH₃)₂); 184 (M⁺-(COCH₃)₂); τ ¹H [90 MHz; CDCl₃] 4.7 (Cp2, 5 4H(t)); 4.5 (Cp3, 4 4H(t)); 2.35 (CH₃, 6H(s));
Integration 2:2:3; τ ¹³C [50 MHz; CDCl₃] 28.21 (C7, C7'); 71.52 (C2, C3', C4, C4'); 74.18 (C2, C2', C5, C5'); 81.15 (C1, C1'); 201.64 (C6, C6'); Vₘₐₓ (KBr) 3098 (Cₐ, C-H); 1662 (C=O); 1281 (CH₃-C=O); 893, 829 (Cₐ, C-H) cm⁻¹.

1,1'-Ferrocenedicarboxylic Acid.

Ferrocene (8.8 g, 47.3 mmol) was dissolved in dry oxygen-free hexane (200 cm³) in a 500 ml three-necked flask under a dry nitrogen atmosphere. n-Butyl-lithium (1.5 m hexane solution: 7.5 g, 117 mmol) was added to tetramethylethylenediamine (TMEDA) (13.6 g, 117 mmol) in hexane (20 cm³) and left to stand for 15 minutes in a dropping funnel under a nitrogen atmosphere. This was then added over a
period of 1 hour to the ferrocene solution and the mixture was stirred for 18 hours. The dilithioferrocene suspension was then injected onto CO$_2$/ether slush. The crude dilithium salt was then filtered and washed with ether and is reported to contain dilithium salt (98%), monolithium salt (1.8%).

The ferrocene salt can be converted into the acid by the addition of water (100 cm$^3$) and then dilute mineral acid to precipitate out the ferrocene acid. This was then filtered and dried. The traces of ferrocene monocarboxylic acid are removed by extraction with benzene in a SohXlet extractor, the ferrocene dicarboxylic acid being insoluble in benzene. The product (12.3g, 95%) was then recrystallised from glacial acetic acid to give an analytically pure sample, m.p. 195° (Lit. 270 m.p. 195°-205° dec);

Found: C, 52.32%; H, 3.58%. C$_{12}$H$_{10}$O$_4$Fe requires C, 52.22%; M, 5.65%; m/e (70eV) 274 (M$^+$); 272 (M$^+$-(H)$_2$); 228 (M$^+$-CO$_2$)(H)$_2$); 184 (M$^+-$(HCO$_2$)$_2$); $^8$H$_{13}$C[62.5 MHz; d$^6$-DMSO] 70.46 (C$^3$, C$^3'$ C$^4$, C$^4'$); 71.83 (C$^2$, C$^2'$ C$^5$, C$^5'$) 72.51 (C$^1$, C$^1'$); 170.06 (C$^6$, C$^6'$); $V_{max}$ (Br) 3098 (C$_p$, C-H); 2925 (O-H); 1765 (C=O); 1170, 1040 (C-O or O-H); 985 (C$_p$, C-H) cm$^{-1}$. 
Dimethyl Ferrocene-1,1'-dicarboxylate

\[
\begin{align*}
\text{C}_7\text{H}_6\text{Fe} & - \text{OOCCH}_3 \\
\text{C}_7\text{H}_6\text{Fe} & - \text{OOCCH}_3
\end{align*}
\]

Lithium-1,1'-ferrocenedicarboxylate (1.6g, 5.6mmol) was suspended in dry methanol (50 cm\(^3\)). Dimethylsulphate (1.76g, 13.98mmol) in dry methanol (25 cm\(^3\)) was added to the salt. The mixture was stirred and refluxed for 3 hours. Methanol (50 cm\(^3\)) was removed by reduced pressure distillation and the solution was allowed to cool to room temperature. Ether (30 cm\(^3\)) was then added and the solution was washed with water (10 cm\(^3\)) and sodium carbonate (10%: 10 cm\(^3\)). The ether layer was washed again with water and then dried (MgSO\(_4\)). The ether was evaporated and the product (1.2g, 71%) was recrystallised from petroleum ether (b.p. 40°-60°), to give an analytically pure sample, m.p. 115.5° (Lit.\(^\text{107}\) m.p. 114°-115°); Found: C, 55.40%; H, 4.56%. \(\text{C}_14\text{H}_{14}\text{O}_4\) requires C, 55.63%; H, 4.63%; m/e (70eV) 302 (M\(^+\)); 272 (M\(^+\)-(CH\(_3\))\(_2\)); 228 (M\(^+\)-CO\(_2\)CH\(_3\)); 184 (M\(^+\)-(CO\(_2\)CH\(_3\))\(_2\)); \(\delta\) \(\text{H}[90\text{ MHz}; \text{CDCl}_3] 5.05 \text{ (Cp, 2,5 4H(t))}; 4.61 \text{ (Cp,3,4 4H(t))}; 3.62 \text{ (CH}_3, 6\text{H(s))}; \text{Integration 2:2:3}; \(\delta\) \(\text{C}[22.5\text{ MHz}; \text{CDCl}_3] 52.39 \text{ (C7, C7')}; 72.29 \text{ (C3, C3', C4, C4')}; 73.27 \text{ (C2, C2', C5, C5')}; 80.88 \text{ (C1,}
Cl') 172.61 (C6, C6'); νmax (kBr) 3089 (Cp, C-H); 1720 (C=O); 1290 (C-O); 960, 895 (Cp, C-H) cm⁻¹.

1,1'-Ferrocenedicarboxyl Chloride

\[
\begin{align*}
&\text{COCI} \\
&\text{Fe} \\
&\text{COCI}
\end{align*}
\]

Lithium 1,1'-ferrocene dicarboxylate was treated with an 8 fold excess of oxalyl chloride in dry dichloromethane. This was stirred for 1 hour then refluxed for 30 minutes. The excess oxalyl chloride and dichloromethane was removed by evaporation and the residue was extracted with dry hexane (soxhlet 4 hours). The hexane was then evaporated and the residue (60%) was recrystallised from dry hexane, m.p. 98° (Lit. 272 m.p. 98°) m/e (35eV) 314; 310 (M+); m/e (70ev) 240 (M+-Cl)₂; 184 (M+-CCl₂); &

\[\begin{align*}
\text{H}[90 \text{ MHz}; \text{CDCl₃}] & 5.05 (\text{Cp}2,5, 4\text{H(t)}); 4.75 (\text{Cp}3,4, 4\text{H(t)}); \text{Integration 1:1; } 8 \text{ }^{13}\text{C}[22.5 \text{ MHz}; \text{CDCl}_3] \\
& 74.33 (\text{C}^3, \text{C}^3', \text{C}^4, \text{C}^4') 75.76 (\text{C}^2, \text{C}^2', \text{C}^5, \text{C}^5'); \\
& 76.19 (\text{C}^1, \text{C}^1'); 168.46 (\text{C}^6, \text{C}^6').
\end{align*}\]
FERROCENE AMIDES.

1,1'-bis(N-methylamido)ferrocene\textsuperscript{107}.

Excess methylamine (10 cm\textsuperscript{3}) was condensed in a round bottomed flask. A solution of 1,1'-ferrocene dicarboxyl chloride (1g, 3.2mmol) in dry benzene (100 cm\textsuperscript{3}) cooled to 0°C, was added to the methylamine. The mixture was allowed to stir for 4-5 hours and was filtered to remove the precipitated methylamine hydrochloride, and the solvent evaporated to yield an orange/brown oily residue which crystallised on cooling. This was then passed down an alumina column with dichloromethane to remove any traces of amine which may still be present, after which 1% methanol in dichloromethane was used to remove the amide from the alumina. The solvent was evaporated and the product (0.89g, 93%) recrystallised from chloroform, m.p. 109°-110°; Found: C, 55.95%; H, 5.36; N, 9.34%. C\textsubscript{14}H\textsubscript{16}N\textsubscript{2}O\textsubscript{2}Fe requires C, 56.0%; H, 5.34%; N, 9.24; m/e (70eV) 300 (M\textsuperscript{+}); 298 (M\textsuperscript{+}-(H)\textsubscript{2}); 268 (M\textsuperscript{+}-(H\textsubscript{2})(CH\textsubscript{3})\textsubscript{2}); 184 (M\textsuperscript{+}-(NH(CH\textsubscript{3})C)\textsubscript{2}); 8 \textsuperscript{1}H[250 MHz; CDC\textsubscript{13}] 7.28 (NH, 2H(sbr)); 4.58 (Cp2,5, 4H(t)); 4.42 (Cp3,4 4H(t)); 3.82 (CH\textsubscript{3}, H(d)); Integration 1:2:2:3;
1,1'-Bis(N,N-Dimethylamido)ferrocene

Excess pure dimethylamine (10 cm³) was injected into a solution of 1,1'-ferrocene dicarboxyl chloride (0.5g, 16mmol) in dry benzene (50 cm³) cooled to 0°C. After stirring for 10 minutes the mixture was filtered to remove precipitated dimethylamine hydrochloride, and the solvent evaporated to yield the crude product. This was then passed down an alumina column with dichloromethane to remove traces of amine which may still be present, after which 1% methanol in dichloromethane was used to remove the amide from the alumina. The solvent was evaporated and the product (0.5g, 95%) recrystallised from chloroform, m.p. 130°C (Lit. 107, m.p. 130°C); Found: C, 58.45%; H, 8.51%; N, 6.02%. C₁₆H₂₀N₂O₂Fe requires C, 58.5%; H, 8.54%; N, 6.10%; m/e (70eV) 328 (M⁺); 298 (M⁺-(CH₃)₂); 268 (M⁺-(CH₃)₄); 184
(M+-(N(Me)2C0)2); δ^1H[90 MHz; CDCl3] 4.66 (Cp2,5 4H(t)); 4.38 (Cp3,4 4H(t)); 3.06 (CH3, 12H(s));
Integration 1:1:3; δ^13C[22.5 MHz; CDCl3] 38.32 (C7, C7'); 71.97 (C3, C3', C4 C4'); 72.85 (C2, C2', C5, C5'); 80.72 (C1, C1'); 170.62 (C6, C6'); νmax (KBr) 3089 (Cp, C-H); 1625 (C=O); 1260 (C-N); 975, 825 (Cp, C-H) cm\(^{-1}\).

1,1'-Bis(N,N-Morpholine amido)ferrocene

Morpholine (1g, 11.5mmol) and triethylamine (2.55g, 25.3mmol) in dry benzene (100 cm\(^3\)) was added to a solution of 1,1'-ferrocene dicarboxyl chloride (1.79g, 5.75mmol) in dry benzene (100 cm\(^3\)) and stirred for 10 minutes. The mixture was then filtered to remove precipitated trimethylamine hydrochloride and the solvent was evaporated to yield the crude amide. This product was passed down an alumina column (grade 1) with dichloromethane to remove any amine present. Methanol (1%) in dichloromethane was then passed through the alumina to remove the amide. The solvent was evaporated and the product (2.18g, 92%) recrystallised from chloroform to give an analytically pure sample, m.p.
180°–181° (Lit.107 m.p. 179°–180°); Found: C, 58.35%; H, 6.84%; N, 5.75%. C_{20}H_{24}N_{2}O_{4}Fe requires: C, 58.29%; H, 6.80%; N, 5.83%; m/e (70eV) 412 (M^+); 356 (M^+-(CH_2)_4); 268 (M^+-(CH_2)_40)_2; 184 (M^+-(CON(CH_2)_4))_2; £ ^1H[90 MHz; CDCl_3] 4.6 (Cp2,5 4H(t)); 4.4 (Cp3,4 4H(t)); 3.66 (CH_2, 16H(s)); Integration 1:1:4; £ ^13C[62.5 MHz; CDCl_3] 45.75 (C_7, C_7'); 67.1 (C_8, C_8') 71.3 (C_3', C_3', C_4, C_4'); 72.21 (C_2', C_2', C_5, C_5'); 80.9 (C_1, C_1') 169.12 (C_6, C_6');

\[ V_{max} (KBr) 3089 (Cp, C-H); 1625 (C=O); 1280 (C-N); 1170, 1100 (C-O); 820, 720 (Cp, C-H) \text{ cm}^{-1}. \]

1,1"-(1,4,10,13-tetraoxa-7,16-diazaacyclo-octadecane-7,16-diylidicarbonyl)ferrocene (Fc[2.2]M).

A 1 litre 3-necked creased flask, equipped with a mechanical stirrer, was flushed with nitrogen and charged with dry benzene (100 cm³). A solution of 1,1'-ferrocene dicarboxyl chloride (1.18g, 3.8mmol) dissolved in benzene 100 ml was placed in a pressure-equalising dropping funnel. In a second similar dropping funnel were placed 1,4,10,13-tetraoxa-7,16-diazaacyclooctadecane (1g, 3.8mmol) and triethylamine.
(0.85g, 8.4mmol) in benzene (100 cm³). The two solutions were added dropwise, simultaneously over a period of 2.5 hours, with vigorous stirring. The mixture became orange and deposited a fine precipitate of triethylamine hydrochloride. When the addition was complete the mixture was stirred for a further 4 hours and left to stand overnight. The solids were separated by filtration and the solvent was then removed to leave an orange residue. This material was chromatographed on a column of alumina using dichloromethane - 0.5% methanol. An orange band was collected, evaporated and the monomeric product (0.75g, 40%) recrystallised from dichloromethane - pentane (1:5), m.p. 183°-184° (Lit. 160 m.p. 183°-184°); Found: C, 57.34%; H, 6.50%; N, 5.65%; C₂₄H₃₂O₆N₂Fe requires C, 57.61%; H, 6.44%; N, 5.6%; m/e (70eV) 500 (M⁺); 226 (M⁺-(CONC₁₂H₂₄O₄)); 184 (M⁺-(CON)₂C₁₂H₂₄O₄); Vₚₚₒₓ (KBr) 3446 (H₂O, O-H); 3098 (Cp, C-H); 2862, m 2360 (Alkane, C-H); 1620 (C=O); 1477, 1413, 1353 (Alkane, C-H); 1260 (C-N); 1140, 1099 (Ether, C-O); 917, 876 (Cp, C-H).

ISOLATION OF THE Fc[2.2]M/ALKALI-METAL COMPLEXES¹

(Fc[2.2]M)ₘ(M⁺X⁻)ₙ⁻

All of the simple Fc[2.2]M salts (m = 1, n = 1) were isolated by the following procedure:-

An M⁺ X⁻ salt and Fc[2.2]M (1-1 molar equivalent)
were dissolved in hot dry methanol and boiled for 15 minutes with stirring, after which the hot solution was filtered. The filtrate was allowed to cool at 0°C for several hours. Crystals thus precipitated were collected, washed with a small amount of methanol and dried in a vacuum. If crystals did not precipitate, the solution was cooled to -15°C after being concentrated.

All the simple inorganic salts used in these complexation reactions outlined were Analar samples or were recrystallised before use. More spectroscopic details of these complex salts may be seen in Chapter 3.

Fc[2.2]M/Lithium Perchlorate.

(Representative Example)

Lithium perchlorate (0.1g, 0.984mmol) and Fc[2.2]M (0.5g, 0.94mmol) were dissolved in hot dry methanol and refluxed for 15 minutes with stirring, after which the hot solution was filtered. The filtrate was allowed to cool at 0°C for several
hours. A bright orange solid (0.27g, 45%) was collected, washed with a small amount of methanol and dried in a vacuum, m.p. 127°-129° dec.

**Fc[2.2]M/Lithium Iodide.**

Using the general procedure outlined previously, lithium iodide (0.13g, 1mmol) and Fc[2.2]M (0.5g, 1mmol) were complexed and a light tan solid (0.931g, 49%) was collected, m.p. 110°-112° dec.

**Fc[2.2]M Lithium/Trifluoromethanesulphonate.**

Using the general procedure outlined previously, lithium trifluoromethanesulphonate (0.16g, 1mmol) and Fc[2.2]M (0.5g, 1mmol) were complexed and a brown tan solid (0.25g, 39%) was collected, m.p. 114°-115° dec.

**Fc[2.2]M/Calcium Trifluoromethanesulphonate.**

Using the general procedure outlined previously, calcium trifluoromethanesulphonate (0.34g, 1mmol) and Fc[2.2]M (0.5g, 1mmol) were complexed and a brown tan solid (0.1g, 12%) was collected, m.p. 135°-136° dec.

**Fc[2.2]M/Silver Iodide.**

Using the general procedure outlined previously, silver iodide (0.24g, 1mmol) and Fc[2.2]M (0.5g,
Immol) were complexed and a dark brown solid (0.39 g (53%) was collected, m.p. 92°-93°.

**Fc[2.2]M/Lithium Tetracyanoquinodimethane.**

![Diagram](image)

Using the general procedure outlined previously, lithium TCNQ (0.21 g, 1 mmol) (Section 7.3) and Fc[2.2]M (0.5 g, 1 mmol) were complexed and a bright green solid (0.34 g, 48%) was collected, m.p. 113°-115° dec.

**Fc[2.2]M/Sodium Tetracyanoquinodimethane.**

Using the general procedure outlined previously, sodium TCNQ (0.23 g, 1 mmol) (Section 7.3) and Fc[2.2]M (0.5 g, 1 mmol) were complexed and a blue/green solid (0.23 g 32%) was collected, m.p. 122°-124° dec.

**1,1''',1''''-bis(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyldicarbonyl)bisferrocene (Fc[2.2]D).**

![Diagram](image)
Larger quantities of dimer were produced by charging a three-necked creased flask, equipped with a mechanical stirrer, a pressure-equalising dropping funnel, and was flushed with nitrogen. With a solution of 1,1'-ferrocene dicarboxyl chloride (1.18g, 3.8mmol) dissolved in dry benzene (100 cm³), 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1g, 3.8mmol) and triethylamine (0.85g, 8.4mmol) in dry benzene (100 cm³) was added dropwise, over a period of 2.5 hours, to the solution in the flask. The mixture was stirred vigorously and over a period of 4 hours a fine precipitate of triethylamine hydrochloride formed. When the addition was complete the mixture was left to stand overnight. The solids were separated by filtration and the solvent was then removed to leave an orange residue. This material was chromatographed on a column of alumina using 0.5% methanol - dichloromethane as eluent. An orange band was collected, evaporated and the monomeric product (0.14g, 27%) was recrystallised from dichloromethane - pentane (1:5).

Further elution of the column using 2% methanol - dichloromethane produced a second orange band. After removal of solvents the dimeric produce (0.86g, 39%) was recrystallised from dichloromethane - pentane (1:5), m.p. 243°-245° (Lit. 160 m.p. 243.5°-245°); Found: C, 57.24%; H, 6.5%; N, 5.48%. C₄₈H₆₄O₁₂N₄Fe₂
requires C, 57.61%; H, 6.44%; N, 5.6%; m/e (35eV) 1000 (M⁺); 500 (M⁺-C₂₄H₃₂O₆N₂Fe). m/e (70eV) 816 (M⁺-C₁₀H₈Fe); 500 (M⁺-C₂₄H₃₂O₆N₂Fe). Fragmentation follows the same pattern as shown in monomeric material; Vₘₐₓ (KBr) 34456 (H₂), 0-H); 3098 (Cₚ, C-H); 2862, 2360 (Alkane, C-H); 1622 (C=O); 1140, 1099 (Ether, C-O); 917, 876 (Cₚ, C-H).

ISOLATION OF THE Fc[2.2]D/ALKALI-METAL COMPLEXES.

Fc[2.2]D/Rubidium Trifluoromethanesulphate.

Using the general procedure previously outlined for the Fc[2.2]M complexes, rubidium trifluoromethanesulphonate (0.12g, 0.5mmol) and Fc[2.2]D (0.5g, 0.5mmol) were complexed and a dark brown solid (0.19g, 32%) was collected, m.p. 180° dec. More spectroscopic details for these complexes are in Chapter 3.


Using the general procedure outlined previously rubidium tetracyanoquinodimethane (0.14g, 0.5mmol) and Fc[2.2]D (0.5g, 0.5mmol) were complexed and a violet solid (0.25g, 39%) was collected, m.p. 180°
Lithium Trifluoromethanesulphonate

Lithium carbonate (0.49g, 6.67mmol) was suspended in water (20 cm³) and to this solution was added trifluoromethanesulphonic acid (2g, 13.3mmol), in water 20 (cm³), dropwise until all the lithium carbonate was completely dissolved. The solution was freeze dried and a white solid (2.07g, ~100%) was collected, m.p. < 300° (Lit. 273 m.p. < 300°); Found: C, 7.62%. \( C_{1}F_{3}S_{1}O_{3}Li \) requires: C, 7.69%.

Calcium Trifluoromethanesulphonate.

Calcium trifluoromethanesulphonate was synthesised by the same general procedure adopted for lithium trifluoromethanesulphonate. Trifluoromethanesulphonic acid (5g, 33.34mmol) in water (20 cm³) was added dropwise to a solution of calcium hydroxide (1.23g, 16.67mmol) in water 20 (cm³). The solution was freeze dried and a white solid (5.50g, 98%) was collected, m.p. < 300° (Lit. 273 m.p. < 300°); Found: C, 7.19%. \( C_{2}F_{6}S_{2}O_{6}Ca \) requires: C, 7.10%.

Rubidium Trifluoromethanesulphonate.

Using the general procedure outlined previously a solution of trifluoromethanesulphonic acid (3g, 20mmol) in water (20 cm³) was added dropwise to a solution of rubidium carbonate (2.3g, 10mmol) in water (20 cm³). The solution was freeze dried and a white solid (4.67g, ~100%) was collected, m.p.
7.3 EXPERIMENTAL PART II (Chapter 4).

**7,7,8,8-Tetracyanoquinodimethane (TCNQ) Salts.**

Tetracyanoquinodimethane was obtained from Aldrich Chemical Company and was recrystallised from acetonitrile. Unless stated, the formation of the "cation TCNQ salts" was by the reaction of a cation source (usually an iodide) with purified tetracyanoquinodimethane. For example, lithium TCNQ is formed by the following reaction:

\[
3\text{LiI} + 2\text{TCNQ} \rightleftharpoons 2\text{LiTCNQ} + \text{Li}^+ + \text{I}_3^{-} \]

**ALKALI METAL TETRACYANOQUINODIMETHANE.**

**Lithium 7,7,8,8-Tetracyanoquinodimethane.**

(Representative Example)

To a boiling solution TCNQ (2.04g, 10mmol) dry acetonitrile (200 cm³) was added a boiling solution of lithium iodide (4.0g, 30mmol) in acetonitrile (30 cm³). Purple crystals started to separate from the dark brown solution on cooling. The mixture stood for 4 hours at room temperature and while still warm the purple solid was collected and washed on a filter with acetonitrile until the washings were bright green. The solid (2.03g, 96%) was then washed with a
large volume of ether to yield an analytically pure sample, m.p. > 300°C (Lit. 220 m.p. > 300°C dec), Found; C, 68.25%; H, 2.0%; N, 25.6%. \( \text{C}_{12}\text{H}_4\text{N}_4\text{Li} \) requires C, 68.3%; H, 1.9%; N, 26.5%.

**Sodium 7,7,8,8-Tetracyanoquinodimethane.**

Cation ion source: NaI Purple Crystals

Yield: 1.30g (58%) m.p. > 300°C dec (Lit. 220 m.p. > 300°C dec); Found: C, 63.71%; H, 2.0%; N, 24.8%.

\( \text{C}_{12}\text{H}_4\text{N}_4\text{Na} \) requires C, 63.4%; H, 1.8%; N, 24.4%.

**Potassium 7,7,8,8-Tetracyanoquinodimethane.**

Cation ion source: KI Red Needle Crystals

Yield: 1.65g (68%) m.p. > 300°C dec (Lit. 220 m.p. > 300°C dec); Found: C, 59.5%; H, 2.1%; N, 22.9%.

\( \text{C}_{12}\text{H}_4\text{N}_4\text{K} \) requires C, 59.2%; H, 1.7%; N, 23.0%.

**Rubidium 7,7,8,8-Tetracyanoquinodimethane.**

Cation ion source: RbI Purple Crystals

Yield: 1.79g (62%) m.p. > 300°C dec (Lit. 220 m.p. > 300°C dec); Found: C, 49.60%; H, 1.4%; N, 19.26%.

\( \text{C}_{12}\text{H}_4\text{N}_4\text{Rb} \) requires C, 49.83%; H, 1.38%; N, 19.38%.

**Ammonium 7,7,8,8-Tetracyanoquinodimethane.**

To a boiling solution TCNQ (2.04g, 10mmol) dry tetrahydrofuran (200 cm³) was added a boiling solution of ammonium iodide (4.35g, 30mmol) in dry methanol (50 cm³). Maroon needles separated from the solution and were collected while the mixture was still warm. The solid (1.31g, 59%) was then washed
with a large volume of ether to give an analytically pure sample, m.p. 212°-215° (Lit. 220 m.p. 210°-215° \text{dec}); Found: C, 65.24%; H, 3.8%; N, 31.7%. C_{12}H_{26}N_{6} requires C, 64.9%; H, 3.6% N, 31.5%.

**ALKALINE-EARTH METAL TETRACYANOQUINODIMETHANE SALTS.**

**Barium, 7, 7, 8, 8-Tetracyanoquinodimethane.**

To a boiling solution TCNQ (1g, 4.9mmol) in dry acetonitrile (100 cm³) was added a boiling solution of barium iodide (1.44g, 3.68mmol) in dry methanol (100 cm³). Fine maroon needles separated out of solution and were collected while the mixture was still warm. The solid (0.94g, 70%) was then washed with a large volume of ether to give an analytically pure sample, m.p. < 300° (Lit. 220 m.p. = < 300°); Found: C, 53.00%; H, 1.5%; N, 20.4%. C_{24}H_{26}N_{6}Ba requires C, 52.84%; H, 1.46%; N, 20.55%.

**Calcium 7, 7, 8, 8-Tetracyanoquinodimethane.**

To a solution of Li^+TCNO^- (1g, 4.74mmol) in water (100 cm³) was added a solution of calcium bromide (0.74g, 2.37mmol) in water (70 cm³). The finely divided purple solid (0.72g, 68%) was collected on a filter and dried in a vacuum, m.p. < 300° (Lit. 220 m.p. < 300°); Found: C, 63.98%; H, 1.72%; N, 24.81%. C_{24}H_{26}N_{6}Ca requires C, 64.28%; H, 1.78%; N, 25%.
TRANSITION METAL TETRACYANOQUINODIMETHANE.

Ferrous 7,7,8,8.-Tetracyanoquinodimethane.

To a solution of Li\textsuperscript{+}TCNQ\textsuperscript{-} (1g, 4.74mmol) in water (100 cm\textsuperscript{3}) was added a solution of iron sulphate septahydrate (0.66g, 2.37mmol) in water (70 cm\textsuperscript{3}).

The finely divided blue solid (1.04g, 95%) was collected on a filter and dried in a vacuum, m.p. 168\textdegree-170\textdegree (Lit.220 m.p. = 170\textdegree); Found: C, 61.88%; H, 1.78%; N, 24.01%. C\textsubscript{24}H\textsubscript{8}N\textsubscript{8}Fe requires C, 62.07%; H, 1.72%; N, 24.14%.

Cupric 7,7,8,8-Tetracyanoquinodimethane.

To a solution of Li\textsuperscript{+}TCNQ\textsuperscript{-} (1g, 4.74mmol) in water (100 cm\textsuperscript{3}) was added a solution of copper sulphate pentahydrate (6g, large excess) in water (70 cm\textsuperscript{3}).

The finely divided green solid (0.89g, 80%) was collected on a filter and dried in a vacuum, m.p. 172\textdegree-174\textdegree (Lit.220 = 170\textdegree); Found: C, 60.39%; H, 1.9%; N, 23.6%. C\textsubscript{24}H\textsubscript{8}N\textsubscript{8}Cu requires C, 61.08%; H, 1.69%, N, 23.75%.

CROWN ETHERS.

All the crown ethers used for the preparative work of Chapter 4, were obtained from Aldrich Chemical Company\textsuperscript{267}. To establish their purity the series of crown ethers used in this study were subjected to combustion analysis.

\textsuperscript{[12]}-Crown-4.

(Lit.\textsuperscript{267} m.p. 16\textdegree); Found: C, 54.29%; H, 9.04%.
C₈H₁₆O₄ requires C, 54.54%; H, 9.09%.

[15]-Crown-5.

(Lit. 267 m.p. 100°-135°/0.2mm); Found: C, 54.25%; H, 9.06%. C₁₂H₂₄O₆ requires C, 54.54%; H, 9.09%.


(Lit. 267 m.p. 43°-45°); Found: C, 54.32%; H, 9.05%. C₁₂H₂₄O₆ requires C, 54.54%; H, 9.09%.

Dibenzo-[18]-Crown-6.

(Lit. 267 m.p. 160°-164°); Found: C, 66.37%; H, 6.6%. C₂₀H₂₄O₆ requires C, 66.67%; H, 6.67%.


(Lit. 267 m.p. 80°-83°); Found: C, 70.22%; H, 8.5%; N, 6.23%. C₂₆H₃₈N₂O₄ requires C, 70.59%; H, 8.59%; N, 6.33%.

ISOLATION OF THE CROWN ETHER/ALKALI-METAL TCNQ COMPLEXES

All of the simple salts (m = 1,2 n = 1) were isolated by the following general procedure:

A cation-TCNQ salt and crown ether (1.2-2 molar equivalent) were dissolved in hot dry methanol and boiled for 15 minutes with stirring, after which the hot solution was filtered. The filtrate was allowed to cool at 0°C for several hours. Crystals thus precipitated were collected, washed with a small amount of methanol and dried in a vacuum. When
crystals were not formed, the solution was cooled to -15°C or to 0°C after being concentrated.

A more detailed spectroscopic analyses of these complexes may be found in Chapter 4.

[12]-Crown-4(12C4)/Lithium TCNQ (1:1 complex)\textsuperscript{11,222}.

(Representative Example)

\[
\text{Lithium-TCNQ} (0.21g, 1\text{mmol}) \text{ and } [12]-\text{crown-4} (0.294g, 1.67\text{mmol}) \text{ were added to dry methanol} (120 cm^3), \text{ after which the solution was refluxed for 15 minutes. The hot solution was filtered, allowed to stand at room temperature, and then cooled to 0°C overnight. The black crystals} (0.09g, 23\%) \text{ were collected, washed with a small amount of methanol and dried in vacuum, m.p. 195^\circ \text{ C decomp.}}
\]


Using the general procedure outlined previously, sodium TCNQ (0.23g, 1\text{mmol}) \text{ and } [12]-\text{crown-4} (0.29g, 1.67\text{mmol}) \text{ were complexed and a blue solid} (0.197g, 49\%) \text{ was collected, m.p. 186^\circ-188^\circ} \text{ (Lit.} 222 \text{ m.p. 183}^\circ-185^\circ) .


(Representative Example)

If the general procedure for [12]-crown-4/lithium
TCNQ is followed, sodium TCNQ and [12]-crown-4 tend to form 1:2 complex (see earlier procedure). In order to gain the 1:1 complex, (0.227 g, 1 mmol) sodium TCNQ and (0.176 g, 1 mmol) of [12]-crown-4 were boiled in methanol for 15 minutes and filtered. The solvent was removed by evaporation and the blue solid (0.4 g, 100%) was collected and dried in a vacuum, m.p. 110°-112°.

[15]-Crown-5(15C5)/Sodium TCNQ (1:1 complex).

Using the general procedure outlined previously, sodium TCNQ (0.23 g, 1 mmol) and [15]-crown-5 (0.37 g, 1.67 mmol) were complexed and a purple solid (0.1 g, 22%) was collected, m.p. 148°-150° (Lit. 222 m.p. 150°).


Using the general procedure outlined previously, potassium TCNQ (0.24 g, 1 mmol) and [15]-crown-5 (0.37 g, 1.67 mmol) were complexed and a purple solid (0.3 g, 45%) was collected, m.p. 210° (Lit. 222 m.p. 210°).


As outlined for the [12]-crown-4 sodium TCNQ complex, potassium TCNQ and [15]-crown-5 also tend to form a 2:1 complex. In order to gain the 1:1 complex, potassium TCNQ (0.24 g, 1 mmol) and [15]-crown-5 (0.22 g, 1 mmol) were refluxed in methanol for 15 minutes and then filtered. The solvent was
completely removed and the purple solid (0.46g, = 100%) was collected and dried in a vacuum, m.p. 154°-156°.

[18]-Crown-6(18C6)/Sodium TCNQ (1:1 complex).

Using the general procedure outlined previously, sodium TCNQ (0.23g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a blue solid (0.21g, 42%) was collected, m.p. 152°-154° (Lit. 222 m.p. 151°-152°).

[18]-Crown-6/Potassium TCNQ (1:1 complex).

Using the general procedure outlined previously, potassium TCNQ (0.24g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a dark purple solid (0.314g, 62%) was collected, m.p. 202°-205° (Lit. 222 m.p. 203°-205°).

[18]-Crown-6/Ammonium TCNQ (1:1 complex).

Using the general procedure outlined previously, ammonium TCNQ (0.22g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a purple solid (0.1g, 20%) was collected, m.p. 168°-170° (Lit. 223 m.p. 170°-172°).

Dibenzo-[18]-Crown-6(DB18C6)/Potassium TCNQ (1:1 complex).

Using the general procedure outlined previously, potassium TCNQ (0.24g, 1mmol) and dibenzo-[18]-crown-6 (0.6g, 1.67mmol) were complexed and a yellow/green solid (0.41g 68%) was collected,
m.p. 204°-205° (Lit. 222 m.p. 202°-204°).

Dibenzo-[18]-Crown-6/Ammonium TCNQ (1:1 complex).

Using the general procedure outlined previously, ammonium TCNQ (0.22g, 1mmol) and dibenzo-[18]-crown-6 (0.6g, 1.67mmol) were complexed and a green solid (0.35g, 60%) was collected, m.p. 170° (Lit. 222 m.p. 168°-170°).

Dibenzyl Diaza-[18]-Crown-6(DDA18C6)/Lithium TCNQ (1:1 complex).

Using the general procedure outlined previously, lithium TCNQ (0.21g, 1mmol) and dibenzyl diaza-[18]-crown-6 (0.74g, 1.67mmol) were complexed and a violet solid (0.29g, 45%) was collected, m.p. 83°-85° dec.

Dibenzyl Diaza-[18]-Crown-6/Sodium TCNQ (1:1 complex).

Using the general procedure outlined previously, sodium TCNQ (0.23g, 1mmol) and dibenzyl diaza-[18]-crown-6 (0.74g, 1.67mmol) were complexed and a violet solid (0.34g, 51%) collected, m.p. 82°-84° dec.

Dibenzyl Diaza-[18]-Crown-6/Potassium TCNQ (1:1 complex).

Using the general procedure outlined previously, potassium TCNQ (0.24g, 1mmol) and dibenzyl diaza-[18]-crown-6 (0.74g, 1.67mmol) were complexed and a green solid (0.41g, 60%) was collected, m.p. 84° dec.

Dibenzyl Diaza-[18]-Crown-6/Ammonium TCNQ (1:1 complex).
Using the general procedure outlined previously, ammonium TCNQ (0.222g, 1mmol) and dibenzyl diaza-[18]-crown-6 (0.74g, 1.67mmol) were complexed and a blue solid (0.21g, 32%) was collected, m.p. 82° dec.

**ISOLATION OF THE CROWN ETHER/ALKALI-METAL TCNQ/NEUTRAL TCNQ COMPLEXES.**

\[(\text{Crown Ether})_m(\text{M}^+\text{TCNQ}^-)_n(\text{TCNQ})_i^{222}\]

All of the complex salts \((m = 1, 2\ n = 1\ i = 1, 2)\) were isolated by the following method.

The original salt \((\text{crown ether})_m(\text{M}^+\text{TCNQ})_n\), synthesised by the method used in the previous section, was dissolved in dry methanol. This solution was added to a dry acetonitrile solution of neutral TCNQ (1-1 molar equivalent), and the mixture was boiled for 15 minutes, after which the hot solution was filtered. The filtrate was allowed to stand at room temperature and then cooled to 0°C. The crystals were collected, washed with a small amount of methanol and dried in a vacuum.

As stated earlier in the isolation of the simple crown ether/alkali-metal TCNQ complex details of spectroscopic evidence for these complexes may be found in Chapter 4.

(Representative Example)

The 1:1 complex of [12]-crown-4/lithium TCNQ (0.39g, 1mmol) was dissolved in dry methanol (150 cm³) and was added to an acetonitrile (30 cm³) solution containing TCNQ (0.2g, 1mmol). The resulting solution was boiled for 15 minutes, filtered and then allowed to cool to room temperature before storing at 0°C overnight. A black solid (0.2g, 34%) was collected, washed with a small amount of a cooled acetonitrile/methanol (50/50) solution and dried in a vacuum, m.p. 213°-214°.


Using the general procedure outlined previously, [12]-crown-4/lithium TCNQ (1:1 complex) (0.39g, 1mmol) and TCNQ (0.4g, 2mmol) were complexed and a dark black solid (0.7g, 88%) collected, m.p. 228°-229°.


Using the general procedure outlined previously, [12]-crown-4/sodium TCNQ (2:1 complex) (0.58g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.38g, 49%) was collected, m.p. 204°-205°.

Using the general procedure outlined previously, [15]-crown-5/sodium TCNQ (1:1 complex) (0.45g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.18g, 30%) was collected, m.p. 172°-173°.


Using the general procedure outlined previously, [15]-crown-5/sodium TCNQ (1:1 complex) (0.45g, 1mmol) and TCNQ (0.4g, 2mmol) were complexed and a black solid (0.8g, 94%) was collected, m.p. 201°-203°.


Using the general procedure outlined previously, [15]-crown-5/potassium TCNQ (2:1 complex) (0.68g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.42g, 48%) was collected, m.p. 231°-233°.


Using the general procedure outlined previously, [18]-crown-6/potassium TCNQ (1:1 complex) (0.49g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.28g, 40%) was collected, m.p. 217°-218°.


Using the general procedure outlined previously, [18]-crown-6/ammonium TCNQ (1:1 complex) (0.49g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.148g, 20%) was collected, m.p.
161°-162° (Lit. 223 m.p. 160°-162°).

**Dibenzo-[18]-Crown-6/Potassium TCNQ/TCNQ (1:1:1 complex).**

Using the general procedure outlined previously, dibenzyl-[18]-crown-6/potassium TCNQ (1:1 complex) (0.6g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.26g, 32%) was collected, m.p. 222°-224° (Lit. 222 m.p. 224°-225°).

**Dibenzyldiaza-[18]-Crown-6/Potassium TCNQ/TCNQ (1:1:1 complex).**

Using the general procedure outlined previously, dibenzyl diaza-[18]-crown-6/potassium TCNQ (1:1 complex) (0.69g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.27g, 30%) was collected, m.p. 102°-103°.

**ISOLATION OF THE CROWN ETHER/ALKALINE-EARTH METAL TCNQ COMPLEXES.**

\[(\text{Crown Ether})_m(M^{2+}(\text{TCNQ})^{-2})_n\] \(^{224}\).

All of the simple salts \((m = 1, 2 \ n = 1)\) in this category were isolated by the general procedure adopted for the formation of the crown ether/alkali-metal TCNQ complexes. Further spectroscopic details may be found in Chapter 4.

**[12]-Crown-4/Calcium TCNQ (1:1 complex).**

Using the general procedure outlined previously, calcium TCNQ (0.4g, 1mmol) and [12]-crown-4 (0.18g,
Immol) were complexed and a violet solid (0.61g, 97\%) collected, m.p. 76°-78°.


Using the general procedure outlined previously, calcium TCNQ (0.45g, 1mmol) and [12]-crown-4 (0.29g, 1.67mmol) were complexed and a violet solid (0.4g, 54\%) was collected, m.p. 99°-100° (Lit. 224 m.p. 100°).


Using the general procedure outlined previously, calcium TCNQ (0.45g, 1mmol) and [15]-crown-5 (0.37g, 1.67mmol) were complexed and a green solid (0.18g, 27\%) was collected, m.p. 180°-182°.


Using the general procedure outlined previously, barium TCNQ (0.55g, 1mmol) and [15]-crown-5 (0.37g, 1.67mmol) were complexed and a green solid (0.30g, 42\%) was collected, m.p. 184°-186°.

[18]-Crown-6/Barium TCNQ (1:1 complex).

Using the general procedure outlined previously, barium TCNQ (0.55g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a violet solid (0.28g, 35\%) was collected, m.p. 222° (Lit. 224 m.p. 220°-222°).

Dibenzo-[18]-Crown-6/Calcium TCNQ (1:1 complex).

Using the general procedure outlined previously, calcium TCNQ (0.45g, 1mmol) and dibenzo-[18]-crown-6 (0.6g, 1.67mmol) were complexed and a solid (0.36g,
45%) was collected, m.p. 201°-203° (Lit. m.p. 200°-202°).

Dibenzo-[18]-Crown-6/Barium TCNQ (1:1 complex).

Using the general procedure outlined previously, barium TCNQ (0.55g, 1mmol) and dibenzo-[18]-crown-6 (0.6g, 1.67mmol) were complexed and a solid (0.61g, 68%) was collected, m.p. 221°-223°.

Dibenzy1 Diaza-[18]-Crown-6/Barium TCNQ (1:1 complex).

Using the general procedure outlined previously, barium TCNQ (0.55g, 1mmol) and dibenzyl diaza-[18]-crown-6 (0.7g, 1.67mmol) were complexed and a solid (0.56g, 57%) was collected, m.p. 85°-86° dec.

ISOLATION OF THE CROWN ETHER/TRANSITION METAL TCNQ COMPLEXES.

(Crown Ether)ₘ(M²⁺(TCNQ)₂⁻)ₙ²²⁵.

All of the simple salts (m = 1 n = 1) in this category were isolated by the general procedure adopted for the formation of the crown ether/alkali, alkaline-earth metal TCNQ complexes. More detailed spectroscopic analysis may be found within Chapter 4.

Cyclam/Ferrous TCNQ (1:1 complex).

Using the general procedure outlined previously, ferrous TCNQ (0.4g, 1mmol) and cyclam (0.33g, 1.67mmol) is complexed and a green solid (0.36g, 54%) was collected, m.p. 243°-245°.
Cyclam/Cuppric TCNQ (1:1 complex).

Using the general procedure outlined previously, cuppric TCNQ (0.47g, 1mmol) and cyclam (0.33g, 1.67mmol) is complexed and a green solid (0.4g, 60%) was collected, m.p. 256°-258°.

ISOLATION OF THE COMPLEX CROWN ETHER/ALKALINE-EARTH METAL TCNQ/NEUTRAL TCNQ COMPLEXES.

(Crown Ether)ₘ(M²⁺(TCNQ)₂⁻)ₙ(TCNQ)ᵢ⁻

All the complex 1:1:1 salts (m = 1,2 n = 1 i = 1) isolated in this section were by the general procedure outlined for the crown ether/alkali-metal TCNQ/neutral TCNQ salts. More detailed spectroscopic analysis may be found within Chapter 4.


Using the general procedure outlined previously, [12]-crown-4/calcium TCNQ (2:1 complex) (0.8g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.29g, 29%) collected, m.p. 240°-244° (Lit.²²⁺²⁴ m.p. 240°-245°).


Using the general procedure outlined previously, [15]-crown-5/calcium TCNQ (1:1 complex) (0.67g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.30g, 35%) collected, m.p. > 30° dec.


Using the general procedure outlined previously,
[15]-crown-5/barium TCNQ (2:1 complex) (0.99g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.63g, 53%) collected, m.p. 234°-235° (Lit.224 m.p. 233°-234°).


Using the general procedure outlined previously, [18]-crown-6/calcium TCNQ (1:1 complex) (0.7g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.5g, 55%) collected, m.p. > 300° (Lit.224 m.p. > 300°).


Using the general procedure outlined previously, [18]-crown-6/barium TCNQ (1:1 complex) (0.81g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.66g, 65%) collected, m.p. 261°-263° (Lit.224 m.p. 260°).

Dibenzo-[18]-6/Calcium TCNQ/TCNQ (1:1:1 complex).

Using the general procedure outlined previously, dibenzo-[18]-crown-6/calcium TCNQ (1:1 complex) (0.81g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.35g, 35%) collected, m.p. 236°-237° (Lit.224 m.p. 235°-236°).

Dibenzo-[18]-Crown-6/Barium TCNQ/TCNQ (1:1:1 complex).

Using the general procedure outlined previously, dibenzo-[18]-crown-6/barium TCNQ (1:1 complex) (0.9g, 1mmol) and TCNQ (0.2g, 1mmol) were complexed and a black solid (0.32g, 29%) collected, m.p. 234°-235°.
Methyl cyanoacetate (347.56g, 3.5mol) was added to a portion of magnetically stirred ethylamine (187.14g, 4.5mol) over a period of 10-15 minutes. The temperature of the mixture rose to about 45° and the product started to crystallise out of solution on cooling. The crude product (211.1g, 54%) was then purified by recrystallisation from ethanol to give analytically pure sample, m.p. 71.5°-72.5° (Lit. 243 m.p. 72°), Found: C, 53.39%; H, 7.10%; N, 24.85%. C₅H₈N₂O requires C, 53.57%; H, 7.14%; N, 25%; δ¹H [90 MHz; d⁶-DMSO] 8.17 (NH, H(s)); 3.58 (CH₂,2H(s)); 3.13 (CH₂,4,2H(q)); 1.07 (CH₃,3H(t)); Integration 1:2:2:2; δ¹³C (22.5 MHz; d⁶-DMSO) 14.44 (c⁵); 25.95 (c²); 35.38 (c⁴); 114.97 (c¹); 161.15 (c³); Vmax (KBr) 3250 (N-H); 2250 (C=O); 1680 (C=O) 1250 (C-N) cm⁻¹.
Potassium hydroxide (22 g, 0.4 mol) in methanol (200 cm³) was added to a stirred solution containing n-ethylcyanoacetamide (35.8 g, 0.32 mol) and ethyl acetoacetate (41.6 g, 0.32 mol) in methanol (70 cm³). From this solution a white solid (21.3 g, 81%) was deposited which was collected and recrystallised from ethanol to give an analytically pure sample, m.p. 245°-246° (Lit. 244 m.p. 246°-248°), Found C, 60.50%; H, 5.58%; N, 15.60%. C₉H₁₀N₂O₂ requires C, 60.67%; H, 5.62%; N, 15.73%. <sup>1</sup>H [90 MHz; d<sup>6</sup> - DMSO] 10.68 (OH, 1H(s)); 5.71 (CH₂, 5H(s)); 3.97 (CH₂, 2H(q)); 2.24 (CH₃, 9H(s)); 1.14 (CH₃, 1H(t)); Integration 1:1:2:3:3; <sup>1</sup>C [22.5 MHz; d<sup>6</sup> - DMSO] 12.94 (C₈); 20.48 (C<sup>10</sup>); 35.83 (C<sup>7</sup>); 88.64 (C<sup>5</sup>); 92.02 (C<sup>4</sup>); 117.38 (C<sup>9</sup>); 158.03 (C<sup>3</sup>); 160.17 (C<sup>2</sup>, C<sup>6</sup>); V<sub>max</sub> (KBr); 3080 (O-H); 2300 (C-H); 2220 (C=O); 1640 (C=O); 1290 (C-N) cm⁻¹.

**OXONOL DYES**<sup>115,188</sup>

Many of the dyes in this section have identical anions. However, only very small differences in the
anion peak chemical shifts (\(^1\)H and \(^13\)C n.m.r. spectra) and absorption band frequencies (i.r. spectra) are observed, as the cation varies. As a consequence the full analytical data characteristic of the first member of each anion class are reported in full; subsequent members show only assignments of the peaks and bands which are in addition to those of the anion.

General Molecular Formula.

\[
\text{PREPARATION OF ALKALI-METAL OXONOL DYES.}
\]

**Lithium Oxonol.**

*(Representative Example)*.

\[m = \text{Li}; \; n = 1\]

A mixture of 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (10g, 56.72mmol), 1,1',3,3'-tetramethoxy propane (4.6g, 28.09mmol) and lithium carbonate (1.04g, 14.04mmol) in dry ethanol (50 cm\(^3\)) was refluxed for 20 hours. On cooling an olive green precipitate was obtained (9.7g, 89%) and after filtering was recrystallised from ethanol to give green cubed crystals, m.p. > 300\(^\circ\) (Lit. 188 m.p. >
Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5.0g, 28mmol), tetramethoxypropane (2.3g, 14mmol) and sodium acetate (1.15g, 14mmol) were refluxed together and a turquoise solid (4.62g, 82%) collected, m.p. > 300° (Lit. 188 m.p. > 300°), Found: C, 60.50%; H, 4.37%; N, 13.27%. C_{21}H_{19}N_{4}O_{4}Na requires C, 60.87%; H, 4.59%; N, 13.53%.

**Potassium Oxonol.**

\[ M = K; \ n = 1 \]

Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5.0g, 28mmol), tetramethoxypropane (2.3g, 14mmol) and potassium acetate (1.38g, 14mmol) were refluxed
together and an olive green solid (4.07g, 67%) collected, m.p. > 300° (Lit. 188 m.p. > 300°), Found: C, 58.85%; H, 4.40%; N, 13.21%. \( \text{C}_{21}\text{H}_{19}\text{N}_{4}\text{O}_{4}\text{K} \) requires C, 58.60%; H, 4.42%; N, 13.02%.

Rubidium Oxonol.

\[ M = \text{Rb}; \ n = 1 \]

Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (2.5g, 14 mmol), tetramethoxy-propane (1.15g, 7mmol) and rubidium carbonate (1.62g, 7mmol) were refluxed together and a dark green solid (1.93g, 58%) was collected, m.p. > 300° (Lit. m.p. > 300°).

Ceasium Oxonol.

\[ M = \text{Cs}; \ n = 1 \]

Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (2.5g, 14mmol), tetramethoxypropane (1.15g, 7mmol) and ceasium acetate (1.34g, 7mmol) were refluxed together and a dark green solid (1.92g, 52%) was collected, m.p. > 300° (Lit. 188 m.p. > 300°).

Ammonium Oxonol.

\[ M = \text{NH}_4; \ n = 1 \]

Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5g, 28mmol), tetramethoxypropane (2.3g, 14mmol) tetra methoxypropane and ammonium iodide (2.04g, 14mmol) were refluxed together and a dark blue solid (3.95g,
69%) was collected, m.p. 223-224 (Lit.115 m.p. 222-224); Found: C, 61.87%; H, 5.57%; N, 16.94%.

\[ \text{C}_{21}\text{H}_{23}\text{N}_{5}\text{O}_{4} \text{ requires C, 61.61%; H, 5.63%; N, 17.11%.} \]

**ALKALINE-EARTH METAL OXONOL DYES.**

**Calcium Oxonol. (Representative Example).**

\[ M = \text{Ca}; \ n = 2 \]

The alkaline-earth metal oxonol dyes were prepared in exactly the same manner as the alkali-metal dyes. A mixture of 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5.0g, 28mmol), tetramethoxypropane (2.3g, 14mmol) and calcium bromide (1.4g, 7mmol) in ethanol (50 cm³) were refluxed for 20 hours. The reaction mixture was allowed to cool and a blue solid (4.7%, 82%) was collected, m.p. > 300° (Lit.188 m.p. > 300°); δ

\[ ^1\text{H}[250 \text{ MHz}; \text{d}^6\text{-DMSO}] 9.01 (\text{CH}, 11, 1\text{H(t)}); 7.71 (\text{CH}, 10, 12, 2\text{H(d)}); 3.9 (\text{CH}_2, 2, 19, 4\text{H(q)}); 2.44 (\text{CH}_3, 7, 15, 6\text{H(s)}); 1.09 (\text{CH}_3, 1, 20, 6\text{H(s)}).
\]

Integration 1:2:4:6:6; δ \[ ^13\text{C} [22.5 \text{ MHz}; \text{d}^6\text{-DMSO}] 13.08 (\text{C}^{1}, \text{C}^{20}); 18.55 (\text{C}^{7}, \text{C}^{15}); 33.82 (\text{C}^{2}, \text{C}^{19}); 92.21 (\text{C}^{6}, \text{C}^{19}); 110.4 (\text{C}^{8}, \text{C}^{13}); 117.72 (\text{C}^{5}, \text{C}^{17}); 120.93 (\text{C}^{11}); 157.36 (\text{C}^{10}, \text{C}^{12}); 158.13 (\text{C}^{4}, \text{C}^{16}); 161.39, 161.97 (\text{C}^{3}, \text{C}^{9}, \text{C}^{18}, \text{C}^{21}). \]

**Magnesium Oxonol.**

\[ M = \text{Mg}; \ n = 2 \]

Using the general procedure outlined previously,
1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5g, 28mmol), tetramethoxypropane (2.3g, 14mmol) and magnesium acetate tetrahydrate (1.5g, 7mmol) were refluxed and a blue solid (4.5g, 76%) was collected, m.p. > 300° (Lit.188 m.p. > 300°): Found C, 59.63%; H, 4.58%; N, 13.15%. C42H38Ng08Mg2H2 requires C, 59.86%; H, 54.51%; N, 13.20%.

Barium Oxonol.

M = Ba; n = 2

Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (5g, 28mmol), tetramethoxypropane (2.3g, 14mmol) and barium iodide (2.99g, 7mmol) were refluxed and a green solid (5.21g, 81%) was collected, m.p. > 300°.

TRANSITION METAL OXONOL DYES.

Cobaltous Oxonol.

M = Co; n = 2

Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (2.5g, 14mmol), tetramethoxypropane (1.15g, 7mmol) and cobaltous acetate tetrahydrate (0.87g, 3.5mmol) were refluxed and a violet solid (2.0g, 68%) was collected, m.p. > 300° (Lit.188 m.p. > 300°).

Copper Oxonol.

M = Cu; n = 2

Using the general procedure outlined previously, 1-ethyl-3-cyano-6-hydroxy-4-methyl pyrid-2-one (2.5g,
14 mmol), tetramethoxypropane (1.15 g, 7 mmol) and cupric acetate monohydrate (0.7 g, 3.5 mmol) were refluxed and a blue green solid (0.22 g, 64%) was collected.

Ferrous and Ferric Oxonol.

\[ M = \frac{Fe^{2+}}{Fe^{3+}}; \quad n = 2/3 \]

Samples of Ferrous and Ferric Oxonol were supplied by Dr. D.J. Edwards of Ilford Ltd274.

**ISOLATION OF THE CROWN ETHER/OXONOL DYE COMPLEXES**

All the oxonol crown/dyes ether complexes in this section were prepared by the following general method. A cation-oxonol dye and crown ether (1.2-2 molar ratio) were dissolved in hot methanol and refluxed for 15 minutes with stirring, after which the hot solution was filtered. The filtrate was allowed to stand at room temperature, and then it was cooled at 0°C for several hours. Crystals thus precipitated were collected, washed with a small amount of methanol, and dried in a vacuum. When crystals did not come out, the solution was cooled to -15°C or to 0°C after being concentrated.

For all these complexes within this section more details on spectroscopic analysis may be found in Chapter 4.
ISOLATION OF CROWN ETHER/ALKALI-METAL OXONOL COMPLEXES.

\((\text{Crown Ether})_m (M^+\text{Ox}^-)_n\).

[12]-crown-4/Lithium Oxonol. (1:1 complex).

(Representative Example).

Lithium oxonol (0.39g, 1mmol) and [12]-crown-4 (0.29g, 1.67mmol) were added to dry methanol (120 ml), after which the solution was refluxed for 15 minutes. The hot solution was filtered and allowed to stand at room temperature for 5-6 hours. Once the solution had cooled to room temperature it was placed in a fridge at 0°C overnight. Bright green solid (0.16g, 28%) was collected, washed with a small quantity of methanol and dried in a vacuum, m.p. 266°-267°.

[12]-crown-4/Sodium Oxonol (2:1 complex).

Using the general procedure outlined previously, sodium oxonol (0.41g, 1mmol) and [12]-crown]-4 (0.29g, 1.67mmol) were complexed and a dark blue solid (0.38g, 50%) collected, m.p. 256-258°.


Using the general procedure outlined previously,
sodium oxonol (0.41g, 1mmol) and [15]-crown-5 (0.37g, 1.67mmol) were complexed and a purple solid (0.2g, 32%) collection, m.p. 224°-226°.

[15]-crown-5/Potassium Oxonol (2:1 complex).

Using the general procedure outlined previously, potassium oxonol (0.43g, 1mmol) and [15]-crown-5 (0.37g, 1.67mmol) were complexed and a violet solid (0.44g, 50%) was collected, m.p. 196°.

[18]-crown-6/Sodium Oxonol (1:1 complex).

Using the general procedure outlined previously, sodium oxonol (0.41g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a light blue solid (0.28g, 43%) was collected, m.p. 242°.

[18]-crown-6/Potassium Oxonol (1:1 complex).

Using the general procedure outlined previously, potassium oxonol (0.43g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a green solid (0.4g, 58%) was collected, m.p. 250°-253°.

[18]-crown-6/Ammonium Oxonol (1:1 complex).

Using the general procedure outlined previously, ammonium oxonol (0.41g, 1mmol) and [18]-crown-6 (0.44g, 1.67 mmol) were complexed and a violet/blue solid (0.15g, 22%) was collected, m.p. 160°-161°.

Dibenzo-[18]-crown-6/Potassium Oxonol (1:1 complex).

Using the general procedure outlined previously, potassium oxonol (0.43g, 1mmol) and dibenzo-[18]-crown-6 (0.6g, 1.67mmol) were complexed and a purple
solid (0.47g, 60%) was collected, m.p. 175°-178°.

Dibenzo-[18]-crown-6/Ammonium Oxonol (1:1 complex).

Using the general procedure outlined previously, ammonium oxonol (0.41g, 1mmol) and dibenzo-[18]-crown-6 (0.6g, 1.67mmol) were complexed and a dark blue solid 0.13g, 17%) was collected, m.p. 266°.

[2.2.2]Cryptand/Sodium Oxonol (1:1 complex).

Using the general procedure outlined previously, sodium oxonol (0.41g, 1mmol) and [2.2.2]cryptand (0.63g, 1.67mmol) were complexed and a blue solid (0.41g, 59%) was collected, m.p. 122°-124°.

[2.2.2]Cryptand/Potassium Oxonol (1:1 complex).

Using the general procedure outlined previously, potassium oxonol (0.43g, 1mmol) and [2.2.2]cryptand (0.63g, 1.67mmol) were complexed and a green solid (0.49g, 62%) was collected, m.p. 125°-127°.

**ISOLATION OF CROWN ETHER/ALKALINE-EARTH METAL OXONOL COMPLEXES.**

\[(\text{Crown Ether})_m(\text{M}^{2+}(\text{Ox}^-)_2)\].

[12]-crown-4/Magnesium Oxonol (1:1 complex).

(Representative Example).

Magnesium oxonol (0.8g, 1mmol) and [12]-crown-4 (0.29g, 1.67mmol) were added to dry methanol (120 ml), after which the solution was refluxed for 15 minutes. The hot solution was filtered and allowed to stand at room temperature for 5-6 hours. Once the
solution had cooled to room temperature it was placed in a fridge at 0°C overnight. A bright blue solid was collected (0.18g, 19%), washed with a small quantity of methanol and dried in a vacuum, m.p. 281-283°.

[12]-crown-4/Calcium Oxonol (2:1 complex).

Using the general procedure outlined previously, calcium oxonol (0.82g, 1mmol) and [12]-crown]-4 (0.29g, 1.67mmol) were complexed and a blue solid (0.63g, 54%) was collected, m.p. 275°.

[15]-crown-5/Magnesium Oxonol (1:1 complex).

Using the general procedure outlined previously, magnesium oxonol (0.8g, 1mmol) and [15]-crown-5 (0.37g, 1.67mmol) were complexed and a violet purple solid (0.44g, 43%) collected, m.p. 276°-278°.

[15]-crown-5/Calcium Oxonol (1:1 complex).

Using the general procedure outlined previously, calcium oxonol (0.82g, 1mmol) and [15]-crown-5 (0.37g, 1.67mmol) were complexed and a purple solid (0.32g, 31%) collected, m.p. 265°-269°.

[18]-crown-6/Calcium Oxonol (1:1 complex).

Using the general procedure outlined previously, calcium oxonol (0.82g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a blue solid (0.42g, 34%) collected, m.p. 286°.


Using the general procedure outlined previously,
barium oxonol (0.19g, 1mmol) and [15]-crown-5 (0.37g, 1.67mmol) were complexed and a purple solid (0.54g, 40%) collected, m.p. 245°.

[18]-crown-6/Barium Oxonol (1:1 complex).

Using the general procedure outlined previously, barium oxonol (0.19g, 1mmol) and [18]-crown-6 (0.44g, 1.67mmol) were complexed and a blue solid (0.764g, 63%) collected, m.p. > 300°.

Dibenzo-[18]-crown-6/Barium Oxonol (1:1 complex).

Using the general procedure outlined previously, barium oxonol (0.92g, 1mmol) and dibenzo-[18]-crown-6 (0.6g, 1.67mmol) were complexed and a purple solid (0.74g, 58%) collected, m.p. 230°.

ISOLATION OF CROWN ETHER/TRANSITION-METAL OXONOL COMPLEXES.

Cyclam/Cuppric Oxonol.

Using the general procedure outlined previously, cuppric oxonol (0.425g, 0.5mmol) and cyclam (0.16g, 0.83 mmol) were complexed and a violet solid (0.19g, 20%) collected, 272°-274°.

Cyclam/Cobaltous Oxonol.

Using the general procedure outlined previously, cobaltous oxonal (0.42g, 0.5mmol) and cyclam (0.16g, 0.83mmol) were complexed and a violet blue solid (0.22g, 21%) collected, m.p. 262°-264°.
Cyclam/Ferrous Oxonol.

Using the general procedure outlined previously, ferrous oxonol (0.42g, 0.5mmol) and cyclam (0.16g, 0.83mmol) were complexed and a green/violet solid (0.21g, 20%) was collected, m.p. 256°-258°.

Cyclam/Ferric Oxonol.

Using the general procedure outlined previously ferric oxonol (0.42g, 0.5mmol) and cyclam (0.16g, 0.83mmol) were complexed and a green/violet solid (0.19g, 23%) was collected, m.p. 262°-263°.

EXPERIMENTAL PART III (Chapter 5).

Methanesulphonic acid was obtained from Aldrich Chemical Company267.

Eatons Reagent.

Methanesulphonic acid was distilled slowly under reduced pressure (b.p. 125° @ 1mmHg, Lit.266 b.p. 167°C @ 10 mmHg) in order to remove any impurities. Phosphorous pentoxide (10% by weight) was added slowly to the freshly distilled methanesulphonic acid, with continuous stirring and gentle heating. As soon as all the phosphorous pentoxide has dissolved the colourless viscous solution was allowed to cool before use.
ISOLATION OF SUBSTITUTED DIBENZENO[18]-CROWN-6 COMPOUNDS.

Dibenzo-[18]-crown-6 was obtained from Aldrich Chemical Company. A spectroscopic characterisation was carried out in order to provide a reference for future compounds within this section; m/e (70eV) 360 (M⁺); 180 (M⁺-C₆H₅(CH₂)₄O₃); 164 (M⁺-C₆H₅(CH₂)₄O₄) 136 (M⁺-C₆H₅(CH₂)₆O₄); 76 (M⁺-C₆H₅(CH₂)₈O₆); δ¹H [200 MHz; CDCl₃] 7.25 (Ar, 8H (s)); 4.3 (Ether, 16H, (m)); Integration 8:16; δ¹³C [22.5 MHz; CDCl₃] 69.79 (C²); 70.78 (C¹); 114.73 (C⁴); 122.16 (C³'); 149.67 (C²'); νₘₐₓ (KBr) 3065 (Ar, C-H); 2881 (Ether, C-H); 1596, 1513 (Ar, C=C); 1331 (Ether, C-H); 1132, 1043 (C-O); 741 (Ar, C-H₉orth) cm⁻¹.

4', 4″ (or 5″) Diacetyl Dibenzo-[18]-crown-6.

(General formula).

A mixture of dibenzo-[18]-crown-6 (10g, 27.8mmol), acetic acid (3.6, 60mmol) and Eaton's reagent (120g) is stirred at room temperature for 18 hours. The mixture is next poured onto ice-water and extracted with chloroform (3 x 100 cm³). The organic layer is then washed with a saturated solution of
sodium bicarbonate, water ($2 \times 200 \text{ cm}^3$) and dried over magnesium sulphate. After evaporation of the solvent, the crude product (10.36g, 84%) was recrystallised from benzene; m.p. 202°-206° (Lit. m.p. 200°-208°); Found: C, 64.71%; H, 6.26%.

$C_{24}H_{28}O_8$ requires C, 64.8%; H, 6.31%; m/e (70eV)

444($M^+$); 401 ($M^+$-COCH$_3$); 358 ($M^+$ - (COCH$_3$)$_2$); δ 1H

[90 MHz; CDCl$_3$] 7.49-6.75 (Ar,6H,(m)); 4.09 (Ether, 16H,(m); 2.47 (CH$_3$,6H,(s)); Integration 3:8:3; δ 13C

[62.5 MHz; CDCl$_3$] 196.7 (C$^7'$,C$^7''$); 153.1 (C$^1'$,C$^1''$);

148.5 (C$^2'$,C$^2''$); 130.5 (C$^4'$,C$^4''$); 120.6(C$^5'$,C$^5''$);

111.5 (C$^6'$,C$^6''$); 111.3 (C$^3'$,C$^3''$); 69.7 (C$^1$);

68.6(C$^2$); 26.2 (C$^8'$,C$^8''$); 1 $\nu_{\text{max}}$ (KBr) 3078 (Ar,C-H);

288.7 (Ether, C-H); 1674 (C=O); 1596, 1515 (Ar,C=C);

1367 (CH$_3$-C=O); 1132, 1043 (C-O) cm$^{-1}$.

$4'$, $4''$ (or 5") Dihexyl Dibenzo-[18]-crown-6.

\[
R' = R'' = CH_2CH_2CH_2CH_2CH_3
\]

Same procedure as the preparation of diacetyl dibenzo-[18]-crown-6 using dibenzo-[18]-crown-6 (3.6g, 10mmol), hexanoic acid (2.5g, 22mmol) and of Eatons reagent (50g). The crude product (4.06g, 73%) was collected and recrystallised from benzene; m.p. 144-146° (Lit. m.p. 144°-147°); Found: C, 69.14%; H, 7.87%. $C_{32}H_{44}O_8$ requires C, 69.06%; H, 7.91%; m/e (35eV) 556 ($M^+$); 414 ($M^+$ - ((CH$_2$)$_4$CH$_3$)$_2$)

358 ($M^+$ - (CO(CH$_2$)$_4$CH$_3$)$_2$); δ 13C[62.5 MHz; CDCl$_3$];

199.2 (C$^7'$,C$^7''$); 152.8 (C$^1'$,C$^1''$); 148.5 (C$^2'$,C$^2''$);
130.5 (c4',c4''); 122.9 (c5',c5''); 112.1 (c6',c6'');
111.4 (c3',c3''); 69.7 (c1); 68.6 (c2); 38.1
(c8',c8''); 31.6 (c9',c9''); 24.4 (c10',c10''); 22.5
(c11',c11''); 13.9 (c12',c12''); \( V_{\text{max}} \) (KBR) 3047
(Ar,C-H); 2850 (Ether,C-H and Alkyl,C-H); 1674 (C=O);
1596, 1519 (Ar, C=C); 1387, 1272 (Alkyl, C-H); 1142
(C-O) cm\(^{-1}\).

4', 4'' (or 5'') Dioctanyl Dibenzo-[18]-crown-6.

\[ R = R'' = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

Same procedure as the preparation of diacetyl
dibenzo-[18]-crown-6 using dibenzo-[18]-crown-6
(3.6g, 10mmol), acetoacetic acid (3.17g, 22mmol) and of
Eatons reagent (50g). The crude product (4.77g, 78%)
was collected and recrystallised from benzene; m.p.
114°-117°; Found: C, 70.44%, H, 8.43. \( \text{C}_{36}\text{H}_{52}\text{O}_8 \)
requires C, 70.59%, H, 8.49%; \( ^1\text{H} [250 \text{ MHz}; \text{CDCl}_3] \):
7.22 (Aromatic, 6H, (m)); 4.12 (Ether, 16H, (m));
2.89 (CH\(_2\), 8H, (t)); 1.70 (CH\(_2\), 16H, (O)); 1.31
(CH\(_2\), 10→13 ,16H, (s)); 0.88 (CH\(_3\), 6H, (t)); Integration
6:16:4:4:16:6; \( ^{13}\text{C} [62.5 \text{ MHz}; \text{CDCl}_3] \) 119.3
(c7',c7''); 152.8 (c1',c1''); 148.5 (c2',c2''); 130.5
(c4',c4''); 122.9 (c5',c5''); 111.9 (c6',c6''); 111.3
(c3',c3''); \( V_{\text{max}} \) similar to previous example.

4', 4'' (or 5'') Didecanyl Dibenzo-[18]-crown-6.

\[ R' = R'' = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

Same procedure as the preparation of diacetyl
dibenzo-[18]-crown-6 using dibenzo-[18]-crown-6 (3.6g, 10mmol), decanoic acid (3.79g, 22mmol) and Eatons reagent (50g). The crude product (4.8g, 72%) was collected and recrystallised from benzene, m.p. 115°-119° (Lit. 250 m.p. 117°-129°); Found: C, 71.27%; H, 8.82%. C_40H_60O_8 required C, 71.6%; H, 8.98%. S 1H [250 MHz; CDCl_3] 7.22 (Ar, 6H, (m)); 4.12 (Ether, 16H, (t)); 1.26 (CH_2, 9, 4H, (Q)); 1.70 (CH_2, 9, 4H, (Q)); 2.89 (CH_2, 8, 4H, (t)); 7.22 (Ar, 6H, (m)); 4.12 (Ether, 16H, (m)); 1.26 (CH_2, 10-15, 24H, (SBr)); 0.87 (Alkyl, CH_3, 6H(t)); Integration 3:8:2:2:12:3; S 13c [62.5 MHz; CDCl_3] 199.1 (C_1', C_2'''); 152.9 (C_1', C_1''); 148.6 (C_2', C_2'''); 1230.6 (C_4', C_4'''); 122.9 (C_5', C_5'''); 112.1 (C_6', C_6'''); 111.4 (C_3', C_3''); 69.7 (C_1); 68.6 (C_2); 32.2 (C_8', C_8''); 31.9 (C_9', C_9''); 29.7 (C_10', C_10''); 29.6 (C_11', C_11''); 29.5 (C_12', C_12'') 29.4 (C_13', C_13''); 24.8 (C_14', C_14''); 22.7 (C_15', C_15''); 14.1 (C_16', C_16''); δ max same as previous compound.

4', 4'' (or 5'') Di-(Trimethyl)acetyl Dibenzo-[18]-crown-6.

R' = R'' = -C(CH_3)_3

Same procedure as the preparation of diacetyl dibenzo-[18]-crown-6 using dibenzo-[18]-crown-6 (3.6g, 10mmol), trimethylacetic acid (2.25g, 22mmol) and Eatons reagent (50g). The crude product (4.5g, 85%) was collected and recrystallised from benzene, m.p. 142°-147° (Lit. 250 m.p. 146°-159°); S 1H [250 MHz; CDCl_3] 7.22 (Ar, 6H, (t)); 4.12 (Ether, 16H,
(m)); 1.68 (CH$_3$, 9, 18H, (S$_5$br)); Integration 6:16:18; s 13C [62.5 MHz; CDCl$_3$] 199.1 (C$^7'$, C$^7''$); 152.9 (C$^{1'}$, C$^{1''}$); 148.6 (C$^2'$, C$^2''$); 130.6 (C$^4'$, C$^4''$); 122.9 (C$^5'$, C$^5''$); 112.1 (C$^6'$, C$^6''$); 111.4 (C$^2'$, C$^2''$); 69.7 (C$^1$); 68.6 (C$^2$); (C$^8'$, C$^8''$); (C$^9'$, C$^9''$); V$_{max}$ (KBr) 3047 (Ar,C-H); 2850 (Alkyl or Ether, C-H); 1674 (C=O); 1596, 1518 (Ar,C=C); 1389, 1356 (C(CH$_3$)$_3$, C-H); 1142 (C-O) cm$^{-1}$.

**ISOLATION OF SUBSTITUTED CROWN ETHERS/ALKALI METAL TCNQ COMPLEXES.**

**Diacetyl Dibenzo-[18]-crown-6/Sodium TCNQ.**

Using the general procedure previously outlined (Section 7.3), sodium TCNQ (0.23m, 1mmol) and diacetyl dibenzo-[18]-crown-6 (0.74g, 1.67mmol) were complexed and a purple solid (0.27g, 40%) collected, m.p. 249°-250°; Found: C, 64.23%; H, 4.70%; N, 8.26%. C$_{36}$H$_{32}$N$_4$O$_8$Na requires C, 64.38%; H, 4.77%; N, 8.35%.

**Diacetyl Dibenzo-[18]-crown-6/Potassium TCNQ.**

Using the general procedure previously outlined, potassium TCNQ (0.24g, 1mmol) and diacetyl dibenzo-[18]-crown-6 (0.74g, 1.67mmol) were complexed and a purple solid (0.41g, 60%) collected, m.p. 238°-239°; Found: C, 62.59%; H, 4.60%; N, 8.03%. C$_{36}$H$_{32}$N$_4$O$_8$K requires C, 63.88%; H, 4.66%; N, 8.15%.
Dihexyl Dibenzo-[18]-crown-6/Sodium TCNQ.
Using the general procedure outlined previously, sodium TCNQ (0.23g, 1mmol) and dihexyl dibenzo-[18]-crown-6 (0.93g, 167mmol) were complexed and a violet solid (0.32g, 40%) collected, m.p. 197-198°; Found: C, 67.31%; H, 6.07%; N, 7.02%.
C_{44}H_{44}N_{40}Na requires C, 67.43%; H, 6.13%; N, 7.15%.

Dihexyl Dibenzo-[18]-crown-6/Potassium TCNQ.
Using the general procedure outlined previously, potassium TCNQ (0.24g, 1mmol) and dihexyl dibenzo-[18]-crown-6 (0.93g, 1.67mmol) were complexed and a purple/blue solid (0.46g, 58%) collected, m.p. 184°-185°; Found: C, 65.89%; H, 5.91%; N, 6.89%.
C_{44}H_{48}N_{40}K requires C, 66.08%; H, 6%; N, 7%.

Dioctanyl Dibenzo-[18]-crown-6/Sodium TCNQ.
Using the general procedure outlined previously, sodium TCNQ (0.23g, 1mmol) and dioctanyl dibenzo-[18]-crown-6 (1.02g, 1.67mmol) were complexed and a blue solid (0.32g, 38%) collected, m.p. 190°-192°. 168°-169°; Found: C68.44%; H, 6.59%; N, 6.55%. C_{48}H_{56}N_{40}Na requires C, 68.65%; H, 6.67%; N, 6.67%.

Dioctanyl Dibenzo-[18]-crown-6/Potassium TCNQ.
Using the general procedure outlined previously, potassium TCNQ (0.24g, 1mmol) and dioctanyl dibenzo-[18]-crown-6 (1.02g, 1.67mmol) were complexed
and a dark purple solid (0.49g, 58%) collected, m.p. 154.4°-155.5°; Found: C, 67.16%; H, 6.48%; N, 6.43%. C₄₈H₇₅N₄O₈K requires C, 67.37%; H, 6.55%; N, 6.55%.

Didecanyldibenzo-[18]-crown-6/Sodium TCNQ.

Using the general procedure outlined previously, sodium TCNQ (0.23g, 1mmol) and didecanyl dibenzo[18]-crown-6 (1.12g, 1.67mmol) were complexed and a purple/blue solid (0.31g, 35%) collected, m.p. 171°-173°; Found: C, 69.24%; H, 6.95%; N, 5.89%. C₅₂H₆₄N₄O₈Na requires C, 69.72%; H, 7.15%; N, 6.26% (Poor Analysis).

Didecanyldibenzo-[18]-crown-6/Potassium TCNQ.

Using the general procedure outlined previously, potassium TCNQ (0.24g, 1mmol) and didecanyl dibenzo[18]-crown-6 (1.12g, 1.67mmol) were complexed and a purple solid (0.48g, 53%) collected, m.p. 159°-162°; Found: C, 68.07%; H, 6.89%; N, 5.87%. C₅₂H₆₄N₄O₈K requires C, 68.50%; H, 7.03; N, 6.15% (Poor Analysis).

Di-(Trimethylacetyl)dibenzo-[18]-crown-6/Sodium TCNQ.

Using the general procedure outlined previously, sodium TCNQ (0.23g, 1mmol) and di-trimethyl acetyl dibenzo-[18]-crown-6 (0.89g, 1.67mmol) were complexed and a purple solid (0.11g, 15%) collected, m.p. 198°-200°; Found: C, 66.39%; H, 5.99%; N, 7.29%. C₄₂H₄₆N₄O₈Na requires C, 66.58%; H, 6.08%; N, 7.40%.
Di-Trimethylacetyl Dibenzo-[18]-crown-6/Potassium TCNQ.

Using the general procedure outlined previously, potassium TCNQ (0.24g, 1mmol) and di-trimethylacetyl dibenzo-[18]-crown-6 (0.89g, 1.67mmol) were complexed and a purple solid (0.23g, 30%) collected, m.p. 184°-187°; Found: C, 65.00%; H, 5.87%; N, 7.12%. C_{42}H_{46}N_{4}O_{8}K requires C, 65.20%; H, 5.95%; N, 7.4%.

MODEL REACTION FOR THE PREPARATION OF POLYMERIC CROWN ETHERS.

Benzo-[15]-crown-5 was obtained from Aldrich Chemical Company. A full spectroscopic characterisation was carried out in order to provide a reference for future compounds within this section, Found: C, 62.51%; H, 7.39%. C_{14}H_{20}O_{5} requires C, 62.68%; H, 7.46%; m/e (70eV), 268 (M^+); 136 (M^+-CH_2CH_2O_3); 108 (M^+-CH_2CH_2O_3); 76 (M^+-CH_2CH_2O_3); 69.83 (C_4); 70.31 (C_3); 71.23 (C_2); 71.72 (C_1); 115.1 (C_4'); 122.1 (C_3'); 149.9 (C_2'); \nu_{\text{max}} (KBr) 3086 (Ar,C-H); 2887 (Ether, C-H); 1594, 1515 (Ar,C=C); 1330 (Ether, C-H); 1134, 1047 (C-O); 741 (Ar,C-H_\text{ortho}) cm\textsuperscript{-1}.  

4'-Acetyl Benzo-[15]-crown-5.

(Method B).

A mixture of benzo-[15]-crown-5 (2.68g, 10mmol), acetic acid (0.66g, 11mmol) and Eaton's reagent is stirred at room temperature for 18 hours. The mixture is next poured onto ice-water and extracted with chloroform (3 x 50 cm$^3$). The organic layer is washed with a saturated solution of sodium bicarbonate (100 cm$^3$), water (100 m$^3$) and dried over magnesium sulphate. After evaporation of the solvent the crude product was extracted was concentrated to give a white solid. The product (2.45g, 79%) was recrystallised from benzene, m.p. 95°-97° (Lit. 253 m.p. 96°-97°); Found: C, 61.66%; H, 6.99%. C$_{16}$H$_{22}$O$_6$ requires C, 61.93%; H, 7.09%; m/e (70eV); 310 (M$^+$); 267 (M$^+$-COCH$_3$); $\delta$ $^1$H [200 MHz; CDCl$_3$] 6.6 (Ar,3H,(m)); 4.4 (Ether,16H,(m)); 2.25 (CH$_3$,3H,(s)); Integration 3:16:3; $\delta$ $^{13}$C [22.5 MHz; CDCl$_3$] 197.25 (C$^7$'); 154.18 (C$^1$'); 149.52 (C$^2$'); 130.31 (C$^4$'); 124.11 (C$^5$'); 113.56 (C$^6$'); 112.57 (C$^3$'); 71.83 (C$^1$); 71.08 (C$^2$); 70.07 (C$^3$); 69.94 (C$^4$); 26.82 (C$^8$'); $\nu_{\text{max}}$(KBr) 3086 (Ar, C-H); 2887 (Ether, C-H); 1680 (C=O); 1596, 1515 (Ar, C=C); 1130, 1060 (C=O) cm$^{-1}$. 
4'-Acetyl Benzo-[15]-crown-5.

(Method A).

A mixture of benzo-[15]-crown-5 (2.56g, 10mmol), acetic anhydride (redistilled) (5ml), polyphosphoric acid (PPA, 15ml) in acetic acid (redistilled) (100ml) is stirred overnight at 60°C. The mixture is allowed to cool to room temperature, subsequently poured into water (200ml) and extracted with chloroform (3 x 100ml). The combined organic layers are washed with saturated sodium bicarbonate until carbon dioxide evolution has ceased, with water (100ml), and dried over magnesium sulphate. After evaporation of the solvent the yellow/brown oil is extracted with hot petroleum ether (60/80, 4 x 200ml) and this extract is condensed to give light yellow crystals (2.4g, 77%) of m.p. 950-970°C (Lit.253 m.p. 960-970°C).

4'-(1-hydroxyethyl) Benzo-[15]-crown-5.

Sodium borohydride (0.26g, 6.77mmol) is added in portions to a stirred solution of 4'-acetylbenzo-[15]-crown-5 (1.59g, 5.13mmol) in dry ethanol (200ml) and stirring is continued for 18 hours at room temperature. The mixture is next poured into water, neutralised with acetic acid and
extracted with chloroform (3 x 50ml). Combined organic layers are washed with saturated sodium bicarbonate (2 x 100ml) and dried over magnesium and concentrated to give a white powder (1.45, 90%) of m.p. 65°-66° (Lit. 253 m.p. 65°-66°); Found: C, 61.37%; H, 7.6%. C_{16}H_{24}O_{6} requires C, 61.54%; H, 7.69%; δ {^1}H [250 MHz; CDCl_3] 6.6 (Ar,3H,(m)); 4.8 (CH,7,lH,(q)); 4.4 (Ether,16H,(m)); 2.74 (OH,1H(s)); 1.44 (CH_3,3H(d)); Integration 3:1:16:1:3; δ {^{13}}C [62.5 MHz; CDCl_3] 149.68 (C'); 122.10 (C'); 118.86 (C'); 114.85 (C'); 112.09 (C'); 111.98 (C'); 71.83 (C); 71.08 (C); 70.47 (C); 69.98 (C); 69.90 (C'); 25.73 (C); V_{max} (KBr) 3436 (O-H); 3063 (Ar,C-H); 2885 (Ether, C-H); 1597, 1510 (Ar,C-H); 1291, 1258 (Alcohol, C-O); 1137, 1079 (Ether, C-O).

4 -Vinylbenzo-[15]-crown-5.

A solution of 4 -(1-hydroxyethyl)-benzo-[15]-crown-5 (1.4g, 4.49mmol) and pyridinium tosylate (0.1g) in dry benzene (50 cm³) is refluxed overnight using a dean-stark trap. The cooled solution is washed with water (50ml) and with saturated sodium chlo rode solution (50ml) to remove the catalyst. The benzene layer is dried with magnesium sulphate and
evaporated to give the crude product which is
column-chromatographed on alumina (activity I) using
chloroform/ethanol (99/1) as eluent to give the pure
product which is a yellow solid (1.17g, 89%) of m.p.
42° (Lit.253 m.p. 43°-44°); Found; C, 65.11%; H,
7.4%. C_{16}H_{22}O_{5} requires C, 65.3%; H, 7.48%; m/e
(70eV) 588 (2M+); 294 (M+); 269 (M+-CH=CH); 6 ^{1}H
[200 MHz; CDCl_{3}] 6.95 (Ar,3H, (m)); 6.6
(Vinyl,1H, (m)); 5.4 (Vinyl,2H, (m)); 4.4
(Ether,16H, (m)); Integration 3:1:2:16.
POLYMERIC DIBENZO-[18]-CROWN-6\textsuperscript{275}.

The preparation of 4',4'' (or 5'') diacetyl
dibenzo-[18]-crown-6 may be found in the beginning of
this section.

Bis 4',4'' (or 5'')-(1-hydroxyethyl) Benzo-[18]-crown-6.

A solution containing diacetyl
dibenzo-[18]-crown-6 (1.5g, 3.34mmol) and sodium
borohydride (1.0g, 26.31mmol) in dry ethanol (50 ml)
was stirred for 2 hours, poured into 250ml of water
and neutralised with sulphuric acid. The mixture was
extracted three times with 15ml portions of
dichloromethane. A white powder (m.p. 196°-198°)
precipitated from the dichloromethane. When the
dichloromethane layer was allowed to stand overnight
a white solid precipitated from the extraction
solution. This solid (0.40g, 27%) was collected by
filtration and recrystallised from dichloromethane,
m.p. 1960-1980° (Lit. 250 m.p. 1970-1990°); Found C,
64.42%; H, 7.2%. C24H32O8 requires C, 64.27%; H,
7.19%.

After the first isomer had been removed by
filtration, the resulting filtrate was vacuum
distilled to yield the solid residue of the second
isomer. This residue was titurated with hot ethyl
ether to give a white solid (0.81g, 54%), m.p.
1660-1680° (Lit. m.p. 1640-1670°); Found: C, 64.47%; H,
7.30%. C24H32O8 requires C, 64.27%; H, 7.19%; Both
isomers show identical spectroscopic data; m/e (70eV)
448 (M+); 418 (M+-CH3)2; 384 (M+-(OH)2(CH3))2; 358
(M+-CH2(OCCH3)); 6 [1H [200 MHz; CDCl3] 6.9
(Ar,6H,(m)); 4.8 (CH,7 ,7",2H(q)); 4.2 (Ether,
CH2,16H,(m)); 2.2 (OH,2H,(s)); 1.42 (CH3,6H,(d));
Integration 3:1:8:1:3; 149.68 (C1"'),C1")]; 122.3
(c2",c2"'); 118.86 (c4",c4"'); 114.85 (c5"c5"'); 112.09
(c6"c6"'); 111.98 (c3",c3"'); 70.75 (c7",c7"'); 69.90
(c1); 69.77 (c2); 25.7 (c8",c8"'); Vmax (KBr)
3175-3101 (OH); 30787 (Ar,C-H); 2887 (Ether, C-H);
1596, 1515 (Ar,C=O); 1315, 1170 (2° Alcohol,OH);
1132, 1043 (Ether,C-O) cm⁻¹.
4',4'-Divinyl Dibenzo-[18]-crown-6.

A solution of bis 4', 4"-(1-hydroxyethyl)-dibenzo[18]-crown-6 (1.5g, 3.35mmol) and pyridinium tosylate (≈ 0.1g) in dry benzene (50 cm³) is refluxed overnight using a dean-stark trap. The cooled solution is washed with water (50 cm³) and with saturated sodium chloride (50 cm³) to remove the catalyst. The benzene layer is dried with magnesium sulphate and evaporated to give the crude product (1.38g, 77%). This product is column chromatographed on alumina (activity I) using chloroform/ethanol (99/1) as eluent to give the pure product which is a light brown solid, m.p. 135°-136° (Lit. 1275 m.p. 137°-138°); Found; C, 69.69%; H, 6.68%. C_{24}H_{28}O_{6} requires C, 69.9%; H, 6.79%; m/e (70eV) 412 (M⁺); 385 (M⁺-\text{CH}=\text{CH}_2); 358 (M⁺-(\text{CH}=\text{CH}_2)_2); 8^{1}H [90 MHz; CDCl₃] 6.92 (Ar, 6H, (m)); 6.57 (Vinyl, 2H, (m)); 5.38 (Vinyl, 4H, (m)); 4.35 (Ether, 16H, (m)); Integration 3:1:2:8.

Polymeric Dibenzo-[18]-crown-6.

4',4"-Divinyl-dibenzo-[18]-crown-6 (0.5g, 1.2mmol) was heated with azodiisobutyronitrile (5mg,
36.7 μmol) at reflux for one hour in dry benzene (50 cm³). A further portion of the radical initiator (5 mg, 36.7 μmol) was added and the heating continued for a further two hours. The resulting solution was vacuum distilled and a very viscous sirruper was collected. The sirruper was added dropwise to a small quantity of vigorously stirred methanol (30 cm³), from which a grey/white solid (0.41 g, 82%) was collected with m.p. 97°-100° (Lit. 275 m.p. 99°-99.5°); Found; C, 67.76%; H, 7.16%. C₂₄H₂₈O₆(CH₃OH) requires C, 67.56%; H, 7.21%; m/e (35 eV) 824 (2M⁺); 412 (M⁺); 180; 164; 136; 76; S [200 MHz; CDCl₃] 7.125 (Ar, (mbr)); 4.36 (ether, (dbr)); 0.32 (Alkyl, (sbr)).

**ISOLATION OF POLYMERIC DIBENZO-[18]-CROWN-6/ALKALI METAL TCNQ SALTS.**

**Polymeric Dibenzo-[18]-crown-6/Sodium TCNQ.**

Using the general procedure previously outlined (Section 7.3), sodium TCNQ (0.11 g, 0.5 mmol) and polymeric dibenzo-[18]-crown-6 (0.34 g, 0.8 mmol) were complexed and a blue/purple solid collected, m.p. 275°-279°. Found; C, 67.42%; H, 5.09%; N, 8.65. C₃₆H₃₂N₄O₆Na requires C, 67.71%; H, 5.00%; N, 8.76%.

**Polymeric Dibenzo-[18]-crown-6/Potassium TCNQ.**

Using the general procedure outlined previously,
potassium TCNQ (0.12g, 0.5mmol) and polymeric
dibenzo-[18]-crown-6 (0.34g, 0.8mmol) were complexed
and a purple solid collected, m.p. 287°-290°. Found;
C, 67.17%; H, 4.93%; N, 8.66%. C_{30}H_{32}N_{4}O_{6}K requires
C, 65.95%; H, 4.89%; N, 8.55%.

POLYMERIC FERROCENE.

Ferrocene was obtained from Aldrich Chemical
Company and was recrystallised from chloroform
prior to use.

Acetyl Ferrocene. (Method A).

To a stirred mixture of ferrocene (10g, 54mmol)
and of acetic anhydride (112.2g, 1.1mol)
(redistilled) was added dropwise phosphoric acid
(20ml, 85%). The flask was then heated for half an
hour on a steam bath. The completed reaction was
poured onto chipped ice (200g) and the mixture was
then neutralised by the addition of solid sodium
bicarbonate. An orange/brown solid was precipitated
and was extracted with chloroform (3 x 100ml). The
combined extracts were dried (MgSO_{4}) and the
chloroform removed by evaporation. The crude product
(6.4g, 52%) was recrystallised from benzene to afford
red crystals of m.p. 85°C (Lit. 85°-86°); m/e
(70eV) 228 (M⁺); 218 (M⁺-CH₃); 185 (M⁺-COCH₃); δ 1H [200 MHz; CDCl₃]: 4.77 (Cp, 2.5, 2H, (t)); 4.5 (Cp, 3, 2H, (t)); 4.2 (CP, 1-5, 5H, (s)); 2.39 (CH₃, (s)); Integration 2:2:5:3; δ 13C [22.5 MHz; CDCl₃]: 201.7 (C6); 79.5 (C1); 72.3 (C2, C5); 69.7 (C3, C4); 69.6 (C1'-C5'); 27.3 (C7); νmax (KBr) 3086 (Cp, C=H); 1620 (C=O); 1420, 1381 (C=O=C); 1006, 893, 829 (Cp, C=H) cm⁻¹.

**Acetyl Ferrocene.** (Method B).

A mixture of ferrocene (5g, 26.9mmol), acetic acid (1.72g, 26.9mmol) and Eaton's reagent (6.0g) is stirred at room temperature for 18 hours. The mixture is next poured into ice water and extracted with chloroform (3 x 50ml). The organic layer is washed with a saturated solution of sodium bicarbonate, water (100ml) and dried over magnesium sulphate. After evaporation of the solvent the crude product was purified by column chromatography. The crude product was then passed down an alumina column (grade 1) with light petroleum (b.p. 60°/80°) to remove any unreacted ferrocene. After the ferrocene was removed the red/orange acetyl ferrocene (3.92g, 64%) may be removed more rapidly with light petroleum diethyl ether (1:1). The acetyl ferrocene was recrystallised from benzene to afford red crystals of m.p. 85°-86° (Lit. 258 m.p. 85°-86°); Found: C, 62.77%; H, 5.24%. C₁₂H₁₂OFe requires C, 63.16%; H, 5.26%.
α-Hydroxyethyl Ferrocene. (Method A).

A 3-neck 250ml flask equipped with a reflux condenser, nitrogen inlet, stirrer and dropping funnel was charged with acetyl ferrocene (2.28g, 10mmol) and dry ether (50 ml). The solution was stirred and treated dropwise with a solution of lithium aluminium hydride (0.19g, 5mmol) in ether and heated under reflux for two hours. The excess lithium aluminium hydride was destroyed with ethyl acetate and the resulting reaction mixture was treated with a solution of 2.68g of ammonium chloride dissolved in water. After being stirred 0.5 hour at 0°, the reaction mixture was filtered and the organic layer separated. After having been washed twice with water the ether solution was concentrated to dryness and the residue was allowed to crystallise. The crude carbinol (2.05G, 89%) was recrystallised from a mixture of ether petroleum ether (1:5) to obtain orange rods, m.p. 75°-77° (Lit. 257 m.p. 77°-78°); m/e (70eV) 230 (M+); 215 (M+-CH₃); 185 (M+-CHOHCH₃); 8 ¹H [200 MHz; CDCl₃] 4.46 (CH₆, 1H, (q)); 4.20 (Cp, 2,5,2H, (t)); 4.11 (Cp, 3,4,2H, (t)), 4.08 (Cp, 1'-5',5H, (s)); 2.21 (OH, 1H, (sbr)); 1.42
Integration 1:2:2:5:1:3; \( V_{\text{max}} \) (KBr) 3171-3101 (HO); 1315, 1171 (2° Alcohol,C-O); 1006, 893, 854, 795 (Cp,C-H) cm\(^{-1}\).

\( \alpha \)-Hydroxyethyl Ferrocene. (Method B).

Sodium borohydride (1.17g, 30.7mmol) is added in portions to a stirred solution of acetyferrocene (5g, 21.9mmol) in 9200ml of dry ethanol and stirring continued for 18 hours at room temperature. The mixture is next poured into water, neutralised with acetic acid (redistilled) and extracted with chloroform (3 x 50ml). Combined organic layers are washed with saturated sodium bicarbonate, dried over magnesium sulphate and concentrated to give a crude orange product. The crude product (4.69g, 93%) was recrystallised from a mixture of ether petroleum ether (1:5) to obtain orange rods, m.p. 76.5°-77.5° (Lit. 257 m.p. 77°-78°); Found; C, 62.26%; H, 6.08%. \( \text{C}_2\text{H}_4\text{OFe} \) requires C, 62.6%; H, 6.09%.

Ferrocene Acetate. (Method A).

\( \alpha \)-Hydroxyethyl ferrocene (1g, 4.35mmol) was dissolved in phridine (4.89g, 61.89mmol) and acetic anhydride (2.1g, 21.22mmol) at 0°C and allowed to stand overnight at room temperature. The solution
was concentrated to dryness in vacuo and the residue allowed to crystallise. The product was suspended in a little petroleum ether and filtered to obtain the crude product (0.99g, 84%). This was further purified by sublimation (<60° @ 0.2mm Hg) to obtain pure acetate, m.p. 66°-67° (Lit. 257 m.p. 67°-68°);

Found; C, 61.59%; H, 5.84%. C14H16O2 requires C, 61.76%; H, 5.88%; m/e (70eV) 272 (M⁺); 257 (M⁺-CH₃);

213 (M⁺-CO₂CH₃); 185 (M⁺-CH₂CH₃CH₂CO₂CH₃); δ ¹H [200 MHz; CDC1₃] 5.81 (CH₆,1H,(q)); 4.24 (Cp,2,5,2H,(t)); 4.18 (Cp,3,4,2H,(t)); 4.12 (Cp, 1-5,5H, (s)); 1.99 (CH₃,9,3H,(s)); 1.53 (CH₃,7,3H, (d)); Integration 1:2:2:5:3:3; δ ¹³C [22.5 MHz; CDC1₃] 170.88 (C8);

88.55 (C6); 70.48 (C1); 68.86 (C2,C5); 69.76 (C3,C4);

69.24 (C1'-C5''); 21.89 (C9); 20.59 (C7); Vmax (KBr) 3086 (C=CH₂); 1723 (C=O); 1281 (CH₃C=O, C-H); 1255 (Ester, C=O); 1006, 893, 829 (Cp,C-H) cm⁻¹.

Vinyl Ferrocene. (Method A).

A sample of the ferrocene acetate (10g, 36.8mmol) distilled under reduced pressure into a tube measuring 2.8 x 20 cm packed with pyrex wool. The tube was heated to 175° and the distillation was carried out at 3 to 5 mm of mercury. The pyrolysis
required about 0.5 hour. The product was washed from
the packing with petroleum ether and the resulting
solution concentrated in vacuo to give the crude
vinyl derivative. The crude product (5.2 g, 56%) was
purified by sublimation (45°-50° @ 0.4 mm Mg) to
afford a pure product, m.p. 47°-49° (Lit: 25 m.p.
48°-49°); m/e (70 eV) 212 (M+); 185 (M+ - CH2)=CH2) S 1H
(+200 MHz; CDCl3) 6.43 (Vinyl, 6,1H,(m)); 5.32
(Vinyl,7,2H,(m)); 4.33 (Cp,2,5,2H,(t)); 4.19
(Cp,3,4,2H,(t)); 4.01 (Cp,1 -5,5H,(s)); Integration
1:2:2:2:5; δ13C [22.5 MHz; CDCl3] 135.4 (C6); 111.77
(C7); 70.49 (C1); 69.96 (C1-C5); 69.43 (C2,C5);
67.42 (C3,C4); Vmax (KBr) 3095 (Vinyl, C-H) 3086
(Cp,C-H); 3011 (Vinyl,C-H); 1557 (Vinyl,C=C); 1101,
1006, 893, 829 (Cp,C-H) cm-1.
Vinyl Ferrocene. (Method B).

A solution of hydroxyethyl ferrocene (1 g,
4.35 mmol) and pyridinium tosylate (Å 0.1 g) in dry
benzene (100 ml) is refluxed for 3 hours using a
Dean-Stark trap. The cooled solution is washed with
water (50 ml) and with saturated sodium chloride
solution (50 ml) to remove the catalyst. The benzene
layer is dried with magnesium sulphate and evaporated
to give the crude produce which is an orange oily
residue. The crude product (0.51g, 55%) was further
purified by sublimation (45°-50° @ 0.4 mm Mg) to give
material which possessed a camphor-like odour, m.p.
Vinyl ferrocene (0.5g, 2.36mmol) was heated with azodiisobutyronitrile (5mg, 36.7μmol) at reflux for one hour in dry benzene (50 cm$^3$). A further portion of the radical initiator (5mg, 36.7μmol) was added and the heating continued for a further two hours. The resulting solution was vacuum distilled and a very viscous sirrup was collected. The sirrup was added dropwise to a small quantity of vigorously stirred methanol (25 cm$^3$), from which a dark brown powder (0.32g 52%) was collected, m.p. 281°-285° (Lit. 257 m.p. 280°-285°); Found; C, 68.07; H, 5.70.

C$_{12}$H$_{12}$Fe requires C, 67.95%; H, 5.66%; m/e (35eV) 636 (3M$^+$); 424 (2H$^+$); 212 (M$^+$); 185 (M$^+$-CH=CH$_2$); $\delta$ $^1$H [200 MHz; CDCl$_3$] 4.37 (Cp,2,5); 4.29 (Cp,3,4, (mbr)); 4.03 (Cp,1-5, (sbr)); 0.37 (Alkyl, (sbr)).
APPENDIX I

Dynamic N.M.R. Studies

The temperature dependence of n.m.r. spectra can be used to obtain information about energy barriers for certain rearrangement processes. From a study of the temperature dependence of the n.m.r. spectrum of the compound the rate constant for the rearrangement can be obtained at a temperature (Tc).

Consider, for example, the spectrum of an N,N-dimethylamide in which the two methyl groups are not in identical environments. When rotation about the CO – N bond is slow there will be two sharp singlets
in the $^1$H n.m.r. spectrum (each of relative area equal to three protons) and two sharp singlets in the $^{13}$C n.m.r. spectrum consistent with the non-equivalence of the two methyl groups. As the temperature at which the spectrum is being recorded is raised the rate of rotation will increase until at higher temperatures only one sharp singlet will be seen at a frequency half way between those of the two original signals. Here both methyl groups will be rapidly interchanging on the $^1$H n.m.r. or $^{13}$C n.m.r. time scale and will thus appear to be in identical environments. If the sample temperature is slowly raised from the "frozen" condition the peak will initially broaden and then merge into one broad signal which eventually sharpens up. The point at which merging occurs is known as the coalescence temperature ($T_c$) and here equation AI.1 holds.

$$K_c = \pi \Delta \nu \sqrt{2}.$$  \hspace{1cm} \text{AI.1}$$

$\Delta \nu$ = the frequency of separation of the two exchanging signals in the "frozen" condition Hz.

From the transition state theory equation AI.2 also holds and combining these two expressions leads to equation AI.3 for which the free energy of activations ($G^+$) for the rearrangement process can be calculated.
\[ K_c = \frac{K}{T_c h} \exp \left( -\frac{\Delta G^\ddagger}{RT_c} \right) \]  \hspace{1cm} \text{AI.2}

\[ \Delta G^\ddagger = \left( \frac{RT_c \log e}{K T_c \sqrt{2/\pi h \Delta V}} \right) \]  \hspace{1cm} \text{AI.3}

\( h = \text{Planks constant} \quad K = \text{Boltzmann's constant} \)

\( T_c = k^0 \).

---

**Figure AI.2** \(^1\text{H N.M.R. Spectra of Fc}[2.2]\)D [250 MHz: CDCl\(_3\)].

**APPENDIX II**

**X-Ray Crystallographic Data.**

**AII.1 1,1' -BIS(N-METHYLAMIDO)FERROCENE (46).**

An orange crystal of approximate dimensions 0.09 x 0.18 x 0.44 mm was glued to the end of a glass fibre. Preliminary photographs indicated it was of good quality. The crystal was mounted on the goniometer head of an Enraf-Nonius CAD4F
diffractometer and the unit cell and orientation matrix were determined using automated search and centering routines. The final unit-cell dimensions were obtained by the least-squares refinement of the setting angles of 25 high angle (28°) 30° reflections. Data were collected with a variable scan speed and the intensities of 3 reflections were remeasured every 2 hours as intensity standards and indicated no substantial decay. Backgrounds were measured at each side of the scan for a total time equal to one-half of the peak scan.

The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on the psi scan data of 3 reflections was applied. The position of the iron atom was determined by Patterson techniques and the remaining non-hydrogen atoms were located by difference-Fourier techniques. Hydrogen atoms were input in idealised positions (C-H = 1.0Å) with isotropic temperature factors. In the final refinements, the positional parameters and anisotropic temperature factors for the non-hydrogen atoms and the isotropic temperature factors for the carbon-bound hydrogen atoms were refined. A 3-term Chebyschev polynomial weighting scheme was used. The final refinement converged with R = 4.56% and no correlation coefficients greater than 0.6 were
observed. The final difference-Fourier map contained no peaks greater than 0.45 e/Å³.

### III.1.1 Crystal Data and Details of Data Collection and Structure Analyses.

**Structure Name:** 1,1'-Bis(N-Methylamido)ferrocene.

**Molecular formula**  
\[ \text{C}_{14}\text{H}_{16}\text{FeN}_{2}\text{O}_{2} \]

**Formula weight**  
324.16

**Crystal data:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>32.672(2)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>5.962(4)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>13.358(1)</td>
</tr>
<tr>
<td>(a/°)</td>
<td>90</td>
</tr>
<tr>
<td>(β/°)</td>
<td>104.088(6)</td>
</tr>
<tr>
<td>(γ/°)</td>
<td>90</td>
</tr>
<tr>
<td>(U/\text{Å}^3)</td>
<td>2535.8</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>C2/c</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>8</td>
</tr>
<tr>
<td>(D_c/\text{g cm}^{-3})</td>
<td>1.7063</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1344</td>
</tr>
<tr>
<td><strong>Linear Absorp. Coeff./cm(^{-1})</strong></td>
<td>96.69</td>
</tr>
<tr>
<td><strong>Crystal size/mm ca.</strong></td>
<td>0.09 x 0.18 x 0.44</td>
</tr>
<tr>
<td><strong>Data Collection:</strong></td>
<td></td>
</tr>
<tr>
<td><strong>X-radiation</strong></td>
<td>Cu K(\alpha),</td>
</tr>
<tr>
<td><strong>(ε) (\text{min.}, \text{max.}/°)</strong></td>
<td>0,70</td>
</tr>
</tbody>
</table>

Cont. ...
\[(\sin \theta / \lambda)_{\text{max}} = 0.6095\]

- **\(\omega\)-scan width parameters**
  - \(A, B(\degree) \ (A+B \tan \theta)\)
  - \(A = 1.0 \quad B = 0.14\)

- **Horizontal aperture parameters**
  - \(A, B(\text{mm}) \ (A+B \tan \theta)\)
  - \(A = 3.0 \quad B = 0\)

- **Scan speed:** min., max. / °min⁻¹
  - 1.3, 4.1

- **Total data**
  - 6540

- **Total unique data**
  - 2393

- **Observed data**
  - 1612

- **\([I > n \sigma(I)]\)**
  - \(n = 3\)

- **Absorption correction:** min., max.
  - 1.00, 1.86

- **Merging \(R\)**
  - 4.28

**Refinement:**

Solved by Patterson and Difference Fourier

- **No. of parameters**
  - 182

- **No. of restraints**
  - 0

- **Weighting scheme type**
  - Chebychev Polynomial

- **Weights**
  - 1043, 1425, 426

- **Extinction parameter**
  - Final shift/error
  - 0.012

- **Max residual electron density/eÅ⁻³**
  - 0.45

- **Final \(R = \Sigma \Delta F / \Delta F_o\)**
  - 4.56

- **\(R_w = [\Sigma \omega \Delta F^2 / \Sigma \omega F_o^2]^{1/2}\)**
  - 5.98

An orange crystal of approximate dimensions 0.11 x 0.33 x 0.33 mm was glued to the end of a glass fibre. Preliminary photographs indicated it was of good quality. The crystal was mounted on the goniometer head of an Enraf-Nonius CAD4F diffractometer and the unit cell and orientation matrix were determined using automated search and centering routines. The final unit-cell dimensions were obtained by the least-squares refinement of the setting angles of 25 high angle (2θ > 25°) reflections. Data were collected with a variable
scan speed and the intensities of 3 reflections were remeasured every 2 hours as intensity standards and indicated no substantial decay. Backgrounds were measured at each side of the scan for a total time equal to one-half of the peak scan.

The data were corrected for Lorentz and polarization effects and an empirical absorption correction based on psi scan data of 4 reflections was applied. The position of the iron atom was determined by Patterson techniques and the remaining non-hydrogen atoms were located by difference-Fourier techniques. The initial identification of the oxygen atoms of the water molecules were based on the heights and positions of peaks in a difference-Fourier map generated after all of the remaining non-hydrogen atoms had been refined. Hydrogen atoms attached to the carbon atoms were then input in idealised positions (C-H = 1.0 Å) with isotropic temperature factors. The hydrogen atoms of the water molecules were located from difference-Fourier syntheses. The refinement is nearly finished and only the positions of the hydrogen atoms of the water molecules are unstable.
### Crystal Data and Details of the Data Collection and Structure Analyses

**Structure Name:** Fc[2.2]M Dihydrate.

**Molecular formula:** $C_{24}H_{36}FeN_{2}O_{8}$

**Formula weight:** 536.40

**Crystal data:**

- **Crystal system:** monoclinic
- **a/Å:** 8.833(7)
- **b/Å:** 21.304(2)
- **c/Å:** 13.253(2)
- **α/°:** 90
- **β/°:** 95.24(3)
- **γ/°:** 90
- **V/Å³:** 2483.5

**Space Group:** P21/n

**Z:** 4

**D$_c$/g cm$^{-3}$:** 1.432

**F(000):** 1264

**Linear Absorp.Coeff./cm$^{-1}$:** 6.537

**Crystal size/mm ca.:** 0.11 x 0.33 x 0.33

**Data Collection:**

- **X-radiation:** Mo, $K_{α}$
- **θ min.,max./°:** 0, 22.5
- **(sinU/λ)max:** 0.5385

**ω-scan width parameters:**

- $A, B(°)$ $(A+B\tan θ)$: $A = 0.9$, $B = 0.35$

Cont. ...
Horizontal aperture parameters

$A, B (\text{mm}) (A + B \tan \theta)$

$A = 2.5 \quad B = 0$

Scan speed: min., max. /°min$^{-1}$

1.4, 2.7

Total data 4096

Total unique data 3036

Observed data 1697

$|I| > n\sigma(I)$

$n = 3$

Absorption correction: min., max.

1.00, 1.05

Merging $R$ 2.88

Refinement:

Solved by Patterson and Difference Fourier

No. of parameters 348

No. of restraints 0

Weighting scheme type

Units Weights

Weights 1

Extinction parameter

final shift/error 0.72

Max residual electron density/eÅ$^{-3}$ 0.19

Final $R = \Sigma \Delta F / \Delta F_o$

3.44

$R_w = \left[ \Sigma w \Delta F^2 / \Sigma w F_o^2 \right]^{1/2}$

3.56
AII.2.2 Microfiche Data of Bond Angles and Bond Lengths.

An orange crystal of approximate dimensions 0.18 x 0.24 x 0.35 mm was glued to the end of a glass fibre. Preliminary photographs indicated it was of good quality. The crystal was mounted on the goniometer head of an Enraf-Nonius CAD4F diffractometer and the unit cell and orientation matrix were determined using automated search and centering routines. The final unit-cell dimensions were obtained by the least-squares refinement of the setting angles of 25 high angle (2θ > 24°) reflections. Data were collected with a variable
scan speed. The intensities of 3 reflections were remeasured every 2 hours as intensity standards and indicated no substantial decay. Backgrounds were measured at each side of the scan for a total time equal to one-half of the peak scan.

The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on psi scan data of 3 reflections was applied. The positions of the iron atoms were determined by Patterson techniques. The remaining non-hydrogen atoms were located by difference-Fourier techniques. Refinements with isotropic temperature factors converged with an R-factor of 13.2%. No correlation coefficients greater than 0.5 were observed. Hydrogen atoms were then input in idealised positions (C-H = 1.0 Å) with fixed isotropic temperature factors. Anisotropic temperature factors for the non-hydrogen atoms were refined. Due to the large number of parameters, the positional parameters and temperature factors had to be refined in consecutive least-squares cycles. The temperature factors for three atoms C(12), C(18) and C(34) refined to non-positive definite values and therefore had to be refined isotropically in the final model. A 3-term Chebyshev polynomial weighting scheme was used for the final refinement. The final refinement converged with R = 9.01%. The
final difference-Fourier map contained no peaks greater than 1.0 e/Å^3.

AII.3.1 Crystal Data and Details of Data Collection and Structure Analyses.

Structure Name: Fc[2.2]D

Molecular formula: C₄₈H₆₄Fe₆N₄O₁₂

Formula weight: 1000.73

Crystal data:

Crystal system: triclinic

a/Å: 11.709(5)
b/Å: 13.310(2)
c/Å: 15.527(8)
a/°: 94.29(3)
β/°: 96.73(4)
γ/°: 101.00(3)
U/Å³: 2347.2

Space Group: PT

Z: 2

D_c/g cm⁻³: 1.419

F(000): 1056

Linear Absorp.Coeff./cm⁻¹: 6.8356

Crystal size/mm ca.: 0.18 x 0.24 x 0.35

Data Collection:

X-radiation: Mo Kα

θ min., max./°: 0-23

(sinθ/λ)max: 0.5498

Cont. ...
ω-scan width parameters
\[ A, B(0) \ (A + B \tan \theta) \]
\[ A = 1.00 \quad B = 0.35 \]

Horizontal aperture parameters
\[ A, B(\text{mm}) \ (A + B \tan \theta) \]
\[ A = 2.00 \quad B = 0 \]

Scan speed: min.\ to max. \( \circ \text{min}^{-1} \)
\[ 0.9, \ 5.5 \]

Total data
7651

Total unique data
6515

Observed data
2830

\[ [I > n\sigma(I)] \]
\[ n = 3 \]

Absorption correction: min.\ to max.
1.00, 1.16

Merging R
2.31

Refinement:
Solved by Patterson and Difference Fourier

No. of parameters
580

No. of restraints
0

Weighting scheme type
Chebychev Polynomial

Weights
192.6, 246.2, 74.5

Extinction parameter
-

final shift/error
0.078

Max residual electron density/\( \text{eÅ}^{-3} \)
0.95

Final R = \( \Sigma \Delta F / \Delta F_o \)
9.01

\[ R_W = [\Sigma \omega \Delta F^2 / \Sigma \omega F_o^2]^{1/2} \]
11.06
AII.3.2 Microfiche Data of Bond Angles and Bond Lengths.

AII.4 METHODS OF CRYSTAL GROWTH FOR X-RAY CRYSTALLOGRAPHY.

Method A.

The solute is dissolved in the minimum amount of boiling solvent and the hot solution is filtered under gravity through fluted filter paper. The hot filtered solution is allowed to cool very slowly by either of the following methods:

(a) The crystallisation process can be carried out in oil, the specific heat capacity of oil being such that the cooling process takes longer than normal.
(b) The flask with the crystallising solution may
be placed in a heated dewar insulated with cotton wool.

Method B.

![Figure AII.1 Solvent Diffusion Technique](image)

**Figure AII.1 Solvent Diffusion Technique**

The solvent diffusion technique of crystallisation involves the following procedure:

(a) Dissolve the solute in solvent B in which the solute is very soluble and fill up the tube (Figure AII.1) up to the mark shown at the interface.

(b) Using a solvent of lower specific gravity (solvent A) than the solvent already placed in the tube (solvent B), carefully pipette solvent A onto solvent B.

(c) Place the tube into a vibration free box or cupboard in which it will not be disturbed. Leave the tube for 10-14 days, allowing the solvent to slowly diffuse together and thus promoting the slow
growth of crystals at the interface. The crystals are removed carefully by filtration and allowed to dry.

The solvents which proved most successful in this study included chloroform (1.48 g/ml) or dichloromethane (1.32 g/ml) as solvent B and hexane (0.66 m/ml) or pentane (0.63 g/ml) as solvent A.

Method C.

Figure AII.2 Solvent Vapour Technique.

The solvent vapour technique of crystallisation involves the following procedure:–

(a) Dissolve the solute in solvent A in which the solute is very soluble and fill one of the tubes of the U-tube system.
(b) Into the other tube of the U-tube system place solvent B which is a very volatile solvent.
(c) As in Method B the U-tube is placed into a vibration free box or cupboard in which it will not
be disturbed. Leave the tube for 3-4 weeks while the volatile solvent B diffused into solvent A. Crystals begin to grow in solvent A and after carefully removing them by filtration they are dried.

APPENDIX III
AIII.1 D.C. CONDUCTIVITY MEASUREMENTS.
AIII.1.1 Sample Preparation.

All of the electrical measurements were carried out on samples in the form of compressed discs. For silver dag contacts, two paper reinforcers were placed on either side of the disc; two copper wires were then connected on either side by the silver dag, which filled the centre hole of the reinforcer, Figure AIII.1

![Figure AIII.1 Sample Preparation for D.C. Conductivity Measurements.](image)

Of the other contacts used, the aluminium and indium were vacuum deposited on to an accurately
defined area on either side of the sample discs, and the pressure contacts involved sandwiching the sample discs between two copper discs of known area. Each of these contacts was then connected to the external circuit via copper wire silver dagged to their surfaces.

AIII.1.2 Low Temperature Measurements.

Measurements below room temperature were made in a liquid nitrogen cryostat system, Figure AIII.2. This system consists of a temperature controller and cooling-heating arrangement. The system used a vacuum of $5 \times 10^{-2}$ mbar in order to avoid moisture condensation on the sample during measurement. Temperature was controlled by balancing the heat flow from the liquid nitrogen reservoir to the cold finder (a copper block) by supplying the required amount of heat through a heating coil wound around the latter. A Eurotherm model 070/008/010 controlled the heating current and a platinum resistance thermometer was used to sense the temperature of the copper block. To ensure that the temperature of the sample was as close as possible to that of the copper-block, good thermal contact was obtained by applying a thin coating of heat-sink compound between the copper and a thin mica sheet which was used as an electrical insulator.
Figure AIII.2  Schematic Diagram of the Cryostat.

AIII.1.3  Instrumentation.

A Kingshill stabilised power supply (Model 36V2C), two 610C solid state electrometers (Keithley Instruments) and a variable resistance box (100Ω - 1MΩ).
AIII.1.4 Experimental

Figure AIII.3 shows the circuit used for all of the measurements. $V_1$ measured the applied voltage and $V_2$ the voltage drop across a known resistance in series with our sample. The known resistance was kept small compared to the sample resistance to maintain as large a voltage drop across the sample as possible. From Ohms Law,

$$ I_2 = \frac{V_2}{R_2} \quad \text{and} \quad I_1 = \frac{V_1}{R_1} $$

where $I_1$ and $I_2$ are the currents flowing through resistances $R_1$ (sample) and $R_2$ (known), respectively. As these resistance are in series ($I_1 = I_2$) and as $R_2$ is known and $V_2$ measured, $I_2$ and
hence $I_1$ can be obtained. Measurements similar to these were made for a range of temperatures.

AIII.4 DIELECTRIC MEASUREMENTS.

AIII.4.1 Instrumentation.

The basic component of the system is a SOLARTRON 1191-FRA. The full system consists of a generator, a correlator, a measuring box together with its interface and a PDP-11/04 computer. The block diagram together with an equivalent circuit is shown in Figure AIII.4.

![Block Diagram of FRA System with Equivalent Circuit of Sample and Measuring Resistor/Capacitor Combination.](image)

Figure AIII.4 The Block Diagram of FRA System with Equivalent Circuit of Sample and Measuring Resistor/Capacitor Combination.
APPENDIX IV.
AIV.1 THE LANGMUIR-BLODGETT TECHNIQUE (LBT).

Thin films fabricated by the Langmuir-Blodgett technique consist of mono-molecular layers sequentially stacked onto a solid substrate. The process employs suitable long chain amphiphillic organic molecules (i.e. long organic molecules with both water attracting and water repelling constituents), dispersed on an aqueous sub-phase. These molecules orientate themselves with their hydrophillic head groups in the water while their hydrophobic tails are free to rotate about their carbon-carbon bonds in the atmosphere above. The molecules are then compressed into two dimensions such that a homogeneous insoluble monolayer is formed, each molecule normal to the water surface, Figure AIV.1.

When a suitably treated substrate is imersed into the water, breaking through the mono-molecular layer, the molecules attach themselves to this substrate. Depending on the nature of the substrate surface, the first layer will adhere either on its first down pass or its first up pass through the air/water interface. A hydrophobic coating will produce deposition on the first down pass as hydrophobic tails adhere to the hydrophobic surface, while no deposition takes place until the first up pass onto a
substrate with a hydrophillic surface. Generally, if the direction of the meniscus (formed at the water surface/substrate boundary) follows the substrate movement, deposition occurs.

Figure AIV.1  Molecules are dissolved in a volatile organic solvent and spread on the water surface. The solvent evaporates, leaving the molecules free to move in a two dimensional plane (a). Upon compression with a barrier system (b), a homogeneous monolayer is formed.

Once the first layer has adhered, a further layer is deposited every time the substrate crosses the air/water interface, Figure AIV.2.

In principle therefore, any desired number of layers may be deposited to produce a film, the thickness of which is the product of the individual molecular chain length and the number of times the substrate has crossed the air/water interface (remembering of course that no deposition takes place on the first down pass onto a hydrophillic surface).
Figure AIV.2 Deposition of mono-molecular film onto a solid substrate is performed by immersing the substrate through the air/water interface. Deposition onto a hydrophobic substrate is illustrated above.

AIV.2 LBT EXPERIMENTS ON CYANINE DYES.

$\text{CH}_3 \text{CH} = \text{CH}_{n-1} \text{CH} = \text{CH} \text{I}^- \text{CH}_3$

$n = 11, 15 \text{ and } 17$

Figure AIV.3 Long Alkyl Chain Cyanine Dyes.

Early work started on the cyanine dyes with the intention of forming a conducting monolayers proved successful. All the dyes shown in Figure AIV.3 had pressure-area isotherm measurements taken and a typical plot is shown in Figure AIV.4. After these initial experiments, monolayers and multilayer
Coating techniques were carried out on microscopy slides. Some of these monolayer transfer results are also shown in Figure AIV.3. The multilayer transfer experiments proved to be successful and examination of the microscopy slides by electron microscopy showed the presence of a cyanine dye/glass interface. Hopefully this minor series of results will provide a useful example of how feasible it is to attempt to make a conducting monolayers which may act as photoelectric and electrical devices.

Figure AIV.3 Pressure-Area Isotherm and Monolayer Transfer Experiments.
REFERENCES


27. Topics in Current Chemistry. (1984), 123.


April 30-May 3 (1973).


55. R.L. Sousa, D.H. Hoffmann, L. Kaplaman


57. G. Eisenham. Glass Electrodes for Hydrogen


Cambridge Crystallographic Data Base.
Department of Crystallography. Oxford University.


188. British Patent 1,278,621
    British Patent 1,512,863
    British Patent 1,521,083.


209. H.J. Keller Low-Dimensional Cooperative


(1929), 334, 409.
(1930), 354, 898.

J.Am.Chem.Soc. (1951), 73, 1087.

238. L.G.S. Brooker, G.H. Keyes and D.N. Heseltine.

239. L.G.S. Brooker, G.M. Keyes, R.H. Sprague,
R.H. van Dyke, E. van Larg, G. van Zanat,

Private Communication.

241. Review see: E.D. Bergmann, D. Ginsburg and


Synth., 1, 179.

244. J.M. Bobbit and D.A. Scola. J.Org.Chem. (1959),
25, 560.

W.J. Feast. Chem and Ind. (1985), 15 April, 263.


267. Aldrich Chemical Co. Ltd. The Old Brickyard, New Road, Gillingham, Dorset, England.
271. Chemical Abstract 68:29843a
Chemical Abstract 68:87384a.
274. Ilford Ltd. Private Communication.