AN INVESTIGATION INTO THE PROPERTIES OF VARIOUS TYPES OF COORDINATION COMPOUNDS OF THALLIUM

A Thesis submitted to the University of London for the Degree of Doctor of Philosophy.

by

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(University of London),
ABSTRACT

A number of complexes of thallium (III) were prepared and several of their properties, including infra-red, visible and ultra-violet spectra, magnetic susceptibility and conductivities were investigated.

Compounds of the type $M \cdot TlX_6$ ($M = $ alkali metal or ammonium ion and $X = $ Cl; and $M = Rb$ and $X = $ Br), $TlTlX_4^-$, $Tl_3TlX_6$ ($X = $ Cl and Br), $R_4NTlX_4$ ($R = $ CH$_3$, C$_2$H$_5$ and $X = $ Cl, Br and I), $R_4NX$ ($R = $ CH$_3$, C$_2$H$_5$ and $X = $ Cl, Br and I), $\overline{Tl0rg_2X_2TlX_4}$ and $\overline{Tl0rg_2X_2X'}$ ($org = $ 2-2' bipyridine, 1:10 phenanthroline and $X = $ Cl, Br and I and $X' = $ I) were prepared and a systematic study of their diamagnetic properties was made. Anionic susceptibility values for the anions $TlX_6^{3-}$ and $TlX_4^{-}$ were found and used in ascertaining the structure of the intermediate compounds, $TlTlX_4$ and $Tl_3TlX_6$ and of the 2-2' bipyridine and 1:10 phenanthroline complexes, $\overline{Tl0rg_2X_2TlX_4}$ and $\overline{Tl0rg_2X_2X'}$. For the intermediate compounds a lowering of diamagnetism due to bond shortening was noted and the magnetic evidence for the dimeric structure of the 2-2' bipyridine and 1:10 phenanthroline complexes was established. Theoretical diamagnetic susceptibility calculations for the above anions were furthermore made and compared with the experimental values.

The preparation of new complexes of thallium (III) halides with quaternary ammonium cations of the type
R\textsubscript{4}NTIX\textsubscript{4} (R = CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}, C\textsubscript{6}H\textsubscript{5}(CH\textsubscript{3})\textsubscript{3} and C\textsubscript{4}H\textsubscript{9} and X = Cl, Br and I) and of mixed halide complexes of the type R\textsubscript{4}NTIX'X\textsubscript{3} (R = CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}, C\textsubscript{6}H\textsubscript{5}(CH\textsubscript{3})\textsubscript{3} and C\textsubscript{4}H\textsubscript{9}, X and X' = Cl, Br or I) was carried out and some of these compounds were studied from an analytical point of view. The tetra-n-butyl and trimethyl phenyl ammonium tetra iodothallates are recommended as promising reagents for the gravimetric determination of thallium in the tervalent state.

Compounds of the type R\textsubscript{4}NTIX\textsubscript{4}, R\textsubscript{4}NTIX'X\textsubscript{3}, \(\text{TL}_{2} \text{org}_{2} \text{X}_{2} \text{TLX}_{4}\) and \(\text{TL}_{2} \text{org}_{2} \text{X}_{2} \text{TX}\) were shown to behave as uni-univalent electrolytes in organic solvents.

The infra-red spectra of the 2-2' bipyridine and 1:10 phenanthroline halogeno complexes in the range 2000-5000 cm\textsuperscript{-1} were investigated. Evidence for the cis configuration of the compound \(\text{TLbipy}_{2} \text{I}_{2} / \text{TLI}_{4}\) was found. The infra-red spectra of the mono, bis and tris complexes of thallium (III) nitrate of 2-2' bipyridine and 1:10 phenanthroline have been studied and evidence for their structures is provided. These infra-red results were found to be in agreement with those of conductivity measurements.

The ultra-violet and visible absorption spectra of the R\textsubscript{4}NTIX\textsubscript{4} (X = Cl, Br or I) in ethanol and acetonitrile solutions were examined. The characteristic TlCl\textsubscript{4}\textsuperscript{-} and TlBr\textsubscript{4}\textsuperscript{-} bands have been assigned and suggestions made as to the origin of the bands observed in the spectra of the tetra
iodothallates. In the case of the intermediate compounds the ultra-violet absorption bands observed were found to arise mainly from thallium (I) transitions. The ultra-violet absorption spectra of the 2-2' bipyridine and 1:10 phenanthroline halogeno complexes in organic solvents were furthermore studied and the characteristic ligand bands observed in each case.

Stability constants of the mono, bis and tris thallium (III):phenanthroline cations were determined in aqueous perchlorate solutions using the method of competitive reactions and a modified continuous variations technique. Further study was carried out in the ultra-violet region using Job's method and a comparison was made with available literature data.
IV.

ACKNOWLEDGEMENTS

I would like to express my most sincere and deep appreciation for the constant help and encouragement that I have received from Dr. V.C.G. Trew during the course of this work. My thanks are also due to Dr. J.W. Smith for his helpful suggestions and to Mr. F.J. Robinson for the reproduction of the graphs.

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Finally I wish to thank my parents, without whose understanding and encouragement, it would have been impossible to devote the time and effort required for this work.
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SECTION I

GENERAL INTRODUCTION

The element thallium has several unique properties which have stimulated interest in its chemistry ever since its discovery in 1861 (1). Volume 38 of Gmelin's Handbook of Inorganic Chemistry on thallium was published in 1940 and a review of its analytical chemistry by Busev and Tiptsova appeared in 1960 (2). Thallium forms two series of salts - thallous and thallic or thallium (I) and thallium (III) - in which the element exhibits +1 and +3 oxidation states respectively; the general properties of the two series being very different. While the thallous compounds are the most stable and best characterised, the thallic are distinctly the less stable and tend to revert to the univalent state unless stabilised by complex formation. The tendency for complex formation with both organic and inorganic ligands is greater in the case of thallium (III). Its complexes are furthermore unstable in aqueous solutions and this is perhaps one of the reasons why the co-ordination compounds of thallium (III) have not been intensively studied.

Current interest in the trihalides of thallium centres on their structure and on the stoichiometry, structure and stability of their co-ordination compounds. Thallium (III) forms well characterised complexes with chlorine and bromine
and to a certain extent with iodine. The existence of solid alkali metal and ammonium chloro and bromo-thallates of the type $M_3\text{TlX}_6$ (where $M = \text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$, $\text{Cs}^+$ and $\text{NH}_4^+$ and $X = \text{Cl}^-$; $M = \text{Rb}^+$ and $X = \text{Br}^-$) has long been known \(5\). X-ray measurements on $\text{K}_2\text{TlCl}_6\cdot2\text{H}_2\text{O}$ and $\text{Rb}_2\text{TlBr}_6\cdot8/7\text{H}_2\text{O}$ \(4\) have shown that the $\text{TlCl}^{3-}$ and $\text{TlBr}^{3-}$ anions are octahedral in structure and the $\text{Tl-Cl}$ and $\text{Tl-Br}$ distances were also measured. Apart from this work no other study appears to have been made on these solid compounds. It was thus thought useful to study their magnetic behaviour in the solid state from a systematic point of view. The dihalides and sesquihalides of thallium with chlorine and bromine are also of interest in this respect. Although it was found by Meier and Garner \(5\) that these salts were diamagnetic no previous systematic work has previously been carried out on them. Structures of the type $\text{TlTLX}_4$ and $\text{Tl}_3\text{TlX}_6$ have been put forward on the basis of their diamagnetism and these structures have furthermore been supported by experiments such as radioactive studies \(6\) on the $\text{Tl}_2\text{Cl}_3$ compound and x-ray crystallographic studies \(7\) on the dibromide. The $\text{Tl-Br}$ distance in the tetrahedral anion of the latter compound was found by Hazell \(7\) to be much shorter than in the caesium compound, $\text{CsTlBr}_4$ \(8\). These facts are of interest in connection with their structure and open up
grounds for further investigation. Their extreme insolubility in both polar and non-polar solvents restrict however the methods available for structure elucidation.

The available data on the halogeno complexes of thallium (III) thus seems to give evidence for the existence of $\text{TlX}_4^-$ and $\text{TlX}_3^-$ ions in the solid state. As a part of an investigation into the study of complexes of thallium containing the above anions, precipitation reactions using large organic groups as cations were thought to be promising from an analytical point of view. Quaternary ammonium cations were used as such reagents since they generally give rise to compounds which are highly insoluble in water and quite stable in the solid state. They are furthermore somewhat soluble in organic solvents and this fact makes them useful for structure determination.

In solution, a number of authors have investigated the halogeno complexes of thallium (III), the chloro and bromo being the most fully studied. Since the mechanism of coordination depends on the structures of the thallium (III) halides $\text{TlX}_2 \cdot 4\text{H}_2\text{O}$ themselves, reference to the work on the structures of these compounds is useful. Berry, Lowry, Goldstein and Gilbert (9) investigated their structures by conductivity and absorption spectra measurements. Conductivity results showed marked deviations from the Onsager plots using water and methanol and are non-
diagnostic of structure at low concentrations whilst with acetonitrile as solvent coordination was very likely. At higher concentration in these solvents the molar conductance results were approximately half the value expected for uni-univalent electrolytes on the assumption that thallic halides are monomers. The existence of dimeric structures $[^\text{TlX}_2]^+[^\text{TlX}_4^-]$ in solution was thus indicated and this was confirmed by conductivity measurements in nitrobenzene at concentrations from 0.002 to 0.05M.

Thallium halogen bonding was indicated from a study of the unit cell dimensions of thallic chloride and it has also been reported by Syrkin and Diatkina (10) that the conductivity of the fused chloride is zero, which suggests that in the solid state the compound has a very high degree of homopolar character. This is further supported by the very low melting point of the solid ($25^\circ$C).

Spencer and Abegg (11) demonstrated the existence of the halogeno complexes by redox potential measurements on Tl$^{3+}$/Tl$^+$ in the presence of halide ions. Later Hughes and Garner (12) confirmed their suggestion and Harbottle and Dodson (13) studied further the chloro complexes by isotopic exchange between TlClO$_4$ and Tl(ClO$_4$)$_2$ using labelled thallium. Although their results did not lead to conclusive identification of the reacting species, evidence for the existence of such anions as TlCl$_2^+$, TlCl$^{2+}$ and TlCl$_4^-$.
was provided. Benoit in 1949 (13) using a potentiometric method obtained stability constants for halothallate anions of the type Tlx$_n^{3-n}$ (where X = Cl or Br and n = 1, 2, 3 and 4). Feshansky and Valledas-Dubois (14) on the basis of spectrophotometric and potentiometric measurements concluded that in solutions containing Tl$^{3+}$ and Cl$^-$ or Tl$^{3+}$ and Br$^-$, complex ions containing up to six halogen atoms existed and they found the stability constants. Nord and Ullstrop (15) using solvent extraction and later Ahrland (16) and coworkers by E.M.F. measurements studied the thallic-chloride system further and concluded that the maximum number of coordinated chloride ions in the above complexes was four. Thus the various results for the thallium (III)-chloride equilibria fall into two groups. The first of which (14) (17) shows that a solution in which chloride ions are in excess contains appreciable concentrations of TlCl$_6^{2-}$ with some TlCl$_5^{2-}$, while the second group (13) (15) (16) (18) find that only TlCl$_3^-$ and TlCl$_4^-$ are mainly present.

The study of complex compounds of thallium (III) with organic amines was begun by Meyer (19) who described the preparation of some alkyl amine complexes of thallium (III) halides. Later Renz (20) and then Heber (21) prepared similar pyridine and ethylenediamine complexes respectively. Kochetkova and Tron'ev (22) described some complexes of thallium (III) halides with ammonia and determined their
thermal stability. Sutton in 1958 (13) reported on complexes of thallium (III) halides with 1:10 phenanthroline and 2-2' bipyridine and carried out some conductimetric and cryoscopic molecular weight determinations in nitro-benzene. On this basis he suggested the following structures for these compounds $\text{[TlCrg}_2X_2\text{]}^{2+}$ where Crg = 2-2' bipyridine and 1:10 phenanthroline. These structures were however by no means settled. Kul'ba and Mironov (24) in a later study described the preparation of some nitrate and perchlorate complexes of thallium (III) containing the above ligands. Using a potentiometric method they found the stability constants for the mono and bis complex ions: $\text{[TlCrg]}^{3+}$ and $\text{[TlCrg}_2\text{]}^{2+}$.

Apart from the above work no other systematic attempts appeared to have been made to determine the structure or chemical behaviour of the coordination compounds of thallium (III) with 1:10 phenanthroline and 2-2' bipyridine in the solid state and in solution. The use of several physical methods is thus required for this purpose and a brief outline of their application to coordination chemistry must now be given.

For solid compounds, magnetochemical methods provide valuable information even when dealing only with diamagnetic compounds as in the present case. Magnetochemical measurements in inorganic chemistry have found their main...
application to coordination compounds of the transition metal ions. In such cases incomplete shells of electrons leading to paramagnetic behaviour are present and it is in such cases possible to correlate the valency, bond type and stereo-chemistry of the atom in question with its effective magnetic moment. Diamagnetic measurements on the other hand are of value provided that systematic studies are made and have been employed in structural determinations in connection with organic molecules. Pascal (25) and a number of subsequent workers (26) have investigated additivity relationships in this field. Systematic work on the diamagnetism of several simple polar inorganic salts have also been carried out by various authors (27) and sets of diamagnetic susceptibility values for several simple ions are now available including alkali and halide ions. Comparison of the experimental values with those predicted by theory have furthermore been made. It was thought useful to investigate the extent to which additivity relationships could be applied to the type of compounds prepared in the present work and thus to use magnetochemical methods in the determination of their structure. Theoretical calculations in these cases should also lead to interesting results.

Although a detailed interpretation of vibrational spectra is impossible for complex molecules, information of
value may be obtained from an empirical study of the infra-red spectra of a series of related substances. Both the 2-2' bipyridine and 1:10 phenanthroline complexes of thallium (III) halides can be examined in this way. Of interest too are the metal-ligand stretching frequencies which give information about the bond strength in the complexes. The latter determination however requires measurements to be made below $500\text{cm}^{-1}$, in the caesium iodide range.

Conductivity measurements in organic solvents enable the number of ions formed in solution on dissociation to be determined, by comparing the mobilities of the ions in question with the values available for various types of compound. The molar conductances for various types of compounds in various solvents are now available in the literature.

Ultra-violet and visible absorption spectra in most cases give in addition evidence about the nature of the complex species present. The determination of the stability constants of the complexes present, particularly in aqueous solutions is perhaps the most fundamental type of measurement.

A fairly large amount of data on stepwise formation constants for complexes of many metals with a diversity of ligands has now been accumulated (28). In the case of the thallium (III) complexes in common with other trivalent
metals the data are scanty. Thus the only measurements on
the stability of complexes of thallium in water are those
of Kul'ba and Mironov on the 2-2' bipyridine and 1:10
phenanthroline complexes determined by a potentiometric
method (24).

Further discussion of the techniques which have been
applied to the present problem and the results obtained
will be introduced later and considered relatively to the
available literature material.
Preparative Work

Owing to the strong tendency of the thallic compounds to go to the thallous state, thallium (III) compounds are relatively unstable and with the exception of the oxide, $\text{Tl}_2\text{O}_3$, cannot be obtained commercially. The laboratory source of thallium (III) is thus generally the thallium (I) compounds: the nitrate, carbonate and chloride being most commonly employed.

Thallium (III) halides can be made by an oxidation reaction of the thallium (I) compounds with the appropriate halogens. The starting point in the preparation of most of the complexes in the present work was thallium (III) chloride tetrahydrate. This was made by passing a stream of chlorine gas into water containing a suspension of thallous chloride. A yellow precipitate of the intermediate compound $\text{Tl}_4\text{Cl}_6$ was first of all obtained, but this dissolved slowly so as to give finally a clear solution of thallium (III) chloride. By careful evaporation of the latter with addition of dilute chlorine water at intervals the tetrahydrate $\text{TlCl}_3 \cdot 4\text{H}_2\text{O}$ separated out as large rather deliquescent needles. The compound was not completely dried and contained a slight excess of chlorine
and chloride ions so as to prevent hydrolysis. This was a bulk preparation, the yield being approximately 400g. in each preparation.

Analar reagents were used in the preparation of compounds whenever possible and the crude samples of the starting materials were all tested for ferromagnetic and paramagnetic impurities (i.e. iron, cobalt and nickel) by the standard tests: (a) **Iron** A purple colouration is given on the addition of an ammoniacal solution of thio-glycollic acid to the test solution: (b) **Nickel** A red colouration of nickeldimethylglyoxime is given when dimethylglyoxime is added to the ammoniacal test solution: (c) **Cobalt** An orange colouration is given on the addition of the reagent α-nitroso-β-napthol together with dilute caustic soda and a little ammonium chloride to the test solution.

The preparation of all the compounds studied in the present work is described here together rather than in the separate sections.

(a) **Alkali Metal and Ammonium chloro and bromothallates**

All these complexes were prepared using the method described by Pratt (3).
Lithium chlorothallate octahydrate, $\text{Li}_2\text{TlCl}_6\cdot3\text{H}_2\text{O}$

Lithium chloride (5g.) was dissolved in water (5ml.) and the resulting solution then added to a solution of thallic chloride tetrahydrate (15g.) in water (5ml.), the mixture was then carefully evaporated, chlorine water (3 drops) was added to prevent the formation of the intermediate compound. The solution was then placed in vacuo over phosphorus pentoxide. The colourless, very detéliquéscent crystals obtained were washed with small amounts of alcohol and ether. The compound was dehydrated over concentrated sulphuric acid in vacuo.

Sodium chlorothallate decadecahydrate, $\text{Na}_2\text{TlCl}_6\cdot12\text{H}_2\text{O}$;
Potassium and Ammonium chlorothallate dihydrates, $\text{K}_2\text{TlCl}_6\cdot2\text{H}_2\text{O}; (\text{NH}_4)_3\text{TlCl}_6\cdot2\text{H}_2\text{O}$

These compounds were similarly prepared by mixing the appropriate quantities of the corresponding alkali and thallium (III) chlorides in concentrated aqueous solutions. The crystals obtained were treated as above.

Rubidium and Caesium chlorothallate monohydrates, $\text{Rb}_2\text{TlCl}_6\cdot\text{H}_2\text{O}; \text{Cs}_2\text{TlCl}_6\cdot\text{H}_2\text{O}$

Approximately 0.1g. and 0.05g. of thallic chloride tetrahydrate were added respectively to aqueous solutions of rubidium chloride (2g.) and caesium chloride (5g.). In the case of the caesium salt the yield was very low and thus after filtering the crystals first obtained, the
filtrate was treated with the calculated fraction of caesium chloride. This process was repeated several times so as to get as much of the salt as possible. The colourless crystals which were obtained in both cases were treated as above.

Rubidium Bromothallate monohydrate, $\text{Rb}_2\text{TlBr}_6\cdot\text{H}_2\text{O}$

Approximately 1g. of thallic bromide tetrahydrate was added to a solution of rubidium bromide (5g.). Because of the low yield, the crystals first obtained were filtered off and the filtrate then treated with a calculated fraction of rubidium bromide. The process was repeated and the golden yellow crystals obtained were washed and treated as above.

(b) Hydrotetrachlorothallic acid trihydrate, $\text{H}\text{TlCl}_4\cdot\text{3H}_2\text{O}$

This compound was prepared as described by Mellor (29). A solution of thallic chloride in concentrated hydrochloric acid was carefully evaporated on a water-bath. The evaporation was completed over sulphuric acid and potassium hydroxide contained in a desiccator. Colourless crystals which rapidly deliquesce in air were thus obtained.

Because of the deliquescent nature of the above compounds, they were stored in a desiccator over calcium chloride. Some of the compounds were stored both in the hydrated and anhydrous forms. The yields were generally
fairly high, approximately 7g. being prepared for each compound.

All the above compounds together with the results of their analysis are listed in Table (1).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Elementary Composition: % Found (calc. in brackets)</th>
<th>Alkali Metal</th>
<th>Thallium</th>
<th>Halide</th>
<th>Water</th>
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<tbody>
<tr>
<td>1 Li₂TlCl₆·8H₂O</td>
<td>3.57 (3.61)</td>
<td>34.91 (35.06)</td>
<td>36.50 (36.59)</td>
<td>22.80 (24.74)</td>
<td></td>
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<tr>
<td>2 Na₂TlCl₆·12H₂O</td>
<td>9.80 (9.83)</td>
<td>29.91 (29.06)</td>
<td>30.41 (30.34)</td>
<td>28.73 (30.77)</td>
<td></td>
</tr>
<tr>
<td>3 K₂TlCl₆·2H₂O</td>
<td>20.49 (20.56)</td>
<td>34.90 (35.83)</td>
<td>37.32 (37.29)</td>
<td>6.09 (6.31)</td>
<td></td>
</tr>
<tr>
<td>4 (NH₄)₂TlCl₆·2H₂O</td>
<td>10.69 (10.64)</td>
<td>40.40 (40.30)</td>
<td>41.98 (41.95)</td>
<td>6.80 (7.09)</td>
<td></td>
</tr>
<tr>
<td>5 Rb₂TlCl₆·H₂O</td>
<td>37.12 (37.09)</td>
<td>29.72 (29.50)</td>
<td>30.53 (30.81)</td>
<td>2.30 (2.60)</td>
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<tr>
<td>6 Cs₂TlCl₆·H₂O</td>
<td>47.79 (47.84)</td>
<td>24.27 (24.46)</td>
<td>25.41 (25.54)</td>
<td>1.93 (2.16)</td>
<td></td>
</tr>
<tr>
<td>7 Rb₂TlBr₆·H₂O</td>
<td>27.02 (27.27)</td>
<td>21.22 (21.33)</td>
<td>50.09 (50.14)</td>
<td>1.70 (1.88)</td>
<td></td>
</tr>
<tr>
<td>8 HTlCl₄·3H₂O</td>
<td>49.98 (50.94)</td>
<td>35.02 (35.35)</td>
<td>12.92 (13.45)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) Intermediate Compounds

With the exception of thallium dichloride, these compounds were prepared by Trew by the methods described below.

Thallium dichloride, TlCl₂

This compound was prepared according to the directions given by Mellor (29), by dissolving thallium sesquioxide in concentrated hydrochloric acid. The compound obtained was
very pale yellow in colour and unstable in the presence of water. Thus all subsequent transfer operations were carried out in a dry box.

Thallium sesquichloride, $\text{Tl}_2\text{Cl}_3$

Following Willm's method (30), it was precipitated as bright yellow crystals by the addition of hydrochloric acid to a mixture of thallium nitrate and thallium (III) chloride tetrahydrate.

Thallium dibromide, $\text{TlBr}_2$

The preparation consisted in heating a solution of thallium (I) nitrate in hydrogen bromide with dilute nitric acid. Partial oxidation resulted with the precipitation of yellow thallium dibromide.

Thallium sesquibromide, $\text{Tl}_2\text{Br}_3$

The most satisfactory method of preparation was as follows: concentrated nitric acid (1ml.) was added to approximately 20g. of thallous nitrate, followed by the gradual addition of hydrogen bromide whilst heating the solution. A whitish yellow precipitate of thallous bromide was found, mixed with the insoluble red precipitate of thallium sesquibromide. On extracting with hot water the red spangles of $\text{Tl}_2\text{Br}_3$ dissolved, leaving the insoluble thallous bromide. On cooling, red crystals were obtained. Continuous extraction with the mother liquor increased the
yield. The crystals were then purified by boiling and recrystallising.

The above compounds together with the results of their analysis, are listed in Table (2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Elementary Composition: % Found (calc. in brackets)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thallium</td>
<td>Chlorine</td>
</tr>
<tr>
<td>1 TlCl₂</td>
<td>74.47(74.24)</td>
<td>26.84(25.76)</td>
</tr>
<tr>
<td>2 Tl₂Cl₃</td>
<td>79.14(79.35)</td>
<td>21.01(20.65)</td>
</tr>
<tr>
<td>3 TlBr₂</td>
<td>55.89(56.12)</td>
<td>43.25(43.88)</td>
</tr>
<tr>
<td>4 Tl₂Br₃</td>
<td>62.98(63.03)</td>
<td>36.45(36.97)</td>
</tr>
</tbody>
</table>

(d) 2-2' Bipyridyl complexes of tervalent thallium

Dichloro(thiophene) Thallium (III) tetrachlorothallate, \( \text{[Tl \text{bipy}_2\text{Cl}_2]} \text{Cl}_4 \)

Using the method of Sutton (23).

Thallium (III) chloride tetrahydrate (1 m.mole) was dissolved in water (10 ml.) and treated with a solution of 2-2' bipyridine (1 m.mole) in ethanol (2ml.). The white precipitate which was obtained was filtered off, washed with water and dried over concentrated sulphuric acid in vacuo.

Calculated: C 25.69; H 2.14; N 5.99; Tl 43.77; Cl 22.78

Found: C 25.71; H 2.13; N 5.94; Tl 43.68; Cl 22.71
Using the method of Sutton (23).

Thallium (III) bromide tetrahydrate (1 m mole) was dissolved in the smallest quantity of water and allowed to react with a solution of 2-2'bipyridine (1 m mole) in ethanol. The white precipitate which was obtained was treated as above.

Calculated:  C 19.98; H 1.67; N 4.66; Tl 34.05; Br 39.93
Found:  C 19.93; H 1.61; N 4.70; Tl 33.97; Br 39.90

Sutton's method (23) was used to prepare this compound.

Thallium (III) chloride tetrahydrate (1 m mole) was dissolved in water (10 ml.) and then treated with 2-2'bipyridine (1 m mole) in ethanol (5 ml.) and sodium iodide (3 m mole) in water (5 ml.) added with stirring. The orange red precipitate which was obtained was filtered off, washed with cold water and 50% alcohol ether, dried at 100°C and in vacuo over concentrated sulphuric acid.

Calculated:  C 16.19; H 1.35; N 3.77; Tl 27.54; I 51.34.
Found:  C 16.26; H 1.39; N 4.00; Tl 27.40; I 51.30.

This was a new compound prepared by a method devised in the course of this work.
Thallium (III) chloride tetrahydrate (0.2g.) was intimately mixed with 2-2’ bipyridine (0.25g.) and sodium iodide (0.55g.) and the mixture heated at 90°C for several hours. Extraction of the mixture with water yielded a black residue. The filtrate obtained after the removal of the residue was evaporated to yield the yellow complex. This was treated in the above manner used for the preceding complex.

Calculated: C 16.19; H 1.35; N 3.77; Tl 27.54; I 51.34
Found: C 15.99; H 1.33; N 3.72; Tl 27.50; I 51.29

Diiodo bis (2-2’bipyridine) thallium (III) iodide, $\text{[Tl}_2\text{bipy}_2\text{I}_2\text{]}_\text{I}$

Using the method of Sutton (23).

Thallium (III) chloride tetrahydrate (1 m mole) in water (10 ml.) was allowed to react with 2-2’ bipyridine (2 m moles) in ethanol in the presence of excess iodide ion. The orange red precipitate obtained was filtered off, washed with cold water and dried over concentrated sulphuric acid in vacuo.

Calculated: C 26.74; H 2.23; N 6.23; Tl 22.72; I 42.42
Found: C 26.70; H 2.21; N 6.20; Tl 22.69; I 42.40

The following 2-2’ bipyridine thallium (III) nitrate complexes were prepared using the method of Kul’ba and Mironov (24).
Diaquo (2-2' bipyridine) thallium (III) nitrate, 
\[ \text{Tl} \text{bipy(H}_2\text{O})_2\text{/(NO}_3\text{)}_3 \]

A molar thallium (III) nitrate solution in one molar nitric acid (10 ml.) was mixed with a molar solution of 2-2' bipyridine (9 ml.) in 92% methyl alcohol. White crystals were obtained on standing. These were filtered off and washed with a little alcohol.

Calculated: C 20.60; H 1.37; N 12.02; Tl 35.09; NO\text{\textsubscript{3}} 31.94

Found: C 19.87; H 1.09; N 11.95; Tl 35.15; NO\text{\textsubscript{3}} 30.89

Bis-(2-2' bipyridine) thallium (III) nitrate, 
\[ \text{Tl} \text{bipy}_2(\text{NO}_3)_2 \]

A 0.25M solution of thallium (III) nitrate hexahydrate was prepared and into 20 ml. of this solution were run 10 - 12 ml. of a 0.5M alcoholic solution of 2-2' bipyridine. A white precipitate was obtained within 5 minutes whilst stirring. It was filtered off, washed with alcohol and dried at 60°C to constant weight.

Calculated: C 29.08; H 2.27; N 13.94; Tl 29.09; NO\text{\textsubscript{3}} 26.49

Found: C 29.00; H 2.20; N 13.87; Tl 28.78; NO\text{\textsubscript{3}} 26.40

Tris-(2-2' bipyridine) thallium (III) nitrate, 
\[ \text{Tl} \text{bipy}_3(\text{NO}_3)_2 \]

Bis-(2-2' bipyridine) thallium (III) nitrate (0.5g) was dissolved in a solution of 2-2' bipyridine (25 ml.) saturated at about 25°C. This yielded a pure product on addition of a saturated solution of 2-2' bipyridine in
diethyl ether. The white precipitate obtained was filtered off and washed with alcohol.

Calculated:  C 41.88; H 2.79; N 14.66; Tl 23.78; NO$_3$ 21.64
Found:  C 41.71; H 2.67; N 14.60; Tl 23.35; NO$_3$ 21.61

Bis-(2-2' bipyridine) thallium (III) perchlorate,

Using the method of Kul'ba and Mironov (24).

Bis-(2-2' bipyridine) thallium (III) nitrate (0.5g.) was dissolved in the minimum quantity of methanol. To the resulting solution the calculated amount of sodium perchlorate was added. A white precipitate was obtained after a few minutes whilst stirring. The precipitate was filtered off and washed with alcohol.

Calculated:  C 29.44; H 1.96; N 6.87; Tl 23.07; ClO$_4$ 36.55
Found:  C 29.31; H 1.87; N 6.80; Tl 24.93; ClO$_4$ 36.01

(e) 1:10 Phenanthroline complexes of tervalent thallium

All the halogeno complexes were prepared using the method of Sutton (23).

Dichloro bis (1:10 phenanthroline) thallium (III) tetrachlorothallate,

Thallium (III) chloride tetrahydrate (1 m mole) was dissolved in water (10 ml.) and then treated with a solution of 1:10 phenanthroline hydrate (1 m mole) in ethanol (2ml.). The white precipitate was washed with a little ethanol and dried over concentrated sulphuric acid.
Calculated: C 29.34; H 1.63; N 5.71; Tl 41.64; Cl 21.67
Found: C 29.21; H 1.61; N 5.68; Tl 41.73; Cl 21.60

Dibromo bis (1:10 phenanthroline) thallium (III) tetrabromothalallate, $\text{Tlphen}_2\text{Br}_2/\text{TlBr}_4$

Thallium (III) bromide tetrahydrate (1 m mole) was dissolved in water (10ml.) treated with a solution of 1:10 phenanthroline hydrate (1 m mole) in ethanol (2 ml.) and the white precipitate obtained was treated as above.

Calculated: C 23.07; H 1.28; N 4.49; Tl 32.75; Br 38.41
Found: C 23.41; H 1.34; N 4.23; Tl 32.99; Br 38.00

Diiodo bis (1:10 phenanthroline) thallium (III) iodothallate, $\text{Tlphen}_2\text{I}_2/\text{TII}_4$

Thallium (III) chloride tetrahydrate (1 m mole) was dissolved in water (10 ml.), treated with a mixture of 1:10 phenanthroline hydrate (1 m mole) and sodium iodide (3 m mole) in 90% aqueous ethanol (10 ml.) and water (10ml.) added with stirring. The orange red precipitate obtained was filtered off and reprecipitated from ethanol by the addition of water. It was then dried as before.

Calculated: C 18.82; H 1.05; N 3.66; Tl 26.71; I 49.74
Found: C 18.76; H 1.13; N 3.60; Tl 26.59; I 49.68

Diiodo Bis (1:10 phenanthroline) thallium (III) iodide, $\text{Tlphen}_2\text{I}_2/I$

Thallium (III) chloride tetrahydrate (1 m mole) was dissolved in water (10 ml.) and then treated with a mixture of 1:10 phenanthroline hydrate (2 m moles) and excess
sodium iodide (1g.) in 90% aqueous ethanol (10 ml.) and water (10 mls.) added with stirring. The orange red precipitate obtained was treated as above.

Calculated: C 30.47; H 1.69; N 5.95; Tl 21.62; I 40.29
Found: C 30.38; H 1.60; N 5.91; Tl 21.59; I 40.20

The following 1:10 phenanthroline thallium (III) nitrate and perchlorate complexes were prepared by using the method of Kul'ba and Mironov (24).

**Di aquo (1:10 phenanthroline) thallium (III) nitrate,**

\[
\text{Tl}^{III}(\text{phen})_{2}^{+2} \left(\text{NO}_{3}^{-}\right)_{3}
\]

A molar thallium (III) nitrate solution in one molar nitric acid (10 ml.) was mixed with a molar solution of 1:10 phenanthroline (9 ml.) in 92% methyl alcohol. A white precipitate was obtained. This was filtered off and washed with a little alcohol.

Calculated: C 23.74; H 1.98; N 11.54; Tl 33.70; NO\(^{-}3\) 30.67
Found: C 23.70; H 1.93; N 11.50; Tl 33.68; NO\(^{-}3\) 30.57

**Bis(1:10 phenanthroline) thallium (III) nitrate,**

\[
\text{Tl}^{III}(\text{phen})_{2}^{+2} \left(\text{NO}_{3}^{-}\right)_{3}
\]

A molar thallium (III) nitrate solution in one molar nitric acid (10 ml.) was mixed with a molar solution of 1:10 phenanthroline (21 ml.) in 92% methyl alcohol. The white precipitate obtained was filtered off and washed with a little alcohol.

Calculated: C 38.38; H 2.13; N 13.06; Tl 27.24; NO\(^{-}3\) 24.79
Found: C 38.29; H 2.09; N 13.10; Tl 27.19; NO\(^{-}3\) 24.70
Tris(1:10 phenanthroline) thallium (III) nitrate, 
\(\text{Tl} \text{phen}_2(\text{NO}_3)_3\)

A molar thallium (III) nitrate solution in one molar nitric acid (10ml.) was mixed with a molar solution of 1:10 phenanthroline (45ml.) in 92% methyl alcohol. The white solid which was obtained was treated as above.  
Calculated:  \(\text{C}: 46.43; \text{H}: 2.58; \text{N}: 13.54; \text{Tl}: 21.97; \text{NO}_3^-: 19.99\)  
Found:  \(\text{C}: 46.38; \text{H}: 2.51; \text{N}: 13.52; \text{Tl}: 21.90; \text{NO}_3^-: 19.87\)

Tris(1:10 phenanthroline) thallium (III) perchlorate 
\(\text{Tl} \text{phen}_2(\text{ClO}_4)_3\)

Tris (1:10 phenanthroline) thallium (III) nitrate (0.6g.) was dissolved in the minimum quantity of methanol. To the resulting solution the calculated amount of sodium perchlorate was added. A white precipitate was obtained almost immediately after mixing. The precipitate was filtered off and washed with alcohol.  
Calculated:  \(\text{C}: 41.43; \text{H}: 2.30; \text{N}: 8.06; \text{Tl}: 19.60; \text{ClO}_4^-: 27.75\)  
Found:  \(\text{C}: 42.34; \text{H}: 2.77; \text{N}: 8.35; \text{Tl}: 19.55; \text{ClO}_4^-: 27.69\)

Anhydrous phenanthroline

Finely powdered 1:10 phenanthroline hydrate (0.4g.) was dried in vacuum at about 100° for two hours. The resulting powder was placed in a desiccator over concentrated sulphuric acid in vacuo for two days. The anhydrous material was then obtained.
Although several quaternary ammonium complexes with metal halides are known, analogous thallium (III) compounds had not been previously prepared. A number of complexes of the type $R_4NTlX_4$ and $R_4NTlX_2X'$ (where $R = CH_3$, $C_2H_5$, $C_6H_5(CH_3)_3$ and $C_4H_9$, and $X$ and $X' = Cl$, Br or I) were successfully prepared as described below.

**Tetra methyl ammonium tetrachlorothallate,**

$\text{(CH}_3\text{)}_4\text{NTlCl}_4$

Tetramethyl ammonium chloride (1 m mole) was dissolved in absolute alcohol (2ml.) and mixed with a solution of thallic chloride tetrahydrate (1 m mole) in the minimum quantity of water. The white precipitate obtained was washed with small quantity of water, alcohol and dried in vacuo over concentrated sulphuric acid.

All the tetra halogenothallates (III) of quaternary ammonium cations were similarly prepared by mixing aqueous alcoholic solution of thallium (III) halides and the corresponding onium halide in 1:1 ratio. When the addition was performed with warm solutions the complex salts usually precipitated on cooling to room temperature. Preparation of the mixed halogeno complexes (i.e. those with two different halogens in the anion) were similarly carried out. All the salts were carefully washed with water and alcohol and dried in vacuo over concentrated sulphuric acid. Table (3) gives a survey of the compounds prepared in this work and contains...
<table>
<thead>
<tr>
<th>Substance</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Tl</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (CH₃)₄NTlCl₄</td>
<td>11.92 (11.42)</td>
<td>3.05 (2.85)</td>
<td>3.70 (3.33)</td>
<td>48.09 (48.62)</td>
<td>32.57 (33.73)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. (CH₃)₄NTlBr₄</td>
<td>7.04 (7.34)</td>
<td>1.69 (1.83)</td>
<td>2.01 (2.13)</td>
<td>31.01 (31.23)</td>
<td></td>
<td>48.00 (48.55)</td>
<td></td>
</tr>
<tr>
<td>3. (CH₃)₄NTlI₄</td>
<td>6.62 (6.74)</td>
<td>1.58 (1.96)</td>
<td>2.04 (1.96)</td>
<td>29.05 (28.70)</td>
<td></td>
<td></td>
<td>70.59 (71.29)</td>
</tr>
<tr>
<td>4. (C₂H₅)₄NTlCl₄</td>
<td>20.89 (20.78)</td>
<td>4.12 (4.19)</td>
<td>2.69 (2.93)</td>
<td></td>
<td></td>
<td></td>
<td>29.76 (29.01)</td>
</tr>
<tr>
<td>5. (C₂H₅)₄NTlBr₄</td>
<td>14.88 (14.68)</td>
<td>3.35 (3.05)</td>
<td>2.42 (2.24)</td>
<td>31.01 (31.23)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. (C₂H₅)₄NTlI₄</td>
<td>11.39 (11.82)</td>
<td>2.37 (2.44)</td>
<td>1.66 (1.70)</td>
<td>24.26 (23.91)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. C₆H₅(CH₃)₃NTlI₄</td>
<td>12.75 (13.06)</td>
<td>1.31 (1.27)</td>
<td>1.58 (1.65)</td>
<td>24.24 (24.08)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>8. ΩH₃(CH₂)₃NTlI₄</td>
<td>20.82 (20.12)</td>
<td>4.16 (3.77)</td>
<td>1.38 (1.46)</td>
<td>21.03 (21.41)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. C₆H₅N(CH₃)₃TlCl₃</td>
<td>20.43 (18.81)</td>
<td>2.41 (2.43)</td>
<td>2.37 (2.43)</td>
<td>35.70 (35.61)</td>
<td>18.68 (18.53)</td>
<td>22.61 (22.11)</td>
<td></td>
</tr>
<tr>
<td>10. C₆H₅N(CH₃)³NTlCl₃</td>
<td>29.3 (28.23)</td>
<td>5.39 (5.29)</td>
<td>2.00 (2.05)</td>
<td>30.20 (30.05)</td>
<td>15.73 (15.63)</td>
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</tr>
<tr>
<td>11. (CH₃)₄NTlCl₃Br</td>
<td>10.64 (10.34)</td>
<td>2.74 (2.58)</td>
<td>3.12 (3.01)</td>
<td>41.01 (40.05)</td>
<td>13.95 (13.89)</td>
<td>32.00 (31.71)</td>
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</tr>
<tr>
<td>12. (C₂H₅)₄NTlCl₃</td>
<td>18.33 (18.42)</td>
<td>4.02 (3.83)</td>
<td>2.54 (2.68)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. (C₂H₅)₄NTlCl₃</td>
<td>17.45 (16.95)</td>
<td>3.89 (3.52)</td>
<td>2.31 (2.47)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. (C₂H₅)₄NTlBr₃</td>
<td>14.07 (13.69)</td>
<td>3.06 (2.85)</td>
<td>2.19 (2.00)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15. (CH₃)₄NTlBr₃</td>
<td>7.50 (7.44)</td>
<td>1.73 (1.86)</td>
<td>2.01 (2.17)</td>
<td>32.00 (31.68)</td>
<td></td>
<td></td>
<td>36.95 (37.17)</td>
</tr>
<tr>
<td>16. (CH₃)₄NTlBr₃Cl</td>
<td>8.41 (8.67)</td>
<td>2.00 (2.16)</td>
<td>2.12 (2.53)</td>
<td>36.32 (36.92)</td>
<td>6.22 (6.40)</td>
<td>43.00 (43.31)</td>
<td></td>
</tr>
<tr>
<td>17. (C₂H₅)₄NTlBr₃Cl</td>
<td>15.43 (15.75)</td>
<td>3.15 (3.28)</td>
<td>2.13 (2.29)</td>
<td>33.75 (33.53)</td>
<td>5.59 (5.81)</td>
<td>39.01 (39.33)</td>
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</tr>
<tr>
<td>18. (CH₃)₃(CH₂)₃NTlBr₃</td>
<td>24.12 (24.36)</td>
<td>4.23 (4.43)</td>
<td>1.69 (1.72)</td>
<td>25.00 (25.14)</td>
<td></td>
<td></td>
<td>29.11 (29.46)</td>
</tr>
<tr>
<td>19. C₆H₅(CH₃)₃NTlBr₃</td>
<td>15.51 (15.27)</td>
<td>1.62 (1.98)</td>
<td>2.01 (1.98)</td>
<td>29.72 (28.91)</td>
<td></td>
<td></td>
<td>34.32 (33.91)</td>
</tr>
</tbody>
</table>
data on the elementary composition.

Method of Analysis

The compounds were analysed for:

(a) Carbon, Hydrogen and Nitrogen

The organic ligand in the various complexes were not determined directly, but the carbon, hydrogen and nitrogen were determined by microanalysis in the laboratory of Drs. Weiler and Strauss (Oxford).

(b) Thallium

The determination of thallium varied for the various complexes: (i) for the alkali metal halothallates (III) and the thallium (I) halothallates (III), the compounds were first of all decomposed by concentrated hydrochloric acid, and after removal of the interfering anions (e.g. I, Br, etc.) the metal was determined gravimetrically either as tetraphenyldarsonium chlorothallate (III) or after reduction to thallium (I) as thallium thionate Tl(C\textsubscript{12}H\textsubscript{10}ON\textsubscript{S})\textsubscript{3}. (ii) In the case of the 2-2' bipyridine, 1;10 phenanthroline and quaternary ammonium compounds the metal was generally determined as follows: An aliquot of the test material was dissolved in a small amount of acetone, about 0.1g. of potassium iodide and a few mls. of 5% Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} then added until the yellow colour of the solution disappeared; the solution plus the precipitate was then allowed to stand overnight; the precipitate was
filtered, washed with 80% acetone and finally dried at 120° – 130° and weighed as thallium (I) iodide.

(c) The Halogens

The halogens were determined either by precipitation with silver nitrate and weighing the silver halides formed, or volumetrically by Volhard's method (31).

(d) The Alkali Metals

All the alkali metals were determined gravimetrically by standard procedures, sodium as zinc uranyl acetate and the rest as the perchlorates.

(e) Nitrate and Perchlorate Anions

Both the nitrate and perchlorate anions were determined gravimetrically as their respective nitron salts (31).

(f) Water of crystallisation

The water of crystallisation in the various complexes was determined by the difference in weight on dehydration in vacuo over concentrated sulphuric acid to constant weight.
SECTION III
PHYSICAL MEASUREMENTS

In order to investigate the properties of the thallium (III) complexes in the solid state and in solution various physical techniques have been employed. An outline of these methods is given in this section.

In the solid state the hexahalothallates of the alkali metals $M_2\text{TLX}_6$, where $M = Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$ and $NH_4^+$ and $X = Cl^-$ or $M = Rb^+$ and $X = Br^-$ can be investigated satisfactorily under dry conditions. It is necessary to exclude water vapour as some of the salts are deliquescent. Magnetochemical studies were carried out on these salts in the solid state. There is evidence however that reaction with the solvent occurs on dissolving in solutions (13-17) and the ions then formed are different from those in the solid state. A potentiometric study of the nature of the solution obtained after removal of the alkali metal cations by an ion exchange column was also carried out.

The quaternary ammonium complexes of thallium (III) of type $R_4\text{NTLX}_4$ (where $R = \text{CH}_3$, $C_2\text{H}_5$, $C_4\text{H}_9$ and $C_6\text{H}_5(\text{CH}_3)_3$ and $X = Cl$, $Br$ or $I$) are only very slightly soluble in water and it was thus of interest to study them from the point of view of their analytical application. Magnetic
susceptibility studies of these complexes and of the quaternary ammonium halides were made from a systematic viewpoint in order to clarify the nature of the ions present in the solid state. Conductivity measurements in nitrobenzene and nitromethane were carried out to determine the number of ions present in solution. These measurements were made for the $R_4NX$, the $R_4NTlX_4$ and the mixed $R_4NTlX_2X'$ salts. The ultra-violet spectra of solutions of all these salts were studied in dilute methanol solution. Reflectance spectra measurements in the visible region were made on the solid state for some of the coloured compounds.

2-2' Bipyridyl and 1:10 phenanthroline thallium (III) complexes of the type $\text{TlOrg}_2X_2\text{TlX}_4$ and $\text{TlOrg}_2X_2\text{X}'$ (where Org = 2-2' Bipyridine or 1:10 Phenanthroline and $X = \text{Cl, Br or I and X'} = \text{I}$), were studied by similar methods to the above. Thus magnetic measurements in the solid state were carried out. Conductivity and ultra-violet measurements in organic solvents were studied. Their near infra-red spectra were also investigated. Solid state reflectance spectra for the coloured iodides were also measured. For the purpose of comparison the infra-red spectra of thallium (III) nitrate complexes with the above ligands were also studied and conductivity
measurements carried out in aqueous solution. A study of the system \(1,10\text{-phenanthroline:thallium (III) perchlorate}\) was furthermore made in order to determine the stability constants of the ions \(\text{Tl.phen}^{n+}\) (\(n = 1-3\)) in aqueous solutions. A spectrophotometric method was employed for this purpose. Continuous variation studies in the ultra-violet region were also carried out for the systems 2,2'-bipyridine- or 1,10-phenanthroline-thallium (III) perchlorate.

Because of the insolubility of the intermediate compounds \(\text{TlCl}_2, \text{Tl}_4\text{Cl}_6, \text{TlBr}_2\) and \(\text{Tl}_4\text{Br}_6\) in most solvents, the methods available for the determination of their structures were limited. Their magnetic susceptibilities were, however, measured in the solid state, and their ultraviolet spectra studied in methanol solution.

A. Magnetochemical Measurements

The magnetic susceptibility was measured by the Gouy method using a type of balance originally designed by Sugden (31) and modified by Trew and Watkins (33) and French and Trew (34). The measurements of magnetic susceptibility depends on the fact that all substances experience a force in a non-homogeneous magnetic field, which induces a tendency for diamagnetic substances to move away from the region of greatest field intensity and for para- and ferromagnetic materials to move into the
regions of maximum field intensity. The resultant force on the specimen is measured by noting the change in mass of the sample when such a differential magnetic field is applied to it.

A maximum field of 8072 gauss was obtained using an electromagnet with a pole gap of 1 cm. A current of 2.7 amps. at 220 volts was used. The latter was controlled by means of a rheostat and the reading on the sensitive ammeter checked through a microscope. Undue heating of the coils was avoided by having the magnet on for as brief a time as possible when taking the measurements. The magnetic thrust was measured by means of a sensitive short-beam balance placed above the electromagnet. The left-hand pan of the balance was replaced by a hook to which was attached a nylon thread carrying a polythene stopper and passing through a hole beneath the left-hand side of the balance case. The susceptibility tube was suspended by the stopper and hung vertically in the centre of the gap between the brass pole pieces. The specimen tube was always placed in the same position and in such a way that one end of it lay exactly at the centre of the field and the other end was in a region where the field was negligible. The position of the tube was carefully noted by means of mirrors and use of a vertical scale placed at the back of the pole gap. The magnet, the pole pieces and the
suspended tube were all enclosed to prevent draughts. It was observed that the temperature in the region of the suspended susceptibility tube remained reasonably constant at 20 ± 1°C at the time of the measurements.

Glass tubes of low susceptibility and uniform area of cross-section were employed. Their dimensions were:
- length 7.00cm, radius 0.45cm and length 6.80cm, radius 0.25cm

the lengths in each case being measured to the calibration mark. Each tube was separately calibrated to find its exact length and volume. The length was measured against a metre ruler and its volume determined by filling the tube in a thermostat at 20°C with water and finding its weight. Knowing the appropriate density its volume was calculated.

The tube was packed with the specimen under investigation by packing as uniformly and tightly as possible for every filling. The tube was filled by addition of the specimen in smaller amounts at a time (2mm length) and the method of tapping was adapted throughout, since it was found that a far more uniform packing of the substance was obtained in this way than by ramming the substance. The latter method as previously suggested by Trew (35) gives reproducible results for well dried crystallised materials but tends to cause caking into regions for microcrystalline powders or soft substances. When dealing with hygroscopic solids, the packing was carried out in a dry-box, the tube
carefully stoppered and the measurement taken immediately.

In order to average any experimental errors, measurements were made with three different fillings of the same substance and an average of three closely agreeing values of the susceptibility thus obtained was taken as the final value of the specific susceptibility of the substance.

Before any measurements were attempted, the magnetic balance was calibrated using "Analar" benzene, conductivity water and "Analar" potassium chloride as magnetic standards. Although several paramagnetic standards have been suggested in the literature (36), it was decided to use the above diamagnetic standards, because of the different order of magnitude of the paramagnetic pulls from the diamagnetic measurements being carried out in this work. Pure benzene of molecular weight grade was further purified by fractional distillation, a middle fraction of about one-third being used. The refractive index, measured by a Pulfrich refractometer using the sodium D line at 20\(^\circ\)C confirmed its purity when a value \(n_D^{20} = 1.50107\) was obtained (37).

Benzene has an accepted susceptibility of \(-0.7023 \times 10^{-6}\) c.g.s. units, water of \(-0.7200 \times 10^{-6}\) c.g.s. units and potassium chloride of \(-0.5224 \times 10^{-6}\) c.g.s. units. Being diamagnetic substances they should have zero temperature coefficients. The diamagnetism of water has been shown to have a small temperature coefficient (36), but it is, however, negligible
Determination of the variation of the field strength with the current flowing in the coils of the electromagnet

Using potassium chloride as standard a preliminary investigation of the way in which the field strength varied with the exciting current was carried out. Different currents were employed by adjusting the sensitive rheostat and measuring the corresponding force on the specimen. The plot of the thrust obtained on the specimen versus the current is shown in graph (1). As can be seen from the graph the thrust increases almost linearly as the power is increased. The maximum current which could be obtained by adjusting the rheostat was 2.9 amp. and so it was not possible to reach the saturation current. Thus it was decided to use a value of 2.7 amp. on the rising part of the curve, as being sufficiently low to prevent undue heating of the coils and giving a margin for slight fall in power supply below 2.9 amp. Considerable care was thus needed to check that the ammeter reading was exactly the same for each measurement. This was achieved by the use of a microscope to magnify the pointer reading on the ammeter dial.

Variation of magnetic force on the specimen with the height of the specimen

Potassium chloride was again used for this measurement. The thrust on the sample and tube for a current of 2.7 amp.
Graph (1)
THRUST ON POTASSIUM CHLORIDE

Graph (2)
THRUST ON POTASSIUM CHLORIDE

Length in cms.
was measured for different lengths of specimen. The plot of thrust versus the length of the specimen is shown in graph (2) and indicates that the minimum length of the specimen should be 5.00 cm. Lengths of 7.00 and 6.80 cm were adopted in the measurements as adequate to allow for the oscillation of the sample when readings on the balance were being taken.

**Determination of the balance constant**

The diagram (1) shows the experimental arrangement of the specimen relative to the field.

Consider the sample in the form of a uniform cylinder of constant area of cross-section:

\[
\begin{align*}
K_1 &= \text{Volume susceptibility of substance} \\
K_2 &= \text{Volume susceptibility of medium (air)} \\
H_1 &= \text{Maximum field at centre of magnet (base of cylinder)} \\
H_2 &= \text{Field at top of cylinder} \\
A &= \text{Area of cross-section} \\
l &= \text{Length of column of substance in cm.} \\
N &\text{S} = \text{North and South poles of electromagnet} \\
F &= \text{Force (a thrust upwards for diamagnetic substances, or downwards for paramagnetic substances)} \\
\mu_1 &= \text{Permeability of material} \\
\mu_2 &= \text{Permeability of medium (e.g. air)}
\end{align*}
\]
The force on a material of permeability $\mu$, in a medium of permeability $\mu_2$ is given by

$$F = \left(\frac{\mu - \mu_2}{\mu_2}\right) A \left(\frac{H_1^2 - H_2^2}{A^2}ight)$$

Substituting $\mu = 1 + 4\pi K$

$$F = \frac{1}{2}(K_1 - K_2) A (H_1^2 - H_2^2)$$

i.e.

$$K_1 = \frac{2F}{A(H_1^2 - H_2^2)} + K_2$$

(1)

Since $\chi = \text{mass susceptibility} = \frac{K}{d}$, where $d = \text{density of the substance}$ and therefore $d = \frac{w}{V}$, $w = \text{weight of column of material}$.

The above expression (1) can be written

$$\chi = \frac{2F}{w(H_1^2 - H_2^2)} + C$$

where C is the air displacement constant and equals $0.0294 \times 10^{-6} \times 1A$ or $0.0294 \times 10^{-6} \times V$ since $1A = V = \text{volume of the material}$.

Since diamagnetic susceptibilities are of the order of $10^{-6}$, multiplying by $10^{-6}$ gives

$$10^6 \chi = \frac{2F \cdot 10^6}{w(H_1^2 - H_2^2)} + 10^6C \text{ c.g.s. units}.$$  

When the length of the cylindrical specimen (1) is sufficiently long then $H_2$ becomes zero and this was arranged to be the condition in the experiment.

Thus

$$10^6 \chi = \frac{2F \cdot 10^6}{w H_1^2} + 10^6C \text{ c.g.s. units}$$

if experiments are carried out using a constant field $H$ and
length of specimen 1
then

$$10^6 \chi = \frac{\alpha F}{w} + \frac{0.0294V}{w} \text{ c.g.s. units} \quad (2)$$

where $\alpha$ is the balance constant for the particular field strength $H$ and length $l$

$$\alpha = \frac{21 \cdot 10^6}{H^2} \quad (3)$$

or if for convenience, the force $F$ is measured in milligrams, $l$ in cms. and $w$ in grams.

$$\alpha = \frac{21 \cdot 10^6 \cdot 98 \cdot 10^{-3}}{H^2} \text{ c.g.s. units} \quad (4)$$

The field strength $H$ is then given by

$$H_1 = \sqrt{\frac{1.962 \cdot L \cdot 10^6}{\alpha}}$$

$$H_1 = 10^3 \sqrt{1.962 \cdot \frac{L}{\alpha}} \quad (5)$$

Thus from equations (2) and (5) both $\alpha$ and $H$ may be calculated. Using 0.20435 for $\alpha$ in equation (5) and $l = 6.80$ cms. gives $H = 8079$ gauss.

Table (4) gives several values obtained using different tubes and water and benzene as standards. A mean value for $\alpha$ per unit length of 0.02947 was thus obtained.
B. Conductivity Measurements

The resistance of any object of constant cross-section is given by

\[ R = \rho \frac{1}{A} \]

where \( R \) is the resistance, \( A \) is the cross-sectional area, \( l \) is the length, and \( \rho \) is the specific resistance.

The conductance \( C'' \) is defined as the reciprocal of the resistance

\[ C'' = K \frac{A}{l} \]

where \( K \) is the specific conductance = \( \frac{1}{\rho} \). The molar conductance is defined as the conductance of that volume \( (V_m \text{ litres}) \) of the solution which contains one molecule of the solute, where this volume is in the form of a cylinder 1 cm. in length (and therefore 1000V_m cm² in cross-section).

If \( C \) is the molar concentration, then the molar conductance is given by
The number of ions formed when a complex compound dissociates is often determined by measuring the electrical conductivity in non-aqueous solvents such as nitrobenzene, nitromethane and acetone. Molar conductances for a number of compounds in these solvents have been quoted in the literature (38)(39)(112). For concentrations of the order $2 \times 10^{-4} - 1 \times 10^{-4}$ M in the above solvents (columns 2, 3 and 4) and in water (column 5), the accepted values of the molar conductances which are generally taken to determine the number of ions present are given in table (5).

<table>
<thead>
<tr>
<th>Electrolyte type</th>
<th>Molar conductance mho/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrobenzene</td>
</tr>
<tr>
<td>Uni-univalent</td>
<td>20-30</td>
</tr>
<tr>
<td>Uni-bivalent</td>
<td>40-60</td>
</tr>
<tr>
<td>Uni-trivalent</td>
<td>75-95</td>
</tr>
</tbody>
</table>

The nitrobenzene used was the Analar reagent dried over calcium chloride. The calcium chloride was removed by filtration and the nitrobenzene distilled under reduced pressure three times; this had a specific conductance of less than $0.4 \times 10^{-6}$ mhos cm$^{-1}$. The nitromethane was dried over phosphorus pentoxide and distilled; the purified solvent had a specific conductance of less than $1 \times 10^{-6}$ mhos cm$^{-1}$. The acetone was the Analar reagent; it was dried over anhydrous sodium sulphate and distilled. The
redistilled acetone had a specific conductance of $10^{-6}$ mhos cm$^{-1}$. For aqueous solutions conductivity water was used; this had an specific conductance of $0.1 \times 10^{-6}$ mho cm$^{-1}$. The Philips conductivity bridge was used. The cell was calibrated by measuring the resistances of $1/50$ and $1/100$ normal solution of potassium chloride, whose specific resistances are exactly known at various temperatures. The calibration constant was found to be 1.26. All measurements were carried out at $25^\circ$C in a thermostat. Solutions of the compounds were prepared either by weighing or by dilution of more concentrated solutions.

C. **Ultra-violet and visible absorption spectra**

Optical densities of the various solutions were measured at $25^\circ$C in matched silica cells, in Unicam S.P. 500 and S.P. 700 Spectrophotometers both fitted with thermostats. The solvents used varied and will be described for each solution. The blank was always the appropriate solvent, containing any salt which had been added or pure as the case may be. All the solvents used were spectroscopically pure. Solid reflectance spectra were measured using the Unicam S.P. 500 spectrophotometer, which was equipped with a reflectance unit.

D. **Infra-red spectra**

A Grubb-Parsons double beam grating instrument was used for the near infra-red measurements. Measurements
could be made in the range 2 - 25 μ (5000 - 400 cm⁻¹).
The mulling agents used were Nujol (5 - 23 μ) and hexachloro-
butadiene (2 - 8 μ). The latter was used for the region
obscured by Nujol absorption bands. The samples were
examined between rock salt (2 - 15 μ) and potassium bromide
(5 - 23 μ) plates. In cases where it appeared likely that
there might be some replacement of a nitrate group by
chloride ion from the rock salt plates, the plates used
were coated with a fine film of polystyrene.
 SECTION IV

Alkali Metal and Ammonium Hexahalothallates

In the presence of excess alkali halides, the halides of trivalent thallium form well defined crystalline compounds which in general show coordination numbers of 6 or 4. The strength of the complex formation increases in the sequence Cl⁻ < Br⁻ < I⁻ (16). As one passed from chloride to bromide to iodide however the maximum number of halide ions coordinated tends to remain at four even in the solid state. Complex bromides and iodides are thus generally of the type TlBr₄⁻ and TlI₄⁻. There are thus well defined hexachlorothallates but only a very few hexabromo-thallates and no hexaiodothallates have been reported.

Hoard and Goldstein (4) studied the crystal structure of potassium hexachlorothallate (III) dihydrate and rubidium hexabromothallate monohydrate and found that they consisted of TlCl₆²⁻ and TlBr₆²⁻ octahedra. They found that the thallium-chlorine and thallium-bromine distances were equal to 2.55Å and 2.70Å respectively. Apart from this work, no other study appeared to have been carried out in the solid state. It was thus considered of interest to prepare a series of complexes of the type M₃TlCl₆ (where M = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ and NH₄⁺ and X = Cl or M = Rb⁺ and X = Br⁻) and to carry out a systematic study of their magnetic susceptibilities, their preparations have already been described in the experimental section.
They are all colourless crystalline solids except for the bromothallate which is yellow in colour. All are extremely deliquescent when hydrated, the lithium and sodium compounds in particular.

**Magnetic Susceptibility Measurements on the Solid Compounds**

The magnetic susceptibilities were measured by a modified Gouy method as described in the "Physical Measurements Section". The hygroscopic nature of these compounds made it necessary to take all precautions to exclude moisture from the specimens; all the packings were thus performed in a dry box.

The compounds of the type $\text{M}_2\text{TlX}_6$ which were investigated, together with the results of their specific (column 2) and molar susceptibilities (column 3) are listed in table (b). The respective anionic susceptibilities for $\text{TlX}_6^{3-}$ are given in column 5 of the same table. These latter values were obtained by subtracting three times the cationic susceptibility values as obtained by Brindley and Hoare (27) [i.e. for $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$ and $\text{Cs}^+$] and Trew and Husain (27) [for $\text{NH}_4^+$] from alkali and ammonium halides in sixfold coordination. These values are listed in column 4 of table (b). The corresponding effective cationic charges are listed in the last column of the same table. Only one bromo compound of the type $\text{M}_2\text{TlBr}_6$,
namely the Rubidium compound, can be obtained and is shown at the bottom of table (6).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-10^6 \chi_a$</th>
<th>$-10^6 \chi_M$</th>
<th>$-3 \times 10^6 \chi_M^+$ (alkali metal)</th>
<th>$-10^6 \chi_{\frac{1}{2}}$</th>
<th>z Cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{NH}_4)_3\text{TLCl}_6$</td>
<td>0.4396 0.4362 0.4390</td>
<td>206.54</td>
<td>37.1</td>
<td>169.5</td>
<td>10</td>
</tr>
<tr>
<td>Li$_3$TlCl$_6$</td>
<td>0.3873 0.3886 0.3893</td>
<td>170.10</td>
<td>2.1</td>
<td>168.0</td>
<td>2</td>
</tr>
<tr>
<td>Na$_3$TlCl$_6$</td>
<td>0.3879 0.3898 0.3914</td>
<td>189.46</td>
<td>18.3</td>
<td>171.3</td>
<td>10</td>
</tr>
<tr>
<td>K$_3$TlCl$_6$</td>
<td>0.3967 0.3988 0.4010</td>
<td>213.16</td>
<td>43.8</td>
<td>169.4</td>
<td>18</td>
</tr>
<tr>
<td>Rb$_3$TlCl$_6$</td>
<td>0.3503 0.3534 0.3514</td>
<td>236.90</td>
<td>66.0</td>
<td>170.9</td>
<td>36</td>
</tr>
<tr>
<td>Cs$_3$TlCl$_6$</td>
<td>0.3369 0.3387 0.3384</td>
<td>275.78</td>
<td>105.3</td>
<td>170.5</td>
<td>54</td>
</tr>
<tr>
<td>Rb$_3$TlBr$_6$</td>
<td>0.3111 0.3122 0.3127</td>
<td>293.3</td>
<td>66.0</td>
<td>227.2</td>
<td>36</td>
</tr>
</tbody>
</table>

From the above results it is observed that the susceptibility value for the anion TlCl$_6^{3-}$ as obtained from the various compounds is quite constant. This indicates that the anion TlCl$_6^{3-}$ behaves as an entity, implying therefore that the susceptibility of these complex compounds can be regarded as the sum of the positive and negative ions. The mean value for the molar susceptibility of the TlCl$_6^{3-}$...
anion is thus found to be $169.9 \pm 0.95$ c.g.s. units.

A good representation of these results can be made graphically. When the molar susceptibility of the alkali and ammonium chlorothallates is plotted against the effective atomic number of the cation (graph 5) a zigzag relationship similar and closely parallel to that obtained by Trew and Hussein (27) for the alkali and ammonium chlorides is obtained. The molar susceptibilities for ammonium chloride and for caesium chloride corrected from 8 to 6 fold coordination are shown by the dotted lines. For the alkali chloride graph it is necessary to multiply the molar susceptibilities by three to obtain comparative results.

The very close parallel character of the two curves shows clearly the polar character of the $3M^+ \text{TlCl}_6^-$ salts since these are here compared with one of the well defined series of polar salts i.e. $M^+ \text{Cl}^-$. It further provides satisfactory support for the experimental accuracy of the present molar susceptibility values, the figures for the alkali halides being recognised as some of the best established values.

A further point worth noting here is the magnetic susceptibility increment obtained on passing from the hexachlorothallate to the hexabromothallate anions. This was found to be 57.3 units for the $\text{MX}_6^{2-}$ ion, a value which
MOLAR MAGNETIC SUSCEPTIBILITIES OF

(a) ALKALI AND AMMONIUM HEXACHLOROORTHALLATES
(b) ALKALI AND AMMONIUM HALIDES

GRAPH (3)
is fairly close to that obtained for the simple halides by Brindley and Hoare. If the value of 57.3 units is considered as equally shared between all the bonds the experimental increment is 9.6 units per \( \text{Tl} - \text{X} \) bond. This must be compared with the value for the simple halides (27) of 10.5 units per bond for chloride and bromide salts with the same coordination number. The agreement is fairly close although the small lowering must be ascribed to a rather high value for the susceptibility of the \( \text{TlCl}_6^{3-} \) ion. This point was revealed when experimental and theoretical susceptibilities for these ions were compared and is further discussed on page (133).
Potentiometric Study of Solutions from Salts of the Hexachlorothallate ion after passing through an ion-exchange column

At an early stage of the present work the nature of the ions present in solutions of the alkali hexachlorothallates was not clearly established. Various workers (11-12) had studied solutions of thallium (III) chloride and bromide and shown that there was a strong tendency towards complex formation in the presence of excess halide ions. Spencer and Abegg showed by redox-potential measurements that halogeno complexes existed in Tl$^{3+}$/Tl$^+$ halide ion solutions. Subsequent workers (13-18) carried out studies by potentiometric and spectrophotometric methods on solutions containing thallium (III) and halide ions and evaluated stability constants for the various species which they considered to be present.

In view of the crystalline and stable character of the salts M$_2$TlCl$_6$, it was thought useful to consider the effect of passing solutions of these alkali metal chlorothallates through a cation exchange column, working on the basis that the three alkali metal ions (3M$^+$) could be removed in this way, leaving the chlorothallate ion as the hexahalothallic acid (H$_2$TlCl$_6$). On extraction of the acid eluate from the column a potentiometric study should then give evidence as to the species present. It was hoped therefore to detect the presence of the TlCl$_6^{3-}$ ion.
The magnetic results already described, but carried out later, support fully the polar character of the $M_2\text{TlCl}_6$ compounds and the existence of $\text{TlCl}_3^-$ and $\text{TlBr}_5^-$ anions in the solid alkali metal chlorothallates and bromothallates. In solution however the ready production on dilution of the brown $\text{Tl(OH)}_3$ gives evidence for the occurrence of marked hydrolysis with the formation of other ionic species. In considering which are present the situation appears to be confused. Results for the thallium (III) chloride equilibria obtained by different workers fall into two groups. According to one group (14) (17) a solution in which the free chloride concentration is 0.1M contains principally $\text{TlCl}_3^-$ with some $\text{TlCl}_2^-$ while the other group (13)(15)(16) (18) find that only $\text{TlCl}_3$ and $\text{TlCl}_4^-$ are present in appreciable concentration.

The results of the present potentiometric studies have not proved as conclusive as was hoped but a summary of the work is included as some interesting points emerge.

Solutions of the alkali metal chlorothallates of the order of $10^{-2}$M were prepared and then passed through a cation resin exchanger Amberlite IR 120(H). The eluate from the column was colourless and apparently clear at concentrations up to 0.001M. Attempts to prepare more dilute solutions led to precipitation of the thallium (III) hydroxide within the column. The 0.01M solutions after
extraction from the column remained clear even after several months. The acid eluate was obtained by dropwise (2 drops per second) elution of the alkali metal halothallate solutions, the first half-bed volume being discarded. The acid solution obtained from each chlorothallate solution was then titrated potentiometrically, using a Pye pH meter with a glass electrode, with standard sodium hydroxide.

Assuming that in solution the TlCl$_2^-$ anion remains as such, the reaction in the exchange column will be expected to be of the type

$$\text{H}_2\text{TlCl}_6 + 3\text{H}^+ + \text{X}^+ \rightarrow \text{HTlCl}_6^- + 3\text{H}^+ + \text{X}_2\text{H}_2\text{O}$$

(1)

the metal cation thus being left in the column. Titration of the resulting solution then leads to

$$\text{H}_2\text{TlCl}_6 + 3\text{NaOH} \rightarrow \text{Na}_2\text{TlCl}_6 + 3\text{H}_2\text{O}$$

(2)

this being the neutralisation reaction. This can furthermore be represented as

$$\text{H}_2\text{TlCl}_6 \overset{\text{K}_1}{\rightarrow} \text{HTlCl}_6^- \overset{\text{K}_2}{\rightarrow} \text{HCl}_6^- \overset{\text{K}_3}{\rightarrow} \text{TlCl}_6^-$$

(3)

where $\text{K}_1$, $\text{K}_2$ and $\text{K}_3$ are the respective stepwise ionisation constants.

It is however possible that decomposition of the hexachlorothallic acid could take place in the solution passing down the column according to the following reaction:

$$\text{H}_2\text{TlCl}_6 \rightarrow 3\text{HCl} + \text{TlCl}_3$$

(4)

Titration of the eluate of this solution with alkali thus leads in this case to neutralisation of the hydrochloric
acid formed and so would require the same number of equivalents for the overall neutralisation as in the first case.

If hydrolytic equilibrium has also occurred to completion in the first case hydrolysis being indicated by the brown colour appearing at neutralisation i.e. about the first strong inflection point, then the following reactions would occur.

\[
\begin{align*}
TlCl_6^{3-} + H_2O &\rightarrow TlCl_5(OH)^{2-} + HCl \\
TlCl_5(OH)^{2-} + H_2O &\rightarrow TlCl_4(OH)^{-} + HCl \\
TlCl_4(OH)^{-} + H_2O &\rightarrow TlCl_3 + HCl
\end{align*}
\]

The overall reaction thus being

\[
3Na^+ + TlCl_6^{3-} + 3NaOH \rightarrow Tl(OH)_3 + 6NaCl \quad (5)
\]

and thus three more equivalents of sodium hydroxide would be required for the reaction and would give in all six equivalents of alkali. In the second case, although the same six equivalents would be required for the overall reaction, the hydrolytic equilibria probably takes place as follows:

\[
\begin{align*}
TlCl_3 + H_2O &\rightarrow TlCl_2(OH)^{+} + HCl \\
TlCl_2(OH)^{+} + H_2O &\rightarrow TlCl(OH)_2^{+} + HCl \\
TlCl(OH)_2^{+} + H_2O &\rightarrow Tl(OH)_3^{+} + HCl
\end{align*}
\]

As will be seen later the results give evidence for the presence of these positive ions (TlCl_2(OH)^{+}, TlCl(OH)_2^{+}). There are further possible interactions in the solution, one of which may be that TlCl_3 + Cl^- \rightarrow TlCl_4^-, the tetrahedral
chlorothallate ion.

The potentiometric titration curves are shown in graph (4); the results are listed in table (7).

**TABLE 7**

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Solution from</th>
<th>Molarity of NaCH = 0.025 except in (1) when the molarity was 0.05M.</th>
<th>Molarity of M₂TlCl₆x10²</th>
<th>Neutralisation Reaction</th>
<th>Hydrolytic Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Obs. E.P.</td>
<td>Calc. E.P.</td>
<td>pH</td>
</tr>
<tr>
<td>1</td>
<td>(NH₄)₃TlCl₆</td>
<td>0.949</td>
<td>6.35</td>
<td>5.69*</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.70*</td>
<td>11.38*</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>Li₂TlCl₆</td>
<td>1.021</td>
<td>10.00</td>
<td>12.25</td>
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<td></td>
<td>10.20</td>
<td>12.00</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>Na₂TlCl₆</td>
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<td>12.30</td>
<td>12.26</td>
<td>4.0</td>
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<tr>
<td>4</td>
<td>K₂TlCl₆</td>
<td>0.974</td>
<td>11.69</td>
<td>11.68</td>
<td>3.9</td>
</tr>
<tr>
<td>5</td>
<td>Rb₂TlCl₆</td>
<td>0.933</td>
<td>13.00</td>
<td>11.20</td>
<td>4.0</td>
</tr>
<tr>
<td>6</td>
<td>Cs₂TlCl₆</td>
<td>0.986</td>
<td>15.00</td>
<td>11.80</td>
<td>4.5</td>
</tr>
</tbody>
</table>

*Calculated from experimental for 0.05M

In an attempt to interpret the figures in table (7) the following points may be noted. The elution process appears satisfactory in the case of the salts of sodium and potassium where a good agreement was found between the experimental and the calculated neutralisation points. In the case of the ammonium, rubidium and caesium salts however, this end point is definitely delayed indicating a higher acid concentration in the eluate than the true neutralisation amount. This could readily be explained if some of the
GRAPH (4)
POTENTIOMETRIC TITRATION CURVES

Li₃TeCl₆
(NH₄)₂TeCl₆

Rb₃TeCl₆
Cs₃TeCl₆

K₃TeCl₆
Na₃TeCl₆

mLs of 0.025 M NaOH
chlorothallic acid has decomposed as

$$\text{H}_2\text{TlCl}_6 \rightarrow \text{TlCl}_3 + 3 \text{HCl}$$

Then with somewhat prolonged contact of the solution with the exchanger in the column a certain amount of decomposition of the \(\text{TlCl}_3\) ions could furthermore take place according to a reaction of the type

$$\text{TlCl}_3 + \text{H}_2\text{O} \rightarrow \text{TlCl}_2\text{OH}^+ + \text{HCl}$$

Some studies of Horne (40) on the adsorption of the cation \(\text{Tl}^{3+}\) with the cation exchange resin Amberlite IR 120(H) appear to have bearing on this point. Horne noted that at a critical molar concentration of hydrochloric acid, added to perchlorate solutions of \(\text{Tl}^{3+}\), there was a decrease in the adsorption of the cation when in contact with the resin for over 72 hours. This occurred at acid strengths of \(10^{-2}\text{M}\) at 8°C and \(10^{-3}\text{M}\) at 35°C and was considered to be due to formation of thallium (III) anionic complexes of the type \(\text{TlCl}_n^{3-n}\). In the present studies with \(\text{M}_3\text{TlCl}_6\) solutions the cationic resin will adsorb only the alkali cations as long as the thallium is in an anionic complex, i.e. remains as \(\text{TlCl}_n^{3-n}\). If on the other hand there is a dissociation to give \(3\text{MCl} + \text{TlCl}_3\), the molar concentration of the equivalent \(\text{HCl}\) of the exchange would be of the order of \(3 \times 10^{-2}\text{M}\). This is in the critical range indicated by Horne's experiments and even though the elution process only took about one hour the possibility of
some adsorption of cationic Tl(III) cannot be ruled out, especially as times of elution were not standardised.

On this basis the above results for the ammonium and rubidium salts indicate about a 10% decomposition of the TlCl$_6^{3-}$ ion in the column. For the caesium compound the decomposition reaction appears considerably greater. As stated above no attempt had been made to standardise the time of contact with the column. The lithium result on the other hand is difficult to explain. The anomaly found in this case may perhaps arise from the extreme hygroscopic nature of the salt which renders the exact weight uncertain.

The suggestion given above that the hydrolytic equilibrium produces positive cations in the solution passing down the column is supported by the following two experiments. When the resin was tested for thallium (III) using a sodium hydroxide solution a light brown colour appeared indicating the formation of thallium (III) hydroxide, showing some residue of thallium (III) ions on the column. The acid eluate obtained originally when the halothallate salts were passed through the column was furthermore analysed in some experiments for its thallium content. Results of these analyses were found to be 6.19% lower than the expected figure. These two facts thus give evidence for the occurrence of some hydrolysis, producing positive ions in the halothallate solutions.
The above explanation for the results in table (7) is further supported by the second end point i.e. that of the total hydrolytic and neutralisation reaction. This end point as can be seen from table (7) occurs at the expected six equivalents of alkali for some of the salts studied, namely the potassium, rubidium and caesium salts. In general the method did not prove to be very exact under the conditions which were obtainable. The fact however that there is a sharp inflexion point which occurs at six equivalents of alkali does however support the fact that the method distinguishes the neutralisation and total hydrolysis of the chlorothallate ion according to the reaction

\[
\text{H}_2\text{TlCl}_6 \xrightarrow{3\text{NaOH}} \text{Na}_2\text{TlCl}_6 + 3\text{H}_2\text{O} \xrightarrow{3\text{NaOH}} \text{Tl(OH)}_3 + 3\text{NaCl}
\]

From the graph, (4) and results in table (7) it would appear that there is no evidence for the intermediate stepwise reactions

\[
\text{H}_2\text{TlCl}_6 \rightarrow \text{H}_2\text{TlCl}^- \rightarrow \text{HTlCl}_3^- \rightarrow \text{TlCl}_4^{3-}
\]

as no inflexion points were found. Kolthoff and Furman have however shown that in order to obtain discrete inflexions all dissociation constants must be less than $10^{-4}$ and each pair of successive constants must differ by $10^4$ or more (41). In a study of the ferri- and ferrocyanic acid systems which are analogous to the present one, Jordan and Ewing showed that in the case of the ferrocyanic acid although no discrete inflexion points were observed,
stability constants of the order of $10^{-1}$ to $10^{-5}$ for $K_1$ and $K_4$ respectively, could be calculated from the difference between the titration curve and the dilution curve of the solution being titrated. Under the present conditions although the dilution curve was not studied the absence of inflection points indicates that the stability constants must differ by a factor of less than $10^4$, since it is known that the overall stability constants are of high value. Ahrland and Johansson have shown very recently that the values of these constants for the Tl$^{3+}$ Cl$^-$ system are:

$$
\beta_1 = 3.0 \times 10^7 \quad \text{(formation of TlCl$_2^{2+}$)}
$$
$$
\beta_2 = 1.8 \times 10^{13} \quad \text{(formation of TlCl$_2^{+}$)}
$$
$$
\beta_3 = 4.5 \times 10^{16} \quad \text{(formation of TlCl$_3^-$)}
$$
$$
\beta_4 = 2.8 \times 10^{19} \quad \text{(formation of TlCl$_4^{-}$)}
$$

From the general relationships between the overall and stepwise constants ($K$) (e.g., $\beta_1 = K_1$, $K_2$, etc.) the values of these stepwise constants are:

$$
K_1 = 3.02 \times 10^7 , \quad K_2 = 6.03 \times 10^5
$$
$$
K_3 = 2.46 \times 10^3 \quad \text{&} \quad K_4 = 6.31 \times 10^2
$$

It is apparent that these only differ by about $10^2$ which is considerably less than the value required to give inflection points.

The problem as to the exact species present in solutions of the hexachlorothallate salts or in the acid
solutions derived from them is evidently more complex than at one time thought. Reference has been made to the fact that some workers consider that there is an appreciable concentration of $\text{TlX}_6^{3-}$ ions in such solutions especially in the presence of excess halide ions. Peschanski and Valladais Dubois have evaluated equilibrium constants from spectrophotometric studies which showed the existence of the $\text{TlCl}_6^{3-}$ and $\text{TlCl}_5^{2-}$. More recently Nord and Ulstrup \textsuperscript{(15)}, from solvent extraction studied and Ahrland and coworkers \textsuperscript{(16)}, from e.m.f. measurements, have shown that the $\text{TlCl}_4^{-}$ anion is definitely the highest chloro-complex. The present study does not clarify this point any further which is certainly one of some complexity.
SECTION V.

QUATERNARY AMMONIUM COMPOUNDS

Cations containing large organic groups are convenient as precipitants of metallic elements from solution because they form stable compounds which are generally only very slightly soluble in water. In recent years several workers have prepared tetrahalogeno metal complexes of a number of the metallic elements. Thus the properties of the complexes of the type \( R_4\text{Me}X_4 \) are well established in the case of zinc and iron. No attempt to obtain similar thallium (III) compounds had so far been made. As there are few good gravimetric methods available for the determination of thallium in the tervalent state it was considered possible that such complexes of thallium (III) might be suitable for analytical methods of determination of thallium in this valency state. Thus their properties, composition and suitability for gravimetric purposes were of interest.

In the presence of halide ions, \( \text{Tl}^{3+} \) ions can be made to interact with quaternary ammonium halides to give sparingly soluble compounds of the type \( R_4\text{NTI}X_4 \) and \( R_4\text{NTI}X_3X' \) where \( R \) can be \( \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5(\text{CH}_3)_3 \) or \( \text{C}_4\text{H}_9 \) as well as possibly other more complex radicals and \( X \) and \( X' \) = Cl, Br or I.
In the present study complexes of thallium (III) with $R = \text{CH}_3$, $\text{C}_2\text{H}_5$, $\text{C}_4\text{H}_9$ and $G = \text{H}_5(\text{CH}_2)_3$ were prepared and their properties studied. The complexes were readily prepared by mixing alcoholic or aqueous alcoholic solutions of thallium (III) halides and the corresponding ammonium halides in the 1:1 ratio. When warm solutions were mixed, the tetrahalogeno complex salts precipitated on cooling to room temperature. The individual preparations have been noted in detail in the "Experimental Section". Some mixed tetrahalogeno thallates were also prepared by mixing the appropriate solutions of mixed halides, e.g. $(\text{CH}_3)_4\text{N Br}$ and $\text{TlCl}_4 \cdot 4\text{H}_2\text{O}$, in the ratio of 1:1.

The properties of this series of complexes were investigated in solution and the solid state both from their possible interest from the analytical point of view and in an attempt to clarify their structure. They are all partially soluble in non-aqueous polar solvents, e.g. nitromethane or nitrobenzene. They are very soluble in acetone and ethanol and methanol dissolve them to a certain extent. The solubilities in organic solvents depend strongly on the cation. The least soluble salts are those containing the tetramethylammonium cation whilst the most soluble are those with the tetrabutylammonium cation. These salts are hydrolysed in aqueous solutions as are
most complex salts of the thallium ion, on dilution giving a brown solution and then a brown precipitate of the hydroxide. Their solubility in water in general decreases in passing from the chloro through the bromo to the iodo complexes. The chlorides and bromides are colourless, the iodides are brick red and the mixed chloride-iodides and chloride-bromides vary in colour from yellow through green to brown. Their colour and their melting points are given in table (8).

Magnetic susceptibility measurements in the solid state were carried out on them. For the iodide and some of the mixed compounds their reflectance spectra were measured. Conductivity measurements in nitrobenzene and nitromethane were carried out to determine the number of ions given by these complexes in solution. Their ultra-violet spectra in methanol was also measured.

Analytical Study of the Complexes

In order to establish the nature and composition of the above-mentioned compounds they were isolated in the pure state and analysis of the percentage compositions of the carbon, hydrogen, nitrogen, thallium and halogen contents were made as described in the "Experimental Section". The possibility of the use of the complexes
<table>
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<tr>
<th>Compound</th>
<th>Colour</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ((\text{CH}_3))_4NTlCl_4</td>
<td>Colourless</td>
<td>305-306(^\circ) with decomposition</td>
</tr>
<tr>
<td>2. ((\text{CH}_3))_4NTlBr_4</td>
<td>Colourless</td>
<td>301 - 302(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>3. ((\text{CH}_3))_4NTlI_4</td>
<td>Brick-red</td>
<td>306-307(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>4. ((\text{CH}_3))_4NTlCl_3Br</td>
<td>Colourless</td>
<td>304-305(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>5. ((\text{CH}_3))_4NTlBr_3Cl</td>
<td>Colourless</td>
<td>305-306(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>6. ((\text{CH}_3))_4NTlBr_3I</td>
<td>Yellow</td>
<td>307-308(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>7. ((\text{C}_2\text{H}_5))_4NTlCl_4</td>
<td>Colourless</td>
<td>240(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>8. ((\text{C}_2\text{H}_5))_4NTlBr_4</td>
<td>Colourless</td>
<td>260-261(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>9. ((\text{C}_2\text{H}_5))_4NTlI_4</td>
<td>Brick-red</td>
<td>220-221(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>10. ((\text{C}_2\text{H}_5))_4NTlCl_3Br</td>
<td>Colourless</td>
<td>234-235(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>11. ((\text{C}_2\text{H}_5))_4NTlBr_3Cl</td>
<td>Colourless</td>
<td>230-231(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>12. ((\text{C}_2\text{H}_5))_4NTlCl_3I</td>
<td>Yellow</td>
<td>240-241(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>13. ((\text{C}_2\text{H}_5))_4NTlBr_3I</td>
<td>Yellow</td>
<td>240-241(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>14. ((\text{C}_4\text{H}_9))_4NTlI_4</td>
<td>Yellowish-red</td>
<td>132(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>15. ((\text{C}_4\text{H}_9))_4NTlCl_3I</td>
<td>Yellow</td>
<td>130-131(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>16. ((\text{C}_4\text{H}_9))_4NTlBr_3I</td>
<td>Yellow</td>
<td>134-135(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>17. ((\text{C}_6\text{H}_5))(\text{CH}_3))_3NTlCl_3I</td>
<td>Yellowish-green</td>
<td>165-166(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>18. ((\text{C}_6\text{H}_5)(\text{CH}_3))_3NTlBr_3I</td>
<td>Yellowish-brown</td>
<td>167-168(^\circ) &quot; &quot;</td>
</tr>
<tr>
<td>19. ((\text{C}_6\text{H}_5)(\text{CH}_3))_3NTlI_4</td>
<td>Yellowish-red</td>
<td>170(^\circ) &quot; &quot;</td>
</tr>
</tbody>
</table>
as analytical reagents for thallium (III) was investigated as follows:

(a) Precipitation of thallium (III) in the presence of chloride ions with tetraethylammonium chloride

An attempted gravimetric determination of thallium (III) by precipitation and weighing as tetraethylammonium tetrachlorothallate was carried out as follows. Solutions containing either thallium (I) as the nitrate or thallium (III) as the sulphate were prepared. In the case of the thallium (I) solutions, oxidation to the tervalent state was carried out by means of hydrogen peroxide in the presence of sodium hydroxide. The solution containing thallium (III) ions were then acidified with 2N hydrochloric acid and to the resulting solution approximately 10mls of 0.1N tetraethylammonium chloride were added slowly whilst stirring. The white precipitate thus obtained was left to stand, heated to boiling so as to coagulate the precipitate and left to cool. The precipitate was then carefully filtered and washed with either a few mls. of solution of the precipitant or a small volume of dilute hydrochloric acid. The precipitate was finally dried at 110°C. This precipitate was not hygroscopic and reached constant weight after an hour. The results of these analyses are shown in table (9).
The above table shows that the method gives results which are systematically 4 - 5% low when the precipitate was washed with water. When a solution of precipitant or 1N hydrochloric acid was employed as washing liquid the results were slightly better, being some 3% low. Organic solvents could not be employed for washing, because of the appreciable solubility of the compound in such solvents.

The starting solutions in the above analyses contained either thallium (I) as the nitrate or thallium (III) as the sulphate or nitrate. By using the method described above it is observed from table (9) that results of the same order were obtained in both cases. The possibility of incomplete oxidation in the case of the thallium (I) solutions can thus be excluded. Hydrolysis of the
compounds which could occur when water and the precipitant are used as washing agents was also prevented in the last group of analyses by the use of 1N hydrochloric acid. The filtrate was furthermore tested for thallium (III) by means of a 1N ammonia solution, whereby a flocculent brown precipitate of the hydroxide was obtained. Thus one can conclude that the only obvious cause of the low results obtained is the still appreciable solubility of the compound in water or even dilute acid under the experimental conditions used.

(b) Precipitation of thallium (III) in the presence of bromide ions with tetraethylammonium bromide

A similar method was used to precipitate thallium (III) as tetraethyl ammonium bromide. Again the starting solutions contained either thallium (I) or thallium (III). In the case of the thallium (I) solutions, oxidation to the trivalent state was carried out by adding 5 mls. of nitric acid, a few mls. of 0.01N potassium bromate and 10 mls. of 2M potassium bromide; excess bromine was removed by careful heating. The thallium (III) solutions were then treated with approximately 10mls. of a 0.1N tetraethylammonium bromide solution. The white precipitate which was obtained, coagulated on agitation. It was allowed to stand for an hour and then filtered off. The precipitate was washed with a few mls. of solution of precipitant and dried at 110°. A constant weight was obtained after
heating for an hour. The results are shown in table (10).

<table>
<thead>
<tr>
<th>Weight of precipitate (in mg.) ((C_2H_5)_4NTlBr_4)</th>
<th>Thallium taken in mg.</th>
<th>Thallium found in mg.</th>
<th>Error in %</th>
<th>Washing Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>320.2</td>
<td>103.3</td>
<td>100.0</td>
<td>-3.3</td>
<td>3.2 Water</td>
</tr>
<tr>
<td>315.3</td>
<td>94.2</td>
<td>90.4</td>
<td>-3.8</td>
<td>4.0 &quot;</td>
</tr>
<tr>
<td>289.2</td>
<td>90.8</td>
<td>87.3</td>
<td>-3.3</td>
<td>3.6 &quot;</td>
</tr>
<tr>
<td>274.2</td>
<td>89.5</td>
<td>85.7</td>
<td>-3.1</td>
<td>3.4 &quot;</td>
</tr>
<tr>
<td>305.7</td>
<td>98.3</td>
<td>95.5</td>
<td>-2.8</td>
<td>2.8 Solution of precipitant</td>
</tr>
<tr>
<td>288.1</td>
<td>92.3</td>
<td>89.9</td>
<td>-2.4</td>
<td>2.6 &quot;</td>
</tr>
<tr>
<td>297.3</td>
<td>95.4</td>
<td>92.9</td>
<td>-2.5</td>
<td>2.6 &quot;</td>
</tr>
<tr>
<td>271.1</td>
<td>86.8</td>
<td>84.7</td>
<td>-2.1</td>
<td>2.4 &quot;</td>
</tr>
<tr>
<td>253.2</td>
<td>81.4</td>
<td>79.1</td>
<td>-2.3</td>
<td>2.8 &quot;</td>
</tr>
<tr>
<td>194.3</td>
<td>52.7</td>
<td>60.7</td>
<td>-1.5</td>
<td>2.4 &quot;</td>
</tr>
</tbody>
</table>

Table (10) shows that the results obtained by the above methods in the absence of the precipitant as washing agent are up to 4% low. However when a solution of the precipitant was employed the results are more favourable. The solubility of the compound is still fairly high, so it would appear unsuitable to employ the method for the gravimetric determination of thallium (III). The filtrate again showed some thallium (III) in solution.

(c) Precipitation of thallium (III) in the presence of iodide ions with tetraethyl, trimethyl phenyl and tetra-n-butyl ammonium iodides

On the assumption that the solubility of a compound decreases with increasing molecular weight it was hoped that more satisfactory results would be obtained by using the quaternary ammonium iodides as precipitants.
method used was as follows: To the solutions containing thallium (III) ions were added a few mls. of hydrochloric acid (1:1) and approximately 10 mls. of 0.5% potassium iodide solution and 10 mls. of a 1 N solution of the quaternary ammonium iodide. Red precipitates were obtained in each case; these were washed with a little solution of precipitant, dried at 110°C for an hour and weighed as $R_4NTI_4$. The gravimetric results obtained for the various quaternary ammonium iodides are shown in table (11).

It can be observed that as the molecular weight of the complexes increases, more satisfactory results are obtained for the thallium (III) estimation. In the case of the tetraethylammonium iodide the results of analyses, when water is used as the washing agent, are up to 3% low. Better results are however obtained when a solution of the precipitant is the washing liquid. With both tetraphenyl and tetra-n-butyl ammonium iodides as reagents, more satisfactory results were found. These results could be used under the given conditions to analyse thallium (III) to a one per cent accuracy. The experiments above were made at 20°C, but preliminary experiments at 0°C, indicated, as shown in table (12) that more accurate results could be obtained at this lower temperature.
<table>
<thead>
<tr>
<th>Weight of precipitate (in mg)</th>
<th>Thallium taken in mg</th>
<th>Thallium found in mg</th>
<th>Error in g</th>
<th>Washing Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) $(C_2H_5)_4NTLI_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>301.1</td>
<td>45.0</td>
<td>73.1</td>
<td>-1.9</td>
<td>2.5</td>
</tr>
<tr>
<td>272.4</td>
<td>68.3</td>
<td>66.1</td>
<td>-2.2</td>
<td>3.1</td>
</tr>
<tr>
<td>225.2</td>
<td>56.3</td>
<td>54.6</td>
<td>-1.7</td>
<td>3.0</td>
</tr>
<tr>
<td>214.3</td>
<td>53.5</td>
<td>52.0</td>
<td>-1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>204.1</td>
<td>51.0</td>
<td>49.5</td>
<td>-1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>291.3</td>
<td>71.8</td>
<td>70.7</td>
<td>-1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>277.7</td>
<td>68.4</td>
<td>67.4</td>
<td>-1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>265.4</td>
<td>64.7</td>
<td>63.9</td>
<td>-0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>(ii) $C_6H_5(CH_3)_3NTLI_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>187.7</td>
<td>46.0</td>
<td>45.2</td>
<td>-0.8</td>
<td>1.7</td>
</tr>
<tr>
<td>204.3</td>
<td>50.2</td>
<td>49.2</td>
<td>-1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>233.2</td>
<td>57.1</td>
<td>56.2</td>
<td>-0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>172.1</td>
<td>42.3</td>
<td>41.5</td>
<td>-0.8</td>
<td>1.9</td>
</tr>
<tr>
<td>304.3</td>
<td>74.1</td>
<td>73.3</td>
<td>-0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>272.3</td>
<td>66.2</td>
<td>65.6</td>
<td>-0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>257.3</td>
<td>62.9</td>
<td>62.0</td>
<td>-0.9</td>
<td>1.4</td>
</tr>
<tr>
<td>123.1</td>
<td>30.0</td>
<td>29.7</td>
<td>-0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>(iii) $C(CH_2)_{2}NTLI_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>267.3</td>
<td>58.2</td>
<td>57.3</td>
<td>-0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>291.2</td>
<td>63.2</td>
<td>62.4</td>
<td>-0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>260.1</td>
<td>56.4</td>
<td>55.7</td>
<td>-0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>307.8</td>
<td>66.5</td>
<td>65.9</td>
<td>-0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>284.5</td>
<td>61.6</td>
<td>60.9</td>
<td>-0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>252.3</td>
<td>54.6</td>
<td>54.0</td>
<td>-0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>251.9</td>
<td>54.6</td>
<td>53.9</td>
<td>-0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>201.2</td>
<td>43.6</td>
<td>43.1</td>
<td>-0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>201.8</td>
<td>43.6</td>
<td>43.2</td>
<td>-0.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>
These results at 0° in the case of the tetra-n-butyl complexes of thallium show good agreement between the calculated and the experimental thallium content. It should be noted that a weight of some 50 mg. of thallium was employed and the one or two milligrams error is not unexpected on such a quantity. This suggests that the quaternary butyl iodide complex could be a satisfactory reagent for the analytical estimation of thallium, especially if larger quantities are employed initially. As the thallium content found by this method of analysis is slightly low throughout a correction could be made for the small amount remaining in solution under standardised conditions. In the present experiments this is about 0.4 mg. in 35-45 mls. of solution at 0° or 0.5 mg. in a similar volume at the higher temperature, when the precipitate is washed by a solution of the precipitant. Further if an additional salt could be found to depress the solubility still further the result would be satisfactory for even smaller amounts of thallium. This aspect was not further investigated.
Magnetic Measurements

The magnetic susceptibilities of compounds of the above type were measured by the Gouy method as already described (page 30). Some of the compounds, especially the tetraiodothallates cake very easily, but by careful packing as described in the "Physical Measurements Section" reproducible results were ensured. A sufficient number of measurements were made on the solid compounds and doubtful results checked by additional measurements so as to enable the diamagnetic susceptibility to be definitely determined. Reliable anionic susceptibility constant values could then be calculated for the anions TlCl$_4^-$, TlBr$_4^-$ and TlI$_4^-$. 

(a) Tetraalkyl ammonium halides

Although a few measurements of the magnetic susceptibilities of some of the quaternary ammonium halides used here as reagents had previously been made (43) new measurements were carried out on all of them. In columns 5 and 6 of table (13) are listed the results obtained by Bedwell (43) and in columns 2 and 3, those obtained during the present work. It will be noted that the general agreement with the earlier work (1941) is good.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Present Work</th>
<th>Literature (43)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-10^6\chi_a$</td>
<td>$-10^6\chi_M$</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{NCl}$</td>
<td>0.6934</td>
<td>0.6945</td>
</tr>
<tr>
<td></td>
<td>0.7117</td>
<td>0.7117</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{NBr}$</td>
<td>0.5499</td>
<td>0.5635</td>
</tr>
<tr>
<td></td>
<td>0.5559</td>
<td>0.5559</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{NI}$</td>
<td>0.5089</td>
<td>0.5023</td>
</tr>
<tr>
<td></td>
<td>0.4981</td>
<td>0.4981</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{NCl}$</td>
<td>0.7498</td>
<td>0.7314</td>
</tr>
<tr>
<td></td>
<td>0.7396</td>
<td>0.7396</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{NBr}$</td>
<td>0.6278</td>
<td>0.6185</td>
</tr>
<tr>
<td></td>
<td>0.6239</td>
<td>0.6239</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{NI}$</td>
<td>0.5681</td>
<td>0.5769</td>
</tr>
<tr>
<td></td>
<td>0.5716</td>
<td>0.5716</td>
</tr>
</tbody>
</table>

Some of the tetra alkyl ammonium halides i.e. the tetra ethyl ammonium chloride and iodide and the tetra methyl ammonium chloride in particular, are very deliquescent and thus the measurements had to be carried out under dry conditions, the specimen being packed in a dry box. From the values of their molar susceptibilities, the now well established values for the halides (27) were subtracted and thus the value for the quaternary ammonium cation was obtained as shown in table (13). The mean value for the molar susceptibility of the tetra methyl ammonium cation is...
51.30 \pm 0.74 \text{ c.g.s. units of susceptibility and for the tetra ethyl ammonium cation is } 97.08 \pm 0.63 \text{ c.g.s. units. These values are used later to determine the susceptibility of the halogenothallate anions.}

Other relationships within the series of alkyl halides can be noted which not only show the additive character of the diamagnetism but afford a useful check on the accuracy of the measurements. Thus halogen increments can be calculated and compared with those obtained for simple halides. By simple subtraction it is possible to obtain the change in the susceptibility on passing from the chloride to the bromide and to the iodide.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta \chi(\text{Br}^-\text{Cl}^-)$</th>
<th>$\Delta \chi(\text{Br}^-\text{I})$</th>
<th>$\Delta \chi(\text{Cl}^-\text{I})$</th>
<th>$\Delta \chi(X^-X_1)$ Literature values \textit{(27)} for alkali halides</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_4\text{NCl}$</td>
<td>9.01</td>
<td></td>
<td></td>
<td>10.5^# 15.8^# 26.3 \textit{(27)}</td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{NBr}$</td>
<td>15.4</td>
<td></td>
<td>24.4</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_4\text{NI}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{NCl}$</td>
<td>9.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{NBr}$</td>
<td>15.7</td>
<td></td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_4\text{NI}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In table \textit{(14)} these are compared with those obtained by Brindley and Hoare \textit{(27)} and by Trew and Husain \textit{(27)} for the simple alkali and ammonium halides. As can be observed from the table the halide differences in the tetra alkyl ammonium salts are in good agreement with those previously
obtained for the simple halides, although the increments involving the chloride ion are somewhat low.

By considering the differences between the molar susceptibilities of the corresponding tetra ethyl and tetra methyl ammonium halides a value for the CH₂ increment in these salts can be calculated as shown in table (15).

<table>
<thead>
<tr>
<th>Compound</th>
<th>-10⁶χM</th>
<th>4Δχ(CH₂)</th>
<th>4Δχ(CH₂)</th>
<th>Literature Values for CH₂ increments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₂)₄NCl</td>
<td>76.7</td>
<td>45.6</td>
<td>11.4</td>
<td>11.86 (26)</td>
</tr>
<tr>
<td>(C₂H₅)₄NCl</td>
<td>122.5</td>
<td>75.8</td>
<td>11.4</td>
<td>11.68 (44)</td>
</tr>
<tr>
<td>(CH₂)₄NBr</td>
<td>85.7</td>
<td>75.8</td>
<td>11.4</td>
<td>11.69 (45)</td>
</tr>
<tr>
<td>(C₂H₅)₄NBr</td>
<td>131.5</td>
<td>46.0</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td>(CH₂)₄NI</td>
<td>101.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C₂H₅)₄NI</td>
<td>147.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The above results give an average value of 11.45 for the CH₂ increment. This is somewhat lower than the three literature values shown, which have been obtained from straight chain aliphatic series of compounds. Further it is known that there is a chain branching effect (46) which modified the increment slightly. A recent study by Abel and Bush of the magnetic susceptibility of homologous series of organo silicon compounds gave values of 11.50 ± 0.09 and 11.60 ± 0.08 for the CH₂ increments in the n-alkyl trimethyl silanes and the n-alkyl trichlorosilanes (41). These two straight chain series thus show a slightly lower increment.
in the case of silicon containing compounds than the pure hydrocarbons. In a more recent paper Abel, Smith, Jenkins and Zobel have made a study of the CH₂ increment in homo-
logous series of silicon, germanium and tin, including a number of quaternary compounds. They obtained considerably lower CH₂ increments for the tetra-n-alkyl silanes and germanes and the corresponding n-alkyl tin compounds. This appears to indicate a small but definite modification of the CH₂ increment in differing types of compounds, which is further supported by the present values.

The systematic agreement of the halide and CH₂ increments calculated from the quaternary ammonium halides with values of earlier workers supports the use of these to obtain anionic susceptibilities for the halogenothallate ions. In calculating the cation susceptibility of the (CH₃)₄N⁺ and (C₂H₅)₄N⁺ ions, ionic halide susceptibility values have been subtracted from the molar susceptibility of the salt. The use of ionic halide rather than covalent halogen susceptibility increments rests on the fact that the quaternary ammonium halides are salts and strong electrolytes. Geddes and Kraus (49) and later Smith and Bauge (50) determined the dipole moment of some of these compounds in benzene and showed their polar character. Furthermore, conductance measurements by Kraus and coworkers (51) have given the following equivalent ionic conductances at 25°C:
(CH$_3$)$_4$N$^+$ = 44.92 and (C$_2$H$_5$)$_4$N$^+$ = 32.66. These as is shown by the table of ionic conductances in Stokes and Robinson (51) are of the same order of magnitude as those for other ionic species such as Li$^+$, Na$^+$, picrate, benzoate and others (52). In estimating the cation susceptibility for the quaternary ammonium salts therefore the ionic halogen susceptibility values have been used and a mean cation figure calculated for interpretation of the compounds with thallium.

(b) Tetraalkyl ammonium tetrahalothallates

The magnetic susceptibilities of the tetraalkyl ammonium tetrahalothallates were determined in a similar manner. These compounds although not deliquescent as were the starting materials still tend to cake rather easily. Their specific and molar susceptibilities are shown in columns 2 and 3 together with the anionic susceptibility values for TlX$_4^-$ in columns 4, 5 and 6 in table (16). The latter were obtained by subtraction of the corresponding mean value for the tetraalkyl ammonium cation previously found.
From the above results, a mean value of 11.36 can be obtained for the CH$_2$ increment in these compounds. This value is in good agreement with that previously found for the quaternary ammonium halides (page 74). The changes in the susceptibility on passing from the chloro to the bromo, bromo to the iodo, and chloro to the iodo complexes, again, agree well with those obtained for the alkali metal halides (27). These increments are shown in table (11).
GRAPH (5)

MAGNETIC SUSCEPTIBILITY OF

(a) Potassium halides
(b) Tetramethylammonium halothallates
(c) Tetraethylammonium halothallates
A further comparison of the susceptibilities of the tetrahalothallates with those of simpler compounds can be made by a graphical method. Graph (5), thus shows a plot of the magnetic susceptibilities for the tetraalkyl ammonium halothallates versus the effective atomic number of the halothallate anion, together with a similar plot for the simple potassium halides (27). It is here observed that there is a definite parallel relationship for the above plots, which indicates that the $\mathrm{TlX}^-$ anion behaves as an entity. There thus seems no doubt that the molar susceptibilities of all these compounds can be treated additively in the manner used above. In other words the magnetic evidence gives a clear indication of the polar character of such compounds.

By considering the various results obtained for the tetrahalogeno complexes, an average value for the susceptibilities of the $\mathrm{TlX}_4^-$ anions can thus be found. These
values are of 120.5, 161.6 and 224.9 c.g.s. units for the tetrachloro, tetrabromo and tetraiodothallate (III) anions respectively.

At this point, it is of interest to compare the halogen increments for all the quaternary ammonium compounds studied above.

Table (18) thus shows the halogen increments for the alkali halides (column 2), for the tetramethyl and tetraethyl ammonium halides (columns 3 and 4 respectively) and tetramethyl and tetraethyl tetrahalothallates (columns 4 and 5 respectively). It is thus observed, that with the exception of the chloride-bromide and chloride-iodide increments for the tetramethyl and tetraethyl ammonium halides which are somewhat low, all the increments are in good agreement with those obtained by Brindley and Hoare (27) for the alkali metal halides.

**Conductivity Measurements**

The number of ions formed on dissociation of the tetraalkyl ammonium complexes of thallium (III) was determined by measuring the electrical conductivity in non-aqueous.
solvents such as nitrobenzene and nitromethane. The results obtained for these complexes are shown in table (19).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nitrobenzene M.conc</th>
<th>mhos</th>
<th>Nitromethane M.conc</th>
<th>mhos</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3\text{)}_4\text{NTI}\text{Cl}_4)</td>
<td>0.0012</td>
<td>31</td>
<td>0.0011</td>
<td>112</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4\text{NTI}\text{Br}_4)</td>
<td>0.0017</td>
<td>29</td>
<td>0.0012</td>
<td>112</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4\text{NTI}^\text{I}_4)</td>
<td>0.0020</td>
<td>27</td>
<td>0.0009</td>
<td>93</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4\text{NTI}\text{Cl}_3\text{Br})</td>
<td>0.0015</td>
<td>33</td>
<td>0.0011</td>
<td>114</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4\text{NTI}\text{Br}_2\text{Cl})</td>
<td>0.0011</td>
<td>31</td>
<td>0.0010</td>
<td>110</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4\text{NTI}_2\text{I})</td>
<td>0.0010</td>
<td>29</td>
<td>0.0011</td>
<td>110</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{)}_4\text{NTI}\text{Cl}_4)</td>
<td>0.0009</td>
<td>29</td>
<td>0.0009</td>
<td>110</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{)}_4\text{NTI}\text{Br}_4)</td>
<td>0.0010</td>
<td>29</td>
<td>0.0012</td>
<td>102</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{)}_4\text{NTI}^\text{I}_4)</td>
<td>0.0011</td>
<td>26</td>
<td>0.0011</td>
<td>92</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{)}_4\text{NTI}\text{Cl}_3\text{Br})</td>
<td>0.0015</td>
<td>30</td>
<td>0.0009</td>
<td>105</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{)}_4\text{NTI}\text{Br}_2\text{Cl}_3)</td>
<td>0.0012</td>
<td>28</td>
<td>0.0009</td>
<td>107</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{)}_4\text{NTI}_2\text{Cl}_4)</td>
<td>0.0011</td>
<td>26</td>
<td>0.0011</td>
<td>106</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5\text{)}_4\text{NTI}_2\text{I}_4)</td>
<td>0.0010</td>
<td>26</td>
<td>0.0012</td>
<td>105</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4(\text{CH}_2\text{)}_3\text{NTI}^\text{I}_4)</td>
<td>0.0011</td>
<td>25</td>
<td>0.0012</td>
<td>90</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4(\text{CH}_2\text{)}_3\text{NTI}\text{Cl}_4)</td>
<td>0.0013</td>
<td>26</td>
<td>0.0010</td>
<td>88</td>
</tr>
<tr>
<td>((\text{CH}_3\text{)}_4(\text{CH}_2\text{)}_3\text{NTI}\text{Br}_4)</td>
<td>0.0012</td>
<td>26</td>
<td>0.0011</td>
<td>88</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5\text{)}_4\text{NTI}_4)</td>
<td>0.0012</td>
<td>26</td>
<td>0.0011</td>
<td>92</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5\text{)}_4(\text{CH}_2\text{)}_3\text{NTI}\text{Cl}_4)</td>
<td>0.0011</td>
<td>27</td>
<td>0.0012</td>
<td>91</td>
</tr>
<tr>
<td>((\text{C}_6\text{H}_5\text{)}_4(\text{CH}_2\text{)}_3\text{NTI}\text{Br}_4)</td>
<td>0.0011</td>
<td>26</td>
<td>0.0010</td>
<td>89</td>
</tr>
</tbody>
</table>
The conductances of some quaternary ammonium salts with simple anions in the two solvents are also listed in table (19) to give a comparison of the mobility of the ions.

As already stated in the physical measurements section, for solutions of $10^{-3} \text{M}$ in nitrobenzene and nitromethane the expected values for uni-univalent electrolytes are $20 - 30$ and $70 - 110 \text{ cm}^{-1} \text{cm}^2$ respectively. The results found for the above-mentioned compounds are in good agreement with the expected ones. Thus they behave as uni-univalent binary electrolytes:

$$R_4N^+ + \text{Tl} \Leftrightarrow R_4N \text{Tl} X^-$$

and

$$R_4N^+ + \text{Tl} \Leftrightarrow R_4N \text{Tl} X'_-$$

where $R = \text{CH}_3$, $\text{C}_2\text{H}_5$, $\text{C}_4\text{H}_9$ and $\text{C}_6\text{H}_5(\text{CH}_3)_2$ and $X$ and $X' = \text{Cl}$, Br or I.

It must be pointed out here that these results were
obtained at one concentration only and not by extrapolation. However the dilutions used were near $\sqrt{V} = 1024$ which is generally considered to represent approximately infinite dilution.

Although the aim of these measurements of electrical conductance was primarily to ascertain the number of ions present in solution, there are certain points concerning the actual molar conductances that are worth noticing. Though the differences in the molar conductances for the various complexes are only small for complexes containing the same quaternary ammonium cation, there is in general a slight fall in the conductance values with increasing anion size. With a few exceptions, which may be due to experimental error, the order with respect to the anions is thus as follows:

$$\text{Tl Cl}_3\text{ Br}^- \succ \text{Tl Cl}_4; \text{Tl Br}_3\text{Cl}^- \succ \text{TlBr}_4; \text{Tl Br}_3\text{I}^- \succ \text{Tl I}_4^-.$$

It is also noted, that for compounds containing the same anion but different tetra alkyl ammonium cation, the molar conductance increase with decreasing size of the cation. The tetra methyl ammonium complexes thus have the highest conductances. This has already been shown to be the case for the simple quaternary ammonium halides (51) and thus appears to hold for their complex compounds. The following order was here obtained:

$$(\text{CH}_3)_4\text{N}^+ \succ (\text{C}_2\text{H}_5)_4\text{N}^+ \succ \text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}^+ \succ (\text{C}_4\text{H}_9)_4\text{N}^+.$$
Ultra-Violet and Visible Absorption Spectra and Reflectance Spectra

For the purpose of interpreting the absorption bands of the halothallate anions in solution, the spectra of the tetraalkyl ammonium halothallate complexes were measured in absolute ethanol solution. Some measurements were also carried out using spectrograde acetonitrile as solvent. In the case of the coloured complexes the reflectance spectra were also measured, using magnesium carbonate as standard. The measurements of the solution spectra were carried out using short path length silica cells (0.1mm) in order to minimise any solvent absorption in this region. The effect of stray light was also tested, using a solution of lithium carbonate as the cut-off filter and was found to be negligible in the region employed. Unicam SP700 and SP500 spectrophotometers were employed. The latter was equipped with a standard reflectance attachment.

As a control the spectra of ethanol and acetonitrile solutions containing halide ions but no thallium were first determined. Tetra ethylammonium chloride, bromide and iodide were employed, after recrystallisation from ethanol-acetone mixtures, as the sources of the halide ions. Their spectra are shown in graph (6) and the position of the bands and extinction coefficients are given in table (20). These values are in good agreement with the literature ones (54). Only the lowest frequency band
GRAPH (b)
(a) IODIDE ABSORPTION SPECTRA IN ETHANOL
(b) " " " ACETONITRILE
(c) BROMIDE " " " "
(d) CHLORIDE " " " "

$E_m \times 10^{-4}$

52 50 48 46 44 42 40 38

Cm$^{-1} \times 10^{-3}$
<table>
<thead>
<tr>
<th>Substance</th>
<th>cm$^{-1}$ Spectra in Ethanol (m$\mu$)</th>
<th>$\varepsilon_{\text{max}} \times 10^{-4}$</th>
<th>cm$^{-1}$ Spectra in acetonitrile (m$\mu$)</th>
<th>$\varepsilon_{\text{max}} \times 10^{-4}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_2H_5)_4NCl$</td>
<td>52,000 (192.3)</td>
<td>--</td>
<td>51,150 (195.5)</td>
<td>0.990</td>
<td>(55)(56)</td>
</tr>
<tr>
<td>$(C_2H_5)_4NTlCl_4$</td>
<td>(I') 40,600 (246.3)</td>
<td>1.85</td>
<td>(I') 41,100 (243.9)</td>
<td>3.84</td>
<td>(55)(56)</td>
</tr>
<tr>
<td></td>
<td>(II') 50,800 (196.8)</td>
<td>2.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(C_2H_5)_4NBr$</td>
<td>(I) 52,000 (192.3)</td>
<td>--</td>
<td>(I) 40,600 (217.0)</td>
<td>1.09</td>
<td>(55)(56)</td>
</tr>
<tr>
<td></td>
<td>(II) 52,000 (192.3)</td>
<td></td>
<td>(II) 49,160 (203.4)</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>$(C_2H_5)_4TlBr_4$</td>
<td>(I') 36,300 (275.4)</td>
<td>2.00</td>
<td>(I') 36,300 (271.0)</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(II') 45,300 (220.8)</td>
<td>3.28</td>
<td>(II') 45,100 (221.7)</td>
<td>4.68</td>
<td></td>
</tr>
<tr>
<td>$(C_2H_5)_4NI$</td>
<td>(I) 45,520 (219.7)</td>
<td>1.41</td>
<td>(I) 40,500 (246.9)</td>
<td>1.45</td>
<td>(54)(56)</td>
</tr>
<tr>
<td></td>
<td>(II) 52,500 (190.4)</td>
<td>1.41</td>
<td>(II) 47,700 (209.6)</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>$(C_2H_5)_4NTlI_4$</td>
<td>(I') 34,500 (289.9)</td>
<td>1.59</td>
<td>(I') 36,500 (273.9)</td>
<td>4.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(II') 39,300 (254.5)</td>
<td>2.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(III') 50,200 (199.2)</td>
<td>4.63</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
for the iodide ion could be obtained in ethanol, since the highest frequency band occurs beyond the instrument limit. With the chloride and bromide ions experimental difficulties arise due to location of both bands in the region above 51,000 cm\(^{-1}\) beyond the instrument limit. Several authors (55) (56) have overcome this difficulty by measuring the spectra of these ions in acetonitrile, which causes a considerable shift compared with those in aqueous and ethanolic solutions. Thus as already stated acetonitrile solutions were also employed here.

A number of workers (53) (54) have put forward various theories to interpret the nature of the halide bands. These theories all point out that the bands arise from charge transfer to the solvent which involves the halogen transitions \( ^1S_0 \rightarrow ^2P_1 \). This is in agreement with the fact that the position of these absorption bands are markedly dependent upon the solvent. The shifts which occur when the solvent is changed from ethanol to acetonitrile are in the range 5,000 - 12,000 cm\(^{-1}\) towards lower frequencies. The intensity of the bands also increases in acetonitrile. This is expected because of the lower polarity of the acetonitrile solvent. Solutions containing bromide and iodide ions are characterised by a double peak. The energy of separation between the two peaks has been considered by several investigators (54) (55) and
it has been found that in the case of both bromide and iodide ions the peaks separations (respectively 3080 and 7200 cm\(^{-1}\)) correspond to the separations 3700 and 7600 cm\(^{-1}\) in the spectra of atomic bromine and iodine. These are known to be the separation of the \(^2P_{\text{z}}\) and \(^2P_{3/2}\) states. In the case of chlorine, Strickler and Kasha (55) have concluded that the doublet splitting is so small (\(\sim 900\text{cm}^{-1}\)) that the peaks are not resolved, but in any case the band has been attributed to an analogous transition.

In the case of the tetra alkyl ammonium halothallate complexes the positions of the bands were found to be independent of the cation as shown by some preliminary experiments with \((\text{CH}_3)_4\text{NTL}_4\) \((X = \text{Cl}^-, \text{Br}^-\) and \(\text{I}^-\) solutions in ethanol. These give the same bands as those recorded in table (20) for the \((\text{C}_2\text{H}_5)_4\text{NXL}_4\) solutions. The extinction coefficients were however only measured accurately for the tetraethyl ammonium compounds and these values are then taken in the interpretation of the spectra. Because of the complexity of the iodide equilibria, which makes the interpretation of the spectra difficult, the chloro and bromo complexes will primarily be discussed.

**Tetra chloro and bromo thallate compounds**

The results in table (20) shows that the chloro and bromo complexes are characterised by two bands at
40,800 and 50,800 cm$^{-1}$, and 36,300 and 45,300 cm$^{-1}$ in ethanol solution respectively. Change of solvent from ethanol to acetonitrile cause but a small change in the position of the bands unlike the large shifts observed in the case of the halide ions which are characteristic of charge transfer to the solvent. This fact and the observation that in the bromothallate complex the shift is in the wrong direction for a charge transfer to the solvent band leads to the tentative suggestion that the halothallate absorption bands must be a result of an internal transition.

Like the spectra of the free halide ions in solution the bands observed for the halothallate complexes move to longer wavelengths on going from the chloro to the bromo complex, but the halothallate ion bands all occur at longer wavelengths than in the case of the free halides and must be therefore clearly associated with the thallium complexes.

The effect of excess halide ion ($\sim 10^{-3}$ M) on the spectra of solutions of these complexes was also examined and it was observed that the positions of the bands were unaffected. Their extinction coefficients increase only slightly in the presence of this excess of halide ions. It is evident from this that for the chloro and bromo complexes the chromophoric species must be the $\text{TlX}_4^-$ ion and not one of the lower species which may be present (i.e. $\text{TiCl}_3^-$, $\text{TiCl}_2^+$, $\text{TiCl}_2^{2+}$). Graphs (8) and (9) show the
GRAPH 1
ULTRA-VIOLET ABSORPTION SPECTRA
(a) C6H5N3I4 in ethanol
(b) C6H5N3I4+ in ethanol plus excess cations

\[ E \times 10^{-4} \]

2.00
2.10
2.20
2.30
2.40
2.50
2.60
2.70
2.80
2.90
3.00

\[ \text{cm}^{-1} \times 10^{-3} \]

31
33
35
37
39
41
43
45
47
49
51

\[ \text{cm}^{-1} \times 10^{-3} \]

90
**GRAPH 13**

**ULTRA VIOLET ABSORPTION SPECTRA**

(a) \((\text{C}_2\text{H}_5)_4\text{N}^+\text{Te}^2\text{C}_4^-\) IN ETHANOL

(b) \((\text{C}_2\text{H}_5)_4\text{N}^+\text{Te}^-\text{Ba}^4^-\) IN ETHANOL PLUS EXCESS Ba\(^{2+}\) IONS
GRAPH (8)
ULTRA VIOLET ABSORPTION SPECTRA
(a) (C₂H₅)₄NTeCl₄ in ACETONITRILE
(b) (C₂H₅)₄NTeBr₄ in

\[ \varepsilon_{\text{max}} \times 10^{-4} \quad 220 \quad 230 \quad 240 \quad 250 \quad 260 \quad 270 \quad 280 \quad 290 \quad 300 \]

\[ \mu \rightarrow 92. \]

\[ \text{cm}^{-1} \times 10^{-3} \]
results in acetonitrile solutions. Graphs (7) and (7a) show the absorption spectra for the chloro and bromo thallates in ethanol solution with and without excess halide ions.

The bands observed for these tetrahalothallate compounds in solution are of interest in connection with the problem of what species exist in solutions of the halothallate salts. A number of workers (13-16) have been interested especially in quite recent times (1964) in the stability constants of the chloro and bromo complexes. These constants have now been determined accurately (16).

Recent work (16) on the chloro and bromo complexes of thallium by Ahrland and co-workers has given further evidence that the TlCl₄⁻ and TlBr₄⁻ are the highest complexes formed in solution seeming to resolve the uncertainty on this point referred to earlier. On this basis it should be possible to identify the transitions in the tetrahedral chromophores Tlx₄⁻ which would give rise to such bands.

An attempt to interpret the transitions can be made with the aid of the energy level diagrams of molecular orbital theory. These are shown for comparative purposes both for tetrahedral and octahedral complexes derived from 5d and 6s orbitals in figures (1) and (2). Figure (1) shows complexes having only $\sigma$ bonding while figure (2) shows the additional effect of $\pi$ bonding on the energy
Figure (1)

Molecular Orbital Energy Level Diagram for Covalent Bonding in (1) Tetrahedral (2) Octahedral Complexes

(1)

6p

6s

5d^{10}

Pure Metal Orbitals

The Orbitals of the United Complex

Pure Molecular Orbitals (Filled)

(2)

6p

6s

5d^{10}

Pure Metal Orbitals

The Orbitals of the United Complex

Pure Ligand 

a Molecular Orbitals (Filled)
**Figure (2)**

**Molecular Orbital Energy Level Diagram for (3) Tetrahedral (4) Octahedral Complexes When Ti Bonding is Added**

(3)

- $t_2g (\pi^*)$
- $e_g (\pi^*)$
- $t_2u (\pi)$
- $t_1u (\pi)$
- $e_g (\pi)$
- $e_g (\pi)$
- $t_2u (\pi)$
- $t_1u (\pi)$

(4)

- $t_2g (\pi^*)$
- $e_g (\pi^*)$
- $t_2u (\pi)$
- $t_1u (\pi)$
- $e_g (\pi)$
- $e_g (\pi)$
- $t_2u (\pi)$
- $t_1u (\pi)$

**Metal Orbitals**

- $5d^{10}$

**Ligand Orbitals**

- $t_2g (\pi^*)$
- $e_g (\pi^*)$
- $t_2u (\pi)$
- $t_1u (\pi)$

**The Orbitals of the United Complex**
levels. This type of diagram was described by Liehr (61) and by Gray (62) and their notation for the metal, the ligand and derived molecular orbitals is employed here.

In the case of the thallium (III) tetrahedral halogeno complexes, 8 electrons from the four ligands and the 10 electrons of the 5 d thallium level must be accommodated. These can be introduced into the $a_1(\sigma)^b$ (2 electrons), $t_2(\sigma)^b$ (6 electrons), $t_2\pi^b$ (6 electrons) and $e\pi^b$ (4 electrons). It must be noted at this point that with the introduction of $\pi$-bonding in the tetrahedral case (Figure (2.3)) the energy positions are more favourable than that for simple $\sigma$-bonding. The non-bonding $e$ orbital becomes $\pi$-antibonding and an additional set of $\pi$-bonding orbitals appears of symmetry $e$, $t$, and $t_2$. Addition of $\pi$-bonding thus enables the electrons to be accommodated in bonding orbitals rather than in the non-bonding and antibonding ones.

When considering the halothallate bands and assigning which orbitals are involved in the electronic transitions, assistance can be obtained from the fact that the TlX$_4^-$ complexes are isoelectronic with the octahedral lead (IV) complexes (PbCl$_6^{2-}$) and the tetrahedral HgCl$_4^{2-}$, HgBr$_4^{2-}$ and HgI$_4^{2-}$) whose bands have been assigned recently by Jørgensen (63). In the octahedral lead complexes he assigned (63) the 32,600cm$^{-1}$ ($\varepsilon = 9,700$) band to the transition $t_{1u}\Pi^b \rightarrow a_1$ i.e. a transition from a $t_{1u}\Pi$ bonding orbital to an $a_1$
α antibonding orbital. In the Bethe notation this is the odd $π τ₂ → εδ σ₁$ transition. The second band at 48,100 cm$^{-1}$ ($ε = 24,000$) was ascribed to the $τ_{1u} π^b → α_1^*$ transition (odd $α τ₂ → εδ σ_1$). The mercury complexes are however of greatest assistance in the present case as these have a tetrahedral symmetry. The single bands of the chloro and bromo mercury complexes have been assigned by Jørgensen as arising from $επ^b → α_1^*$ (or $π 5 τ_2 → εδ σ_1$). These bands occur for the mercury chloro and bromo complexes at 43,400 and 40,300 cm$^{-1}$. By analogy with the isoelectronic mercury compounds it would seem reasonable to suggest that the corresponding halothallic bands considered above at 40,600 cm$^{-1}$ (TlCl$^-$) and 36,300 cm$^{-1}$ (TlBr$^-$) must arise from similar transitions in the tetrahedral chromophore. The oscillator strength ($P$) for the HgCl$^-$ and HgBr$^-_4$ bands were also given by Jørgensen (63) as 60,000 $x 10^{-5}$ and 70,000 $x 10^{-5}$ (0.6 and 0.7) respectively. Approximate calculations of these oscillator strengths can be carried out using the formula:

$$P = \frac{1000}{N} \cdot \frac{mc^2}{ε^2} \cdot 2.30 \int ε \, dα \sim 9.20 \times 10^{-9} ε_0 δ$$

(taking the approximation that $ε_0 δ$ is given by $ε_0 \cdot$ width at $ε_0/2$.)

Where $N$ is the Avogadro's number, $ε$ the charge and $m$ the mass of the electron, $c$ the velocity of light, $ε_0$ the extinction coefficient at the maximum and $δ$ - the half width of the curve.
The oscillator strengths for the TlX₄⁻ bands were calculated on this basis from the graphs (7) and (7a) and figures in table (20) and found to be 0.76 and 0.65 for the chloro and bromo thallate bands respectively. Table (21) shows the positions of the maxima, the extinction coefficients and oscillator strengths for both the mercury (63) and thallium complexes for comparative purposes.

### Table (21)

<table>
<thead>
<tr>
<th></th>
<th>cm⁻¹ (mμ)</th>
<th>ε x 10⁴</th>
<th>*F</th>
<th>cm⁻¹ (mμ)</th>
<th>ε x 10⁴</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl²⁻</td>
<td>43,400</td>
<td>2.8</td>
<td>0.6</td>
<td>TlCl⁻</td>
<td>40,600</td>
<td>1.85</td>
</tr>
<tr>
<td>(230.5)</td>
<td></td>
<td></td>
<td></td>
<td>(246.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgBr²⁻</td>
<td>40,400</td>
<td>2.8</td>
<td>0.7</td>
<td>TlBr⁻</td>
<td>36,300</td>
<td>2.00</td>
</tr>
<tr>
<td>(248.0)</td>
<td></td>
<td></td>
<td></td>
<td>(275.4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Jørgensen (63) gives P in units of 10⁻⁵.

At this point one must mention the high frequency bands observed in the spectra of the TlCl₄⁻ (at 50,800 cm⁻¹) and TlBr₄⁻ (at 45,300 cm⁻¹) solutions. These are probably the chloride and bromide charge transfer bands (transfer to the solvent) observed for Cl⁻ (at >52,000 cm⁻¹) and Br⁻ (at ~52,000 cm⁻¹) solutions respectively. These are somewhat shifted towards lower frequencies in the complex solutions. The halogen bands have already been discussed on page (87).

**Tetra iodo Compounds**

The ultra-violet absorption spectra of the tetra iodo
thallate compounds were measured in ethanol and acetonitrile solutions and their spectra are shown in graphs (9) and (10). The positions of the maxima and their extinction coefficients are listed in table (20).

In the ultra-violet spectral region the iodothallate solutions give rise to three bands at $34,500\, \text{cm}^{-1} (289.9\, \mu\text{m})$, $39,300\, \text{cm}^{-1} (254.5\, \mu\text{m})$ and $50,200\, \text{cm}^{-1} (199.2\, \mu\text{m})$. The latter band shows a broad shoulder at $47,000\, \text{cm}^{-1} (212.8\, \mu\text{m})$. The spectra of these compounds in acetonitrile solutions show similar characteristics except that only a single broad band with a maximum at $36,500\, \text{cm}^{-1}$ is observed. This thus replaces the two bands in ethanol solution at $34,500$ and $39,300\, \text{cm}^{-1}$. The non-Gaussian shape of the band in acetonitrile gives furthermore an indication that overlapping of the above two bands ($34,500$ and $39,300\, \text{cm}^{-1}$) must have taken place.

The complexity of the thallium (III) iodide equilibria however makes the interpretation of all these bands uncertain. Busev and Tiptsova (114) have suggested the following equilibria for solutions containing thallium (III) and excess of iodide ions:

$$
\text{Tl}^{3+} + 2\text{I}^- \rightleftharpoons \text{Tl}^+ + \text{I}_2
$$

$$
\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-
$$

$$
\text{Tl}^+ + \text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^+ + \text{Tl}^+
$$

When the dissociation of the tetra alkyl ammonium tetra iodothallate compounds is considered, similar equilibria
GRAPH (9)
ULTRAVIOLET ABSORPTION SPECTRA
(a) (C₂H₅)₄NI⁺ IN ETHANOL
(b) " " " PLUS EXCESS IODIDE IONS

\[ \varepsilon_m \times 10^4 \]

\[ \begin{array}{c}
5.0 \\
4.0 \\
3.0 \\
2.0 \\
1.0 \\
\end{array} \]

\[ \begin{array}{c}
51 \\
49 \\
47 \\
45 \\
43 \\
41 \\
39 \\
37 \\
35 \\
33 \\
31 \\
\end{array} \]

\[ \text{cm}^{-1} \times 10^{-3} \]
GRAPH (10)
ULTRA VIOLET ABSORPTION SPECTRUM OF
\((\text{C}_2\text{H}_5)_4\text{HTeI}_4\) IN ACETONITRILE.
would be expected:

\[ R_4\text{NTlI}_4 \rightarrow R_4\text{N}^+ + \text{I}^- + \text{TlI}_3^+ \]

\[ \text{Tl}^+ + \text{I}^- \]

On this basis one would expect some \( \text{I}_3^- \), \( \text{Tl}^+ \) and \( \text{I}^- \) absorption to take place and hence some of their characteristic bands should be observed.

Katzin (51) studied the absorption spectra of solutions containing the \( \text{I}_3^- \) ions and observed bands at \( 34,483\text{cm}^{-1} \) (290\text{m\mu}) and \( 28,571 - 27,778\text{cm}^{-1} \) (350 - 360\text{m\mu}). The two bands at \( 45,520\text{cm}^{-1} \) (219.7\text{m\mu}) and \( 52,500\text{cm}^{-1} \) (190.4\text{m\mu}) observed in the case of solutions containing iodide ions have already been discussed on page (87). With regard to the thallium (I) iodide absorption Jørgensen has quoted bands at \( 42,918\text{cm}^{-1} \) (233\text{m\mu}) and \( 35,461\text{cm}^{-1} \) (282\text{m\mu}) for absorption bands of thallium (I) phosphors in potassium iodide (58).

A consideration of the above indicates that a complete interpretation of the bands in these iodo complexes is difficult. However, a few suggestions as to their origin can be made. The \( 34,500\text{cm}^{-1} \) (289.9\text{m\mu}) band observed for the iodothallate solutions agrees very closely with both the \( \text{I}_3^- \) band (at \( 34,483\text{cm}^{-1} \)) observed by Katzin and with the \( \text{Tl(I)I} \) band (at \( 35,461\text{cm}^{-1} \)) quoted by Jørgensen. The fact that this band is shifted towards \( 33,000\text{cm}^{-1} \) (330\text{m\mu}) (Graph (9)) when excess iodide ion is added however indicates
that some $I_2^-$ absorption must be involved here. On con-
sidering the $39,300\text{cm}^{-1}$ bands (for the iodothallate
solutions) it is observed that this is fairly close in
position to the $42,918\text{cm}^{-1}$ band in the case of thallium (I)
iodide. The phosphor spectra are however measured in
the solid state and if the normal shift towards lower
frequencies on passing from the solid state into solution
is considered an even better agreement would be expected.

The far ultra-violet band (at $50,200\text{cm}^{-1}$) and its
shoulder (at $\sim 47,000\text{cm}^{-1}$) observed for the iodothallate
solution appear to be simple $I^-$ charge transfer (transfer
to the solvent) bands perhaps slightly modified in these
complex solutions.

The visible region spectra of solutions of the iodo-
thallate compounds are characterised by a single band at
$25,200\text{cm}^{-1}$ (396.8 $\mu\text{m}$) with an extinction coefficient of
$1.03 \times 10^4$ (graph (ii)). This band has been observed by
other workers for solutions of thallium (III) containing
an excess of iodide ions ($\text{I}_2^-$) and appears characteristic of
the $\text{TlI}_4^-$ ion. In fact when the position of the maximum,
the extinction coefficient ($\mathcal{E}$) and the oscillator strength
($F$) are compared, as in the case of the chloro and bromo
complexes (page 98), with the corresponding values for
the mercury iodide complex, a close analogy is observed.
Thus:
GRAPH (11)

VISIBLE ABSORPTION SPECTRUM OF

$(\text{C}_2\text{H}_5)_4\text{NTeI}_4$ IN ETHANOL.
Hence one can make the tentative suggestion that if this band is characteristic of the TlI₄⁻ chromophore, it must arise from an analogous transition i.e. \( e_n^b \rightarrow a_1^* \) (figure (a.3)).

The situation in the solid state is however different. The reflectance spectra of solids of the type \( R_4NTlI_4 \) are characterised by two bands at 25,641\( \text{cm}^{-1} \) (390\( \mu \text{m} \)) and at 21,277\( \text{cm}^{-1} \) (470\( \mu \text{m} \)) of almost equal intensity. A comparison of the reflectance (solid state in the visible region) with the visible absorption spectra (in solution) for the TlI₄⁻ compounds suggests that an overlap of the two bands occurs in solution which is distinguishable in the solid state. This would lead to the broad band. However an alternative possibility is that one band is absent in solution from a change in structure. The first suggestion appears more likely since the band in solution is broad and almost Gaussian in shape indicating that the two components from which it arises must be of equal intensity. A shift of the position of the bands on passing from solid to solution is furthermore expected.

The 25,641\( \text{cm}^{-1} \) band observed in the solid state could then arise from the I₃⁻ absorption (at 28,571 - 27,778\( \text{cm}^{-1} \))
GRAPH (12)

REFLECTANCE SPECTRA OF
(a) (C₂H₅)$_4$NTEI₄
(b) [CH₃(CH₂)₃]₄NTEI₄
(c) C₆H₅(CH₃)$_3$NTEI₄
whilst the $21,277\text{cm}^{-1}$ could be an iodine band (104). This interpretation is however only a tentative one and further study into the iodide compounds of thallium (III) both in the solid state and in solution seems necessary to obtain a conclusive result.
Some Intermediate Compounds of Thallium

The empirical formulae of the thallium dichloride TlCl₂, sesquichloride Tl₂Cl₃, dibromide TlBr₂ and sesquibromide Tl₂Br₃ suggest that thallium is divalent, whereas the common valencies of group IIIB elements are one and three. However the empirical formula for a crystalline substance is often misleading and it has been suggested (5) that the composition arises from equal proportions of univalent and tervalent metal atoms. They are thus regarded as thallium (I) halothallates (III) i.e. Tl⁺Tlx₄⁻ and 3Tl⁺[Tlx₆]²⁻ where X = chloride or bromide ion.

Meier and Garner (5) measured the magnetic susceptibilities of the di and sesquichlorides and, finding they were diamagnetic, concluded that there could not be thallium (II) in these compounds. Thallium (II) would contain an unpaired electron and exhibit paramagnetism. There is still however the possibility, suggested by these authors that the thallium may be present as the dimeric dipositive Tl₂²⁺ ion. McConnell and Davidson (6) have shown however by the use of radioactive Tl²⁰⁴ that the thallium atoms in Tl₂Cl₃ are not all equivalent and thus the structure Tl₂⁺TlCl₆ was again supported.

Because of their extreme insolubility in polar and non-polar solvents, the methods available for determining their structure are restricted. It was thought of
interest to measure their magnetic susceptibilities in the solid state and to see if any systematic relationship could be found in their molar susceptibilities. In the previous sections experimental molar susceptibility values for anions of the type TlX₄⁻ and TlX₆³⁻ (where X = Cl or Br) were obtained. Thus, assuming that the structures can be written as Tl₂[TlX₄⁻] and Tl₃[TlX₆⁻], simple subtraction of the respective anionic susceptibilities from the molar susceptibilities of the intermediate compound, would yield the ionic susceptibility for the thallium (I) ion. The latter can accordingly be compared with susceptibility values for the thallium (I) ion found by other workers (44, 45) using various thallium (I) compounds.

The above dihalides and sesquihalides were prepared following the methods which were described in the experimental section. The deliquescent nature of the dichloride, TlCl₂, made it necessary to handle this compound in the absence of moisture. The magnetic susceptibility measurements of all these compounds were carried out by the Gouy method, as described earlier.

Values for the specific and molar susceptibilities of the above compounds are shown in table (2). Columns 3 shows the susceptibility values for the anions TlCl₄⁻, TlBr₄⁻, TlCl₆³⁻ and TlBr₆³⁻ as found in sections (21, 22). The resultant ionic susceptibility value for thallium (I) for
It is observed from the above results that the ionic thallium (I) susceptibility as obtained from the various compounds is constant. A mean value of 29.15±0.17 c.g.s. units is thus obtained for this ion in these intermediate compounds. This susceptibility value is however lower than the corrected one obtained by Rew, Hussain and Siddiqui (66) of -33.8x10^{-6} c.g.s. units. In a later work Stephen (15) obtained a mean susceptibility of -32.9x10^{-6} c.g.s. units for Tl^+ from measurements on various thallium (I) salts such as the chloride and the perchlorate. This latter value is also higher than the one obtained in the present work.

A graphical comparison of the above results with those obtained for the compounds of thallium (III) with tetraalkyl
ammonium (section VI), 2-2' bipyridine and 1:10 phenanthroline (section VHI) groups can furthermore be made. This can be done by plotting the molar susceptibilities of the above compounds containing the same anion versus the effective atomic number of the cation. The resultant plots are shown in graphs (13) and (14) for the tetrachlorothallates and tetrabromothallates respectively. It is then observed that in both cases the values for the two intermediate compounds namely, $\text{Tl}^+\text{TlCl}_4^-$ and $\text{Tl}^+\text{TlBr}_4^-$ fall well below those for the other complexes.

An explanation of the above results may however be reached by considering various properties of these intermediate compounds. They are, with the exception of the dichloride or $\text{TlTlCl}_4^-$, very stable in the solid state and are markedly insoluble and inert. The low value for the thallium (I) ion susceptibility as found from these compounds can thus be regarded as arising from an appreciable reduction in the spread of the electronic field. Crystal structure measurements furthermore indicate that in the case of the $\text{TlTlBr}_4^-(\text{Tl-Br} = 2.51\text{Å})$ compound the Tl-Br distance is much shorter than in the analogous caesium compound namely $\text{CsTlBr}_4^-(\text{Tl-Br} = 2.65\text{Å})$. This thus indicates that a more condensed structure exists in these compounds.

The structures $\text{Tl}^+\text{TlX}_4^-$ and $\text{Tl}^+\text{TlX}_6^-$ furthermore suggest
GRAPH (13)
MOLAR MAGNETIC SUSCEPTIBILITIES OF
THE TETRACHLOROTHALLATES
○ (CH₃)₄NTeCl₄ × (C₆H₅)₄NTeCl₄
△ [TePh₄]Cl₂ TeCl₄
○ [TePh₂Cl₂]TeCl₄
• TeCl₄

GRAPH (14)
MOLAR MAGNETIC SUSCEPTIBILITIES OF
THE TETRA BROMOTHALLATES
○ (CH₃)₄NTeBr₄ × (C₆H₅)₄NTeBr₄
△ [TePh₄]Br₂ TeBr₄
○ [TePh₂Br₂]TeBr₄
• Te[TeBr₄]
the possibility of \( \pi - d \) bonding between \( \text{Tl}^+ \) and the \( \text{TlX}^- \) or \( \text{TlX}_6^- \) anions. This type of orbital mixing seems reasonable for atoms containing filled \( d^0 \) orbitals as in the \( \text{TlX}_4^- \) and \( \text{TlX}_6^3^- \) anions. The thallium (III) ion in these anions is stabilised by coordination with the halogen orbitals. The possibility of a further interaction between the empty outer orbitals of the thallium (I) with those of the complex anions \( \text{TlX}_4^- \) cannot then be ruled out. Such an interaction would cause a bond shortening effect, as noted by Hazell (7) in the crystal structure determination. It would lower the diamagnetism of the thallium (I) ion provided it is assumed that a normal allocation of the diamagnetism is given to the \( \text{TlX}_4^- \) anion.

**Reflectance and Ultra-Violet Absorption Spectra**

The insolubility of these dihalides and sesquihalides of thallium in most solvents made the study of their structures difficult. They are however deeply coloured and thus it was thought useful to determine their reflectance spectra. The positions of the maxima are given in table (23) while their reflectance spectra in the visible region are shown in graphs (15) and (16).

**TABLE 23**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{cm}^{-1} ) (( \text{m} \mu ))</th>
<th>Compound</th>
<th>( \text{cm}^{-1} ) (( \text{m} \mu ))</th>
<th>( \Delta \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{TlTlCl}_4 )</td>
<td>29,410 (340)</td>
<td>( \text{Tl}_2\text{TlCl}_6 )</td>
<td>26,040 (384)</td>
<td>3,370</td>
</tr>
<tr>
<td>( \text{TlTlBr}_4 )</td>
<td>(a) 28,169 (355)</td>
<td>(a) 25,120 (398)</td>
<td>3,049</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) 24,590 (410)</td>
<td>(b) 21,739 (460)</td>
<td>2,651</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c) 22,631 (438)</td>
<td>(c) 19,505 (518)</td>
<td>3,526</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Mean) 29,075</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[^1]: The symbol \( \Delta \) represents the change in frequency.

[^2]: \( \text{cm}^{-1} \) stands for centimeters per inverse centimeter.

[^3]: \( \text{m} \mu \) stands for millimicrons.
GRAPH (15)
reflectance spectra
(1) $T_{2-d}$
(2) $T_{4-d}$
It will be noted that in the solid state there is only evidence for a single broad band which in the case of the bromo complexes shows several small maxima. In the case of the chloro complexes the peaks differ in position for the two compounds, the band for the TlTlCl₄ occurring at shorter wavelengths than that for the Tl₂TlCl₆ compound. The spectra of the bromo compounds show three maxima as indicated in the above table with the positions shifted in the same sequence. It has been suggested that the colours of these compounds and hence the above bands arise from charge transfers involving the two states of thallium, i.e. univalent and tervalent thallium. In solution these compounds lose their colour.

Solutions of the order of 10⁻⁵ M in spectroscopically pure methanol were made up for these compounds and their ultraviolet spectra then measured. Graphs (17) and (18) show these spectra for the chlorides and bromides respectively in the range 50,000 - 33,000 cm⁻¹ (200-300 m). The positions of the maxima and respective extinction coefficients are listed in table (24).
In solution the absorption bands thus arise in the ultra-violet region. In both the chloro and the bromo compounds the positions of the maxima are coincident for each pair of compounds, their molar extinction coefficients however differ. The chlorides show three bands at 49,600 cm\(^{-1}\) (201.6 m\(\mu\)), 45,800 cm\(^{-1}\) (218.3 m\(\mu\)) and 38,600 cm\(^{-1}\) (259.1 m\(\mu\)). The bromides on the other hand are characterised by two bands at 46,000 cm\(^{-1}\) (217 m\(\mu\)) and 36,700 cm\(^{-1}\) (272.5 m\(\mu\)).

The bands observed in solution show no apparent resemblance to those of the TlCl\(_4^-\) and TlBr\(_4^-\) cations observed in section (VI). Furthermore they do not occur in the range where bands are observed in solutions of simple halide ions (section (V)). It will be noted that they are considerably more intense than the bands for the halothallates.

A comparison of the positions of the maxima obtained in the present work for solutions of these dihalides and sesquihalides shows that they are in close agreement with

<table>
<thead>
<tr>
<th>Compound</th>
<th>cm(^{-1})(m(\mu))</th>
<th>(\varepsilon) (\times) 10(^{-3})</th>
<th>cm(^{-1})(m(\mu))</th>
<th>(\varepsilon) (\times) 10(^{-3})</th>
<th>cm(^{-1})(m(\mu))</th>
<th>(\varepsilon) (\times) 10(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl(_2)Cl(_6)</td>
<td>49,600 (201.6)</td>
<td>62.5</td>
<td>45,800 (218.3)</td>
<td>56.0</td>
<td>38,600 (259.1)</td>
<td>12.0</td>
</tr>
<tr>
<td>Tl(_2)Br(_6)</td>
<td>46,000 (217.4)</td>
<td>44.5</td>
<td>36,700 (272.5)</td>
<td>16.2</td>
<td>36,700 (272.5)</td>
<td>24.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>cm(^{-1})(m(\mu))</th>
<th>(\varepsilon) (\times) 10(^{-3})</th>
<th>cm(^{-1})(m(\mu))</th>
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<td>56.0</td>
<td>38,600 (259.1)</td>
<td>12.0</td>
</tr>
<tr>
<td>Tl(_2)Br(_6)</td>
<td>46,000 (217.4)</td>
<td>44.5</td>
<td>36,700 (272.5)</td>
<td>16.2</td>
<td>36,700 (272.5)</td>
<td>24.2</td>
</tr>
</tbody>
</table>
GRAPH(17)

ULTRA VIOLET ABSORPTION SPECTRA OF
(a) Te₄Cl₆ in METHANDL
(b) Te₂Cl₄ in METHANDL
GRAPH (18)
ULTRAVIOLET ABSORPTION SPECTRA
(a) Tl₂Br₄ in methanol
(b) Te₄Br₆ in methanol
those previously observed by other workers (61-61) in the spectra of thallium (I) incorporated in crystals of the alkali halides. Seitz in 1938 observed for all these alkali halide phosphors a characteristic pattern of three peaks, namely at about 40,100 (peak A), 47,500 (peak B) and 50,500 (peak C) cm\(^{-1}\). The latter two were found however to be incompletely resolved. This incomplete resolution was also found to be the case for the dibromide and sesquibromide compounds in the present work. These spectra show only two peaks (see table (24)). A theoretical interpretation of the absorption and emission spectra of the thallium (I) halide phosphors at various temperatures was made by Williams and Johnson (69). They tentatively deduced that the absorption bands of KCl:Tl at 51,020 cm\(^{-1}\) (196 μ) and 40,160 cm\(^{-1}\) (249 μ) having oscillator strengths of approximately 0.1 electron volt arise from the \(^{3}P_{0} \rightarrow ^{3}P_{1}\) and \(^{3}P_{0} \rightarrow ^{3}P_{1}\) transitions in the thallium ions respectively.

As already stated the methanolic solutions of the thallium dihalides and sesquihalides give analogous absorption bands to those of the phosphors though slightly shifted towards lower wave numbers. This type of shift on passing from solid to solutions was also observed by Glasner and Reisfield (70) for antimony (III) and bismuth (III) halide phosphors studied in solution and the solid state and
thus the assignment of these bands to be a thallium (I) transition here would appear reasonable.

The separation of the bands observed here for the chloride and bromide complexes of thallium are furthermore shown in table (25).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(A-B) cm(^{-1}) (e.v.)</th>
<th>(A-C) cm(^{-1}) (e.v.)</th>
<th>(B-C) cm(^{-1}) (e.v.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorides</td>
<td>3,800 (0.471)</td>
<td>11,000(1.363)</td>
<td>7,200 (0.893)</td>
</tr>
<tr>
<td>Bromides</td>
<td></td>
<td>9,300(1.153)</td>
<td></td>
</tr>
</tbody>
</table>

It should furthermore be noted that Merrit and Co-workers in their analytical study of thallium (I) halide compounds observed some absorption bands which are in close agreement with those discussed above. Solutions of thallium (I) in 6M HCl and 6M NaBr showed bands at 39,840 cm\(^{-1}\)(251 m\(\mu\)) and 37,740 cm\(^{-1}\)(265 m\(\mu\)) respectively.

In view of the above facts it seems appropriate to suggest that the absorption bands observed here from solutions of the thallium dihalides and sesquihalides must also arise from transitions involving the Tl\(^+\) energy levels. On considering the straightforward dissociation of the compound as

\[ \text{Tl}_3\text{TL}_2\text{X}_6 \rightarrow 3\text{Tl}^+ + \text{TlX}_2^- \rightarrow 3\text{Tl}^+ + \text{TlX}_4^- + 2X^- \]

it can be seen that the thallium (I) cation and the TlX\(_4^-\) anions should both be present in solution and should be the
the sources of spectroscopic transitions. If it is assumed that there is no complete decomposition of the TlX$_4^-$ ion, one thus would expect the characteristic bands of the TlCl$_4^-$ (40,600 cm$^{-1}$) and TlBr$_4^-$ (45,300 and 36,300 cm$^{-1}$) also to appear. The fact that no clear indication of the tetrahalothallate bands is found (graph (17)) on initial inspection can be clarified by considering the intensity of the various bands and examining the shape of the 45,800 cm$^{-1}$ band.

From the extinction coefficients in table (24) it is observed that the absorption bands from the Tl$^{4+}$TlX$_4^-$ and Tl$_3^+TlX_6^-$ solutions are very intense. The halothallate bands which are discussed in section (17), on the other hand are considerably weaker with extinction coefficients of $1.85 \times 10^4$ (TlCl$_4^-$), $2 \times 10^4$ and $3.28 \times 10^4$ (TlBr$_4^-$). Restricting the discussion to the chloride complexes it can be seen from graph (17) that the TlCl$_4^-$ bands will be entirely masked in the range 51,000-45,000 cm$^{-1}$, but will give a small contribution to the observed spectrum over the range 45,000-42,000 cm$^{-1}$. Since any observed spectrum is additive for the various absorbing species present the non-Gaussian shape of the broad 45,000 - 42,000 cm$^{-1}$ band in this region can be ascribed to a contribution from the TlCl$_4^-$ absorption. This argument was furthermore supported by means of a more quantitative although approximate treatment as follows.
The intensities of the thallium (I) absorption bands ($\varepsilon_{\text{max}} \sim 3 \times 10^5$) as those of the $\text{TlCl}_4^-$ bands obtained in the present work, were plotted together and compared. Addition of the separate intensities gave then a total absorption curve which showed a characteristic distortion of the $45,300\text{cm}^{-1}$ band as in the experimental curve (graph (17)). This thus indicates that the contribution of the $\text{TlCl}_4^-$ in this range must be a significant one, although the treatment is only approximate because it is not possible to make an allowance for the shift of the phosphor bands on passing from the solid state to solution.

For the $\text{TlTlBr}_4$ and $\text{Tl}_3\text{TlBr}_6$ compounds the situation is analogous. In this case however the $\text{TlBr}_4^-$ bands ($45,300$ and $36,300\text{cm}^{-1}$) are entirely masked by the thallium (I) bands, although the total intensity must again be partly determined by a contribution from the thallium (I) and $\text{TlBr}_4^-$ bands.
Comparison between Theoretical and Experimental Diamagnetic Susceptibilities

Diamagnetism is a property of all atomic systems arising from the precession of the electronic orbits under the action of the external magnetic field. For a poly-electronic atom both classical mechanics and quantum mechanics lead to the expression

\[ \chi_A = -\frac{Ne^2}{6mc^2} \sum \vec{r}_n^2 \] (71)

for the atomic susceptibility. This is the Langevin equation for diamagnetic susceptibility of a spherically symmetrical gram atom or ion, deduced on a simple classical model of a point nuclear charge with a single electron rotating in an orbit at a distance \( a_0 \). In this expression \( N \) (6.025 x 10^{23} \text{ mol}^{-1}) is the Avogadro's number, \( e \) (4.80294 x 10^{-10} \text{ e.s.u.}) the unit of electrostatic charge, \( c \) (2.9979 x 10^{10} \text{ cm sec}^{-1}) the velocity of light and \( m \) (9.1086 x 10^{-28} \text{ gm}) the mass of the electron. The expression \( \sum \vec{r}_n^2 \) represents the sum of the squares of the projections of the orbits for all the electrons on a plane perpendicular to the field direction. On substituting for the above constants the following expression is obtained

\[ \chi_A = -2.829 \times 10^{10} \sum \vec{r}_n^2 \]

but when \( \vec{r} \) is expressed in units of \( a_0 \) (0.53 x 10^{-8} \text{ cm}), the normal radius of the hydrogen atom, this becomes
Calculations of diamagnetic susceptibilities of atoms or ions thus depend on the determination of the value for the mean square radius of the atomic or ionic orbitals. The term $\sum_n \xi^2$ can be calculated for atoms and ions by a number of different semi-empirical methods and in a few simple cases (such as light ions) may be evaluated by use of Hartree's self-consistent field functions. From this the radial charge distribution function in the atom or ion is obtained. Of the other methods available \(11\) for the determination of $\sum_n \xi^2$, Brindley \(12\) has shown that the Slater method \(7\) gives results in good agreement with experimental susceptibilities for most atoms and ions. This method was thus employed here to calculate the susceptibilities of the thallium atom and thallium ions.

In this method the mean square radius is derived for the various electronic shells from the nuclear charge, the effective quantum number of the atom and the screening constant for the particular shell. Then

$$\sum_n \xi^2 = \frac{(n')^2(n' + 1)(n' + 1)}{(Z - S)^2}$$

for the atomic system. $n'$ is the principal quantum number modified for screening of nuclear charge, $(Z - S)$ is the effective nuclear charge for each electron considered, $Z$ being the actual nuclear charge of the atom or ion and $S$ the screening constant giving the fraction of the nuclear charge screened by core
electrons for any particular shell. Following Slater's rules for determining \( n' \) and \( S \), the susceptibility is obtained by summing over all the electronic shells in the ion.

Slater's rules for determining \( n' \) and \( S \) are as follows:

1. For given values of \( n \), values of \( n' \) are assigned:

   \[
   \begin{align*}
   n & : 1 \text{ } 2 \text{ } 3 \text{ } 4 \text{ } 5 \text{ } 6 \\
   n' & : 1 \text{ } 2 \text{ } 3 \text{ } 3.7 \text{ } 4.0 \text{ } 4.2
   \end{align*}
   \]

2. The electrons are then divided into groups, with \( S \) and \( p \) electrons of the same \( n \) together, but with \( d \) and \( f \) electrons taken separately. When dealing with \( d \) electrons the \( S \) and \( p \) electrons of the same principal quantum number count as the group below. For each group of electrons the screening constants are calculated by the following method. The individual screening constant for all \( S \) electrons is taken as 0.30. For \( S \) and \( p \) electrons for the group immediately below, it is 0.85. For all other lower groups the screening constant for each electron is 1.00. For \( d \) and \( f \) electrons in lower groups it is 1.00.

By using these rules the screening constants and hence the \( \Sigma \xi^2 \) values were obtained for the various electronic shells of thallium atom and ions derived from it as shown to two places in Table (26). The susceptibilities are then obtained from \( \Sigma \xi^2 \) using the Langevin equation.
The following values are thus obtained for the susceptibilities of the central metal atom in various oxidation states:

\[-10^6 \chi_{\text{Tl}^0} = 0.7923 \geq 101.15 = 80.14\]
\[-10^6 \chi_{\text{Tl}^+} = 0.7923 \geq 79.50 = 62.99\]
\[-10^6 \chi_{\text{Tl}^{2+}} = 0.7923 \geq 62.64 = 49.63\]
\[-10^6 \chi_{\text{Tl}^{3+}} = 0.7923 \geq 49.37 = 39.12\]

Theoretical Calculations of the Ionic Susceptibilities of the Tetrahalothallate and Hexahalothallate anions

A theoretical value for the ionic susceptibilities of anions of the type TlX$_4^-$ and TlX'$_6^-$ (where X = Cl, Br or I and X' = Cl or Br) can be obtained for comparison with the experimental values obtained in the previous section. Allowance is made for the electronegativity difference between the atoms forming the bonds. The ionic suscepti-
bility calculated in this way is however uncorrected for any bond effect or bond depression. The method is similar to that used by Trew and Husain in calculating the susceptibilities of the \( \text{NO}_3^- \) ion and developed subsequently by Trew, Husain and Siddiqi (paper in press) and Trew and Stephen (65). It is applied as follows to the ions concerned here. Consider the tetrahedral anion

\[
\begin{align*}
\text{X} & \quad \text{Tl} \\
\text{X} & \quad \downarrow \\
\text{X} & \quad \text{X}
\end{align*}
\]

where \( \text{X} = \text{Cl}, \text{Br} \) or \( \text{I} \).

Pauling has suggested that the negative charge is distributed over the whole surface of the ion, each halogen atom being assigned a quarter of the whole charge.

For the \( \text{TlCl}_4^- \) anion, the electronegativity difference between thallium and chlorine is 1.2 units as the respective electronegativities are \( \text{Tl} = 1.8, \text{Cl} = 3.0 \) (74). From the graph which relates the electronegativity difference between atoms and the percentage ionic character of the bond, the above difference gives a 30% ionic character. The single thallium-chlorine bond may then be represented as:

\[
\begin{align*}
+0.3 & \quad \text{Tl} \\
-0.5 & \quad (-0.25) \\
\text{Cl}
\end{align*}
\]

adding the 0.25 charge from the negative charge of the ion to that already on the halogen. On considering the four bonds, a total charge of 1.2 is thus found on the central metal atom. The ionic and atomic susceptibility constants
for thallium (i.e. for Tl\textsuperscript{0}, Tl\textsuperscript{+}, Tl\textsuperscript{2+}, and Tl\textsuperscript{3+}) and those for the halogens (i.e. Cl\textsuperscript{0}, Cl\textsuperscript{-}, Br\textsuperscript{0}, Br\textsuperscript{-}, I\textsuperscript{0}, I\textsuperscript{-}) obtained by Slater and corrected by Stephen were then employed to determine the susceptibilities of the thallium anions.

Allowing for the appropriate charge distribution:

\[
-10^6 \chi_{(\text{TlCl}_4^-)} = (0.2 Tl^{2+} + 0.8 Tl^+) + 4(0.55 Cl^- + 0.45 Cl^0)
\]

\[
= \left(0.2 \times 49.03 + 0.8 \times 62.99\right) + 4(0.55 \times 25.32) + \\
\]

\[
-10^6 \chi_{\text{TlCl}_4^-} = 152.08 \text{ c.g.s. units (ergs oersted}^{-1}\text{mole}^{-1})
\]

This value of the ionic susceptibility is uncorrected for bond depression. An estimate of the lowering of diamagnetism produced by bond formation (i.e. the bond depression) can be made by use of the covalent radii of the atoms corrected by a bond shortening effect calculated from the known bond lengths derived from crystal structure determinations. Since the diamagnetic susceptibility is related to the mean square radius, by the Langevin equation

\[
-10^6 \chi = 0.7923 \sum r^2
\]

a corrected value for the bond effect for the ionic susceptibility is given by

\[
-10^6 \chi \text{ (corrected)} = -10^6 \chi \frac{r_1^2}{r_2^2}
\]

where \(r_1^2\) is obtained from the square of the experimental bond lengths between thallium and the halogen and \(r_2^2\) is the square of the sum of the normal ionic radii deduced by
Pauling. Thus for the \( \text{TlCl}_4^- \) ion:

\[
-10^6 \chi_{\text{TlCl}_4^-} (\text{corrected}) = 152.08 \times \frac{(2.55)^2}{(2.86)^2}
\]

\( r_1 = 2.55\text{Å} (4) \) and \( r_2 = 2.86\text{Å} (115) \)

\[
-10^6 \chi_{\text{TlCl}_4^-} (\text{corrected}) = 120.84
\]

This figure agrees very well with the experimental value of 120.5.

The anionic susceptibilities for \( \text{TlBr}_4^- \) and \( \text{TlI}_4^- \) can be calculated similarly.

The electronegativity difference between thallium and bromine is one unit (\( \text{Tl} = 1.8; \text{Br} = 2.8 \)) and the corresponding ionic character for the bond is 22%. Thus the bond can be represented as:

\[
\begin{array}{c}
\text{Tl} \\

\hline
+0.22
\end{array}
\begin{array}{c}
\text{Br} \\

-0.22+(0.25)
\end{array}
\]

On summing for the four bonds a total charge of +0.88 is obtained on the central metal.

\[
-10^6 \chi_{(\text{TlBr}_4^-)} = (0.88\text{Tl}^+ + 0.12\text{Tl}^0) + 4(0.47\text{Br}^0 + 0.53\text{Br}^-)
\]

\[
= (0.88 \times 62.99 + 0.12 \times 80.14) + 4((0.47 \times 32.81 + 0.53 \times 59.40))
\]

\[
= 210.25 \text{ c.g.s. units.}
\]

The literature shows two values for the \( \text{Tl-Br} \) bond length in \( \text{MTlBr}_4 \) complexes (8). In the case of \( \text{KTLBr}_4\cdot2\text{H}_2\text{O} \) a bond length for the \( \text{Tl-Br} \) bond of 2.75Å is recorded and for \( \text{CsTlBr}_4 \) the value is 2.65Å. If the ionic radius of 3.01Å is used for \( \text{Tl-Br} \) and calculations made for a
corrected susceptibility as above, using each of these two experimental values, figures of 175.4 c.g.s. units and 162.9 c.g.s. units are obtained respectively. It is evident that the shorter bond length derived from the anhydrous CsTlBr$_4$ gives the better agreement with the experimental susceptibility of 161.6 c.g.s. units.

In the case of the TlI$_4^-$ anion the electronegativity difference between the atoms is 0.7 units (Tl = 1.8; I = 2.5). This value corresponds to 11% ionic character as obtained from Pauling’s graph. Furthermore a total charge of 0.44 is obtained when the four bonds are considered:

$$\chi(TlI_4^-) = (0.56Tl^+ + 0.44Tl^0) + 4(0.36I^0 + 0.64I^-)$$

$$= (0.56 \times 62.99 + 0.44 \times 80.14) + 4(0.36 \times 50.12 + 0.64 \times 58.74)$$

$$= 293.05 \text{ c.g.s. units.}$$

A search through the literature for an experimental Tl-I distance indicated that no published value was available. An approximate value was however obtained by plotting the covalent distances (for Tl-Cl, Tl-Br, Tl-I) and the known experimental distances for Tl-Cl and Tl-Br versus the respective atomic numbers as in graph (19). The covalent plot was found to approximate to a straight line and thus by extrapolation of the experimental plot for the Tl-Cl and Tl-Br distances a value of 2.76 was obtained for the Tl-I distance. Using this value and the covalent distance
GRAPH (12)
(a) COVALENT Te-X DISTANCES
(b) EXPERIMENTAL Te-X DISTANCES

(TE - X) DISTANCE

ATOMIC NUMBER
for Tl—I it is thus possible to correct the above susceptibility value for the $(\text{TlI}_4)^-$:

$$\chi_{\text{TlI}_4\text{(corrected)}} = 293.1 \times \frac{(2.76)^2}{(3.16)^2} = 223.6 \text{ c.g.s. units}$$

$$r_2 = \text{Tl—I} \text{ (covalent radii)} = 3.16.$$ 

This method therefore gives a value which is in good agreement with the experimental one of 224.0. The susceptibility measurements thus indicate a bond length for the Tl—I bond of 2.76Å from this comparison with those of the Tl—Cl, Tl—Br bonds.

The theoretical calculation for the TlCl$_6^{3-}$ and TlBr$_6^{3-}$ anions can be made similarly. Consider the octahedral anion

$[\begin{array}{ccc} X & \vdots & X \\ X & \vdots & X \\ & Tl & X \\ X & \vdots & X \end{array}]_{3-}$

where $X = \text{Cl}$ or $\text{Br}$. The electronegativity difference between the two atoms is as above, 1.2 units, giving a percentage ionic character of 30%. The single thallium chlorine bond in this anion may then be represented as

$$\begin{array}{ccc} +0.3 & -0.3+(0.5) \\ \text{Tl} & \text{Cl} \end{array}$$

adding the 0.5 charge from the negative charge of the whole ion. On considering the six bonds, a total charge of 1.8 is thus assigned to the thallium atom. By allowing for the charge distribution, the susceptibility for the anion TlCl$_6^{3-}$ can be obtained:
\[-10^6 \chi_{\text{TlCl}_6^{3-}} = (0.8\text{Tl}^{2+} + 0.2\text{Tl}^+) + 6(0.8\text{Cl}^- + 0.2\text{Cl}^0) \]
\[= (0.8 \times 49.63 + 0.2 \times 50.99) + 6(0.8 \times 25.32 + 0.2 \times 20.22) \]
\[= 197.85 \]
Correcting for bond depression
\[-10^6 \chi_{\text{TlCl}_6^{3-}} = 197.85 \times \left(\frac{2.55}{2.86}\right)^2 \]
\[-10^6 \chi_{\text{TlCl}_6^{3-}} \text{ (corrected)} = 157.2 \]

This is somewhat lower than the experimental value of 169.9. This point will be considered later.

For the TlBr\(_6^{3-}\) anion the electronegativity difference is again one unit and hence the percentage ionic character is 0.22. The bond may thus be represented as

\[
\begin{array}{c}
\text{Tl} \\
\hline
+0.22 \\
\end{array} \quad \begin{array}{c}
\text{Br} \\
-0.22+(-0.5) \\
\end{array}
\]

On considering the six bonds a total charge of +1.3 is obtained. Similarly allowing for the charge distribution
\[-10^6 \chi_{\text{TlBr}_6^{3-}} = (0.32\text{Tl}^+ + 0.68\text{Tl}^{2+}) + 6(0.77\text{Br}^- + 0.23\text{Br}^0) \]
\[= (0.32 \times 62.99 + 0.68 \times 49.63) + 6(0.77 \times 39.4 + 0.23 \times 23.81) \]
\[= 281.25 \]
Correcting for bond depression then
\[-10^6 \chi_{\text{TlBr}_6^{3-}} \text{ (corrected)} = 281.3 \times \left(\frac{2.70}{3.01}\right)^2 \]
\[-10^6 \chi_{\text{TlBr}_6^{3-}} \text{ (corrected)} = 226.3 \]

This value is in reasonable agreement with the experimental value of 227.7.
At this stage it seems of interest to make a general comparison of the various theoretical susceptibilities for the anions $\text{TlX}_4^-$ and $\text{TlX}_6^{3-}$ with those values obtained by experiment. Table (21) shows the various anions studied here (column 1), their respective calculated susceptibilities uncorrected for the effect of bond length (column 2) and those values calculated and corrected for the above effect (column 3). The experimental anionic susceptibilities are shown in column 4 and the compounds from which these experimental values were obtained listed in column 5 of the same table.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Calculated Molar Susceptibilities</th>
<th>Experimental Molar Susceptibilities</th>
<th>Derived from</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uncorrected</td>
<td>Corrected</td>
<td></td>
</tr>
<tr>
<td>$\text{TlCl}_4^-$</td>
<td>$152.1 \times 10^{-6}$</td>
<td>$120.8 \times 10^{-6}$</td>
<td>$120.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{TlBr}_4^-$</td>
<td>$210.3 \times 10^{-6}$</td>
<td>$162.9 \times 10^{-6}$</td>
<td>$161.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{TlI}_4^-$</td>
<td>$293.1 \times 10^{-6}$</td>
<td>$223.6 \times 10^{-6}$</td>
<td>$224.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{TlCl}_6^{3-}$</td>
<td>$197.9 \times 10^{-6}$</td>
<td>$157.2 \times 10^{-6}$</td>
<td>$169.9 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{TlBr}_6^{2-}$</td>
<td>$281.3 \times 10^{-6}$</td>
<td>$226.3 \times 10^{-6}$</td>
<td>$227.7 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

$R$ = alkyl group and $M$ = alkali metal or ammonium ion.

The table shows that on the whole, agreement is good between the calculated susceptibilities corrected for the effect of bond length and the experimental values. The lower bond length in the case of Tl-Br appears to be the more correct value, since it gives a calculated figure in
good agreement with the experimental. Furthermore it is a value derived from an anhydrous salt (CsTlBr$_4$). The figure derived from K$_4$TlBr$_4$.2H$_2$O, may show some effect of hydration. The only considerable discrepancy between experimental and calculated susceptibilities is in the case of the TlCl$_6^{2-}$ ion. The susceptibility of the TlCl$_6^{2-}$ ion was derived from the series of alkali chlorothallates. These are all hygroscopic compounds and in addition contain water of crystallisation in the normal crystalline form. In preparing them for the magnetic measurements the water, including that of crystallisation, was removed by dehydration in vacuo over sulphuric acid at room temperature and measurements were made after packing in a dry box. The good agreement for the anion susceptibility for the whole series of salts (Na$^+$ and Li to Cs) would indicate that any experimental error is comparable for the whole series. The method of dehydration however might involve leaving the lattice arrangement of the hydrated form rather than that of a true anhydrous salt. This effect would lead to an enhanced molar susceptibility. The other hexahalothallate measured, namely the Rb$_3$TlBr$_6$ salt, although hydrated, is much less hygroscopic and the anion susceptibility from this was found to be closer to the calculated value though still slightly above it.
SECTION VIII
2-2' Bipyridine and 1:10 Phenanthroline Complexes

Halide Complexes

In the general introduction reference was made to the earlier work of Sutton (23) on the 2-2' bipyridine and 1:10 phenanthroline complexes. He prepared a number of complexes of thallium (III) containing three ligands with various anions and made an attempt to establish their structure on the basis of molecular weight determinations and conductance measurements in nitrobenzene. He suggested the following dimeric structures for these cationic complexes of type \[\text{Tl Org}_2\ X_{2'}X\] and \[\text{Tl Org}_2\ X_{2}X\text{Tl X}_4\], but their structures were by no means fully established. (In the formulae Org = 2-2' bipyridine or 1:10 phenanthroline and X = Cl, Br, I and X' = I.)

No further work appears to have been done on these complexes probably as they are relatively insoluble in most solvents. It was considered, however, that systematic magnetic susceptibility measurements on the solid compounds would be of interest which together with a further study of their conductances in other solvents should throw further light on their structure. In addition the infrared and reflectance spectra of the solids and the ultraviolet absorption spectra of solutions in methanol were investigated. These complexes are sufficiently soluble.
in nitrobenzene, nitromethane, acetone, methanol and ethanol to give solutions of a strength appropriate for conductance and absorption spectroscopy measurements to be attempted. The solubility in methanol and ethanol is less than in the other solvents.

During the course of the preparation of the iodine containing compounds of bipyridine, two isomeric forms of the iodothallate complex $\text{[Tl}bipy_2I_2\text{]}^-$ were obtained, depending on the method of preparation (see page (11)). A yellow and a red form were isolated, the red compound being the less soluble of the two when aqueous alcoholic solutions were employed as solvents. It seemed possible from their analytical composition that they were two different geometrical isomers and experimental measurements of the various properties were carried out to investigate this possibility. An attempt was made to prepare isomeric 1:10 phenanthroline complexes by similar methods to those used for bipyridine but with no success.

Magnetic measurements were carried out in the solid state; conductance measurements were obtained in nitrobenzene, nitromethane and acetone. Conductivity measurements in nitrobenzene (used by Sutton) were carried out as
a check. Their near infra-red spectra were studied and their ultra-violet absorption spectra measured in methanol solutions. For the only coloured compounds, the iodides, their visible and reflectance spectra were measured.

**Magnetochemical Measurements**

The magnetic susceptibilities of these compounds were measured at room temperature by the Gouy method details of which have been given in the 'Physical Measurements Section'. Because of the fine nature of these solids and thus their tendency to cake on packing similar precautions to those mentioned in the case of the quaternary ammonium compounds, had to be taken.

The magnetochemical evidence and the structure of 2-2' Bipyridine and 1:10 Phenanthroline complexes

Table (48) shows both the specific and molar susceptibilities of these complexes.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$-10^6 \chi_a$</th>
<th>$-10^6 \chi_M$</th>
<th>Compound</th>
<th>$-10^6 \chi_a$</th>
<th>$-10^6 \chi_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>${\text{TlBipy}_2\text{Cl}_2} \text{Cl}_4$</td>
<td>0.3739</td>
<td>351.4</td>
<td>${\text{TlPhen}_2\text{Cl}_2} \text{Cl}_4$</td>
<td>0.3881</td>
<td>381.9</td>
</tr>
<tr>
<td></td>
<td>0.3749</td>
<td></td>
<td></td>
<td>0.3899</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3787</td>
<td></td>
<td></td>
<td>0.3891</td>
<td></td>
</tr>
<tr>
<td>${\text{TlBipy}_2\text{Br}_2} \text{Br}_4$</td>
<td>0.3255</td>
<td>395.5</td>
<td>${\text{TlPhen}_2\text{Br}_2} \text{Br}_4$</td>
<td>0.3393</td>
<td>427.7</td>
</tr>
<tr>
<td></td>
<td>0.3281</td>
<td></td>
<td></td>
<td>0.3411</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3296</td>
<td></td>
<td></td>
<td>0.3427</td>
<td></td>
</tr>
<tr>
<td>${\text{TlBipy}_2\text{I}_2} \text{I}_4$ (Red)</td>
<td>0.3055</td>
<td>459.2</td>
<td>${\text{TlPhen}_2\text{I}_2} \text{I}_4$</td>
<td>0.3202</td>
<td>490.1</td>
</tr>
<tr>
<td></td>
<td>0.3101</td>
<td></td>
<td></td>
<td>0.3230</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3136</td>
<td></td>
<td></td>
<td>0.3177</td>
<td></td>
</tr>
<tr>
<td>${\text{TlBipy}_2\text{I}_2} \text{I}_4$ (Yellow)</td>
<td>0.3103</td>
<td>465.5</td>
<td>${\text{TlPhen}_2\text{I}_2} \text{I}_4$</td>
<td>0.3351</td>
<td>316.5</td>
</tr>
<tr>
<td></td>
<td>0.3150</td>
<td></td>
<td></td>
<td>0.3371</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3165</td>
<td></td>
<td></td>
<td>0.3324</td>
<td></td>
</tr>
<tr>
<td>${\text{TlBipy}_2\text{I}_2} \text{I}$</td>
<td>0.3201</td>
<td>288.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3199</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3251</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The magnetic evidence as obtained in this work can be shown to support the dimeric structures of these complexes with two of the halogen atoms inside the coordination sheath. These structures as mentioned above are given by the formulae:

$\{\text{Tl} \text{Bipy}_2 \text{X}_2 \} \text{Tl} \text{X}_4$  where $X = \text{Cl, Br or I}$

$\{\text{Tl} \text{Bipy}_2 \text{X}_2 \text{X'} \}$  where $X' = \text{I}$ and

$\{\text{Tl} \text{Phen}_2 \text{X}_2 \} \text{Tl} \text{X}_4$  where $X = \text{Cl, Br or I}$

$\{\text{Tl} \text{Phen}_2 \text{X}_2 \text{X'} \}$  where $X' = \text{I}$
In Table (29) the comparative molar susceptibility increments from halogen to halogen are shown for compounds of the type $\text{Tl Org}_2 X_2 \text{Tl} X_4$ where Org = 2-2' bipyridine or 1:10 phenanthroline and X as stated above. In columns 3 - 5 the increments between the chloride-bromide, bromide-iodide and chloride-iodide complexes are given, while in column 6 there is shown four times the ionic susceptibility of the halide ions.

As previously stated the work of Brindley and Hoare (21) and later of Trew and Hussein (21), has shown that for a single halide ion the increments are $\text{Br} - \text{Cl} \Delta \chi = 10.5$


$$\text{Br}^- - I^- \Delta \chi = 15.8; \quad \text{Cl}^- - I^- \Delta \chi = 26.3. \quad \text{It would be expected from the empirical formula of these complexes}$$

$$[\text{Tl}_2 \text{Crg}_2 \text{X}_2]^+ \text{Tl} \text{X}_4$$

$$\text{that the increments on passing from chloride to bromide, bromide to iodide and chloride to iodide would be those for six halogen atoms /e.g.}$$

$$\text{Tl}_2 \text{Crg}_2 \text{Br}_6 - \text{Tl}_2 \text{Crg}_2 \text{Cl}_6$$.

$$\text{This would give in the three cases total increments of 63.0, 94.8 and 157.8 for the chloride-bromide, bromide-iodide and chloride-iodide transitions respectively.}$$

$$\text{The results in Table (29) show however that the increments are considerably lower than for six halogens and in fact are only slightly greater than those for four.}$$

$$\text{It is clear that two of the halogen atoms are contributing far less than their normal amount to the diamagnetism in the large cation.}$$

$$\text{In the previous section experimental values for the anion susceptibilities of } \text{TlCl}_4, \text{TlBr}_4 \text{ and } \text{TlI}_4 \text{ were obtained.}$$

$$\text{On the assumption that the dimeric formula is correct subtraction of these ionic values from the molar susceptibilities of these compounds gives an ionic susceptibility for the cations } [\text{Tl}_2 \text{Crg}_2 \text{Cl}_2]^+, [\text{Tl}_2 \text{Crg}_2 \text{Br}_2]^+ \text{ and } [\text{Tl}_2 \text{Crg}_2 \text{I}_2]^+$$

$$\text{as shown in column 6 of Table (30). Columns 2, 3, 4 and 5 of the same table show the molar susceptibilities, effective atomic number of the anions, mean magnetic susceptibilities of anion and effective atomic number of the cations respectively.}$$
TABLE 30

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-10^6 \chi_M$</th>
<th>$\varepsilon Z$ Anion</th>
<th>$-10^6 \chi_M$ Cation</th>
<th>$\varepsilon Z$ Cation</th>
<th>$-10^6 \chi_M$ Cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TlBipy$_2$Cl$_2$)$_2$</td>
<td>351.4</td>
<td>150</td>
<td>120.5</td>
<td>278</td>
<td>230.9</td>
</tr>
<tr>
<td>(TlBipy$_2$Br$_2$)$_2$</td>
<td>395.5</td>
<td>222</td>
<td>161.6</td>
<td>314</td>
<td>233.9</td>
</tr>
<tr>
<td>(TlBipy$_2$I$_2$)$_2$</td>
<td>459.2</td>
<td>294</td>
<td>224.9</td>
<td>350</td>
<td>234.3</td>
</tr>
<tr>
<td>(TlBipy$_2$I$_2$)$_2$(Red)</td>
<td>465.5</td>
<td>294</td>
<td>224.9</td>
<td>350</td>
<td>240.6</td>
</tr>
<tr>
<td>(TlBipy$_2$I$_2$)$_2$(Yellow)</td>
<td>288.7</td>
<td>54</td>
<td>50.6*</td>
<td>350</td>
<td>238.1</td>
</tr>
<tr>
<td>(TlPhen$_2$Cl$_2$)$_2$</td>
<td>381.9</td>
<td>150</td>
<td>120.5</td>
<td>302</td>
<td>261.4</td>
</tr>
<tr>
<td>(TlPhen$_2$Br$_2$)$_2$</td>
<td>425.7</td>
<td>222</td>
<td>161.6</td>
<td>338</td>
<td>264.1</td>
</tr>
<tr>
<td>(TlPhen$_2$I$_2$)$_2$</td>
<td>490.1</td>
<td>294</td>
<td>224.9</td>
<td>374</td>
<td>265.2</td>
</tr>
<tr>
<td>(TlPhen$_2$I$_2$)$_2$(I)</td>
<td>316.5</td>
<td>54</td>
<td>50.6*</td>
<td>374</td>
<td>265.9</td>
</tr>
</tbody>
</table>

*For these compounds the anionic value is that of the iodide ion. (27)

The figures in column 6 show that there is very little increase in the ionic susceptibility of the cation on passing from the chloro to the bromo, and the bromo to the iodo compound. In the case of the 2-2' bipyridine complexes there is a susceptibility increase of less than two units between the chloro and the bromo compound while the increment between the bromo and the red iodo complex is almost zero. For the bromo and yellow iodo complex the
increment is of about seven units, and that between the bromo and iodide complex is of about five units. Similar small increments occur for the 1:10 phenanthroline complexes. If the normal increment for two halogen atoms had been found the susceptibility should have increased by 21 units between the chloro and the bromo and 32 units between the bromo and iodo complexes.

This evidence further supports the suggestion that the halogen contribution to the diamagnetism is very much repressed in the cation with large organic groups in the co-ordination sheath. The cation structures of these complexes may be written as follows:

Where I and II are the 2:2' bipyridine and 1:10 phenanthroline thallium (III) cations respectively and X is chloride, bromide or iodide atoms. It is thus observed that the two halogen atoms tend to be surrounded by the large organic molecules. Regarding the cationic molecule as a much sphere of the charge contribution of the halogen tends to be swamped by that of the organic groups even in the
case of the iodo complex. This effect makes the halogen susceptibilities almost negligible in their contribution to the overall cationic susceptibility in the 1:10 phenanthroline complexes and small in the 2-2' bipyridine complexes.

A representation of the \( \text{Tl Org}_2 X_2 F^+ \) cations can be made by building up a model. A photograph of a model of \( \text{Tl Bipy}_2 Cl_2 F^+ \) cation is shown in Figure (3). As can be observed from the photograph the halogen atoms project clearly in the model in the vertical plane beyond the organic groups. This might seem to weaken the above argument, but it should be noted that only an average susceptibility measurement has been made using a powdered sample. It is probable that measurements on a single crystal along various axes would detect a difference in
the susceptibility i.e. show an anisotropic effect. Furthermore it must be remembered that the $\pi$ electron cloud cannot be shown by the model. For benzene and other non-condensed polynuclear compounds the mean radius of the magnetic orbits of the $\pi$ electrons in the molecular plane is given as equal to about $1.53\text{Å}$. For condensed polynuclear compounds this mean radius increases as the number of rings increases e.g. for naphthalene it is equal to about $1.64\text{Å}$. Considering thus, the radius of these magnetic orbits for benzene to be equal to about $1.53\text{Å}$ and comparing this magnitude with the normal thallium (III) -chlorine ($2.86\text{Å}$ (4)) and thallium (III) bromine ($2.65\text{Å}$ (8)) bond lengths it seems obvious that the halogens are well within the influence of the $\pi$ bond field. This would thus support the idea that the two halogen atoms inside the co-ordination sheath do not contribute fully to the volume of the electron field which determines the bulk diamagnetism. The negatively charged halogens and $\pi$ electron cloud would appear to form a non-localised field giving a more or less spherical ion of dimensions determined by the organic group.

Comparison of the magnetic susceptibilities of the 2-2'Bipyridine and 1:10 Phenanthroline complexes

Before attempting a comparison between calculated and experimental susceptibilities of the complexes containing
the above ligands, it is of interest to observe the changes in susceptibility in passing from the bipyridine complexes to the corresponding phenanthroline ones. These changes are shown in table (31).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-10^6 \chi_M$</th>
<th>$\Delta \chi$ (Bipy$_2^-$Phen$_2^+$)</th>
<th>Compound</th>
<th>$-10^6 \chi_M$</th>
<th>$\Delta \chi$ (Bipy$_2^-$Phen$_2^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TlBipy$_2Cl$)</td>
<td>2351.4</td>
<td>30.5</td>
<td>(TlBipy$_2I_2$)</td>
<td>459.2</td>
<td>31.5</td>
</tr>
<tr>
<td>(TlPhen$_2Cl$)</td>
<td>331.9</td>
<td></td>
<td>(TlBipy$_2I_2$) <em>TlI_4</em> (Red)</td>
<td>465.5</td>
<td>27.6</td>
</tr>
<tr>
<td>(TlBipy$_2Br$)</td>
<td>395.5</td>
<td>32.2</td>
<td>(TlPhen$_2I_2$) <em>TlI_4</em> (Yellow)</td>
<td>490.1</td>
<td></td>
</tr>
<tr>
<td>(TlPhen$_2Br$)</td>
<td>427.7</td>
<td></td>
<td>(TlBipy$_2I_2$)I</td>
<td>288.7</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(TlPhen$_2I_2$)I</td>
<td>316.5</td>
<td></td>
</tr>
</tbody>
</table>

If a mean of all except the yellow iodide complex (which is later shown to be of different structure) is taken the value is $30.50 \pm 1.64$ units. When, however, the yellow form of the $[\text{Tl Bipy}_2 \text{I}_2 \text{I}_2 \text{Tl I}_4]$ complex is considered a much lower increment of 24.6 units is obtained. This low increment in susceptibility can be attributed to the probably different structure of the yellow bipyridine complex to that of the analogous red complex. The increment between the $[\text{Tl Bipy}_2 \text{I}_2 \text{I}_2 \text{I}]$ and the corresponding 1:10 phenanthroline complex is somewhat low.
Lewis and Wilkins (15) give molar magnetic susceptibility values for 2-2’ bipyridine and 1:10 phenanthroline of 105 and 128 units respectively but without any indication as to whether the figures are experimental or calculated. These figures result in a difference of 23 units between the two ligands. For the cations each containing two organic groups $\text{Tl Org}_2 X_2^{-}$ this would give a difference of 46 units. The experimental increment found of 31.4 units is about 15 units less than that suggested by these authors for the free ligands. There is therefore a decrease in the increment between these two organic ligands in the co-ordination complexes. In order to clarify the problem it was found necessary to determine the experimental molar susceptibilities of the two organic ligands and to calculate theoretical susceptibilities by the Pascal-Pacault method.

**Calculated Magnetic susceptibilities of 2-2’ Bipyridine and 1:10 Phenanthroline molecules**

By employing Pascal’s method developed by Pacault for calculating theoretical susceptibilities (26), the molar susceptibilities for the free ligands can be obtained. From these, by making certain assumptions, a calculated value for the thallium (III) complexes can be estimated. The free ligands 2-2’ bipyridine and 1:10 phenanthroline are first considered. For
both molecules, Pascal's atomic susceptibilities (25) were employed but additional structural factors introduced by Pacault have to be considered for this type of molecule. For aromatic and condensed ring systems according to Pacault's first rule for constitutive ligand effects (26), the correction factor characteristic of the pyridine ring is $+0.5$ units. A second rule which applies to condensed rings accounts for the shared bonds between the condensed rings. This increment is given as $\Delta \chi = -5.3 \times 10^6$ units $\times$ the number of shared bonds. This need only be considered here in the case of the 1:10 phenanthroline molecule.

Accordingly, using the figures given by Pacault (26):

$$\chi_M(\text{2-2'}\text{Bipyridine}) = \sum (10\chi_c + 8\chi_H + 2\chi_N + 2\chi_{py} - 10\chi_{benzene})$$

$$= \sum (10(-6.00)+8(-2.93)+2(-5.55)$$

$$+2(+0.5))$$

$$= -93.54$$

$$\chi_M(\text{1:10Phenanthroline}) = \sum (12\chi_c + 6\chi_H + 2\chi_N + 2\chi_{py} + 2\chi_{benzene})$$

$$= \sum (12(-6.00)+6(-2.93)+2(-5.55)$$

$$+2(+0.5)+(-1.4)+2(-5.3)$$

$$= -117.64$$

The increment between the two organic ligands in these theoretical susceptibilities is 24.10 units on passing from 2-2' bipyridine to 1:10 phenanthroline. Experimental molar susceptibilities for these ligands were also determined and these are shown in table (32) below.
As can be seen from the table, the theoretical and experimental susceptibilities agree quite well for the 1:10 phenanthroline molecule. In the case of 2-2' bipyridine the experimental value is 1.55 units lower than that found by calculation. This is of interest in relation to the crystal structure. It has been shown by Cagle (1a), by crystal structure studies that the 2-2' bipyridine molecule exists in the crystal with the rings coplanar and with the nitrogen atoms trans to the bonds joining the ring. In co-ordination with a single metal ligand the cis form that is involved and the calculated susceptibility includes no factor for change from the cis to the trans isomer. The difference obtained between the calculated and the experimental susceptibilities could then be interpreted as the difference in diamagnetism between the cis- and trans-2-2' bipyridine structures. A higher susceptibility value would be expected in the case

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-10^6\chi_a$</th>
<th>$-10^6\chi_M$ Exptl.</th>
<th>$-10^6\chi_M$ Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2' Bipyridine</td>
<td>0.5936</td>
<td>91.99</td>
<td>93.54</td>
</tr>
<tr>
<td></td>
<td>0.5827</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5910</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5852</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.5922</td>
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<tr>
<td>1:10 Phenanthroline</td>
<td>0.6013</td>
<td>117.56</td>
<td>117.64</td>
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<tr>
<td></td>
<td>0.5913</td>
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<td></td>
<td>0.5817</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>0.5963</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of the cis-isomer: \[ \text{cis} \] since here the lone pair of electrons of the two nitrogen atoms on the same side of the ring exert a repulsion on each other. This would lead to an increase in the diamagnetism as the electronic cloud is spread. In the trans structure a loose hydrogen bonding will tend to be formed between the nearest hydrogens of the adjacent ring and the nitrogens. This will tend to restrict the diamagnetism.

Several workers have pointed out that there will be a difference in the diamagnetic susceptibility of different isomeric substances and a few experimental results are available for various types of isomerism (36). Only a few studies have however been carried out on cis- and trans-isomers. Selwood (36) observed that in the cis-trans isomers of dicahydronaphthalene, the decalins, there was a lowering of susceptibility in the case of the cis-form and ascribed this to the effect of the Van Vleck high frequency paramagnetism on the rings of different conformation. The effect here is however due to the difference in conformation and is quite different from the present case. No earlier work has been found which includes nitrogen containing systems with lone pairs which could interact in the manner discussed above.
Calculated magnetic susceptibilities of 2-2' Bipyridine and 1:10 Phenanthroline complexes of thallium (III) halides

Using the above Pascal's susceptibility values for the organic ligands, calculated susceptibilities for the cations [Tl Bipy2 X2]+ and [Tl Phen2 X2]+ can be obtained. Two ways of deriving such ionic susceptibility values can be considered. Since the resultant cation has a single positive charge an extreme possibility is to calculate the cationic susceptibility by using a susceptibility value for thallium (I), the calculated values for the organic molecules and Pascal's values (25) for covalently bonded halogens. This would give the correct charge. The following susceptibility values for the cations found in this way are shown in column 2 of table (33).

<table>
<thead>
<tr>
<th>Cation</th>
<th>(-10^6 \chi M (\text{Calc.}))</th>
<th>(-10^6 \chi M (\text{Calc.}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Tl Bipy}_2 \text{Cl}_2]^+)</td>
<td>260.08</td>
<td>260.18</td>
</tr>
<tr>
<td>([\text{Tl Bipy}_2 \text{Br}_2]^+)</td>
<td>281.08</td>
<td>281.18</td>
</tr>
<tr>
<td>([\text{Tl Bipy}_2 \text{I}_2]^+)</td>
<td>309.08</td>
<td>312.72</td>
</tr>
<tr>
<td>([\text{Tl Phen}_2 \text{Cl}_2]^+)</td>
<td>281.28</td>
<td>281.38</td>
</tr>
<tr>
<td>([\text{Tl Phen}_2 \text{Br}_2]^+)</td>
<td>302.28</td>
<td>302.38</td>
</tr>
<tr>
<td>([\text{Tl Phen}_2 \text{I}_2]^+)</td>
<td>330.28</td>
<td>333.98</td>
</tr>
</tbody>
</table>

A value of 32.8 for thallium (I) previously found by Stephen (65) was employed.

At the other extreme these cationic susceptibilities
can be obtained by using a susceptibility value for thallium (III), values for the organic ligands as used above and the ionic susceptibility values for two halogen ions. This would give the correct single positive charge on the cation. The values found in this way are shown in column 3 of table (33). A value of 24.5 units was used here for the susceptibility of thallium (III) from some unpublished results of Trew on simple thallium (III) halides and the nitrate. Thus, whichever method is used these two calculated set of values are in close agreement, the iodides showing the greatest difference.

The manner in which the charge is assigned thus seems immaterial. These calculated values may be compared with the experimental figures for the cations $\left[\text{Tl Org}_2 \ X_2\right]^+$ tabulated above when it is seen that the latter are very much lower than the former. This was expected, as the halogen contribution to the cationic susceptibility is much lower than the normal. This is shown in table (34) where calculated cationic susceptibilities with and without the halogen contribution are given for comparison with the experimental.
Column 2 shows the experimentally determined cationic susceptibility (i.e. calculated from the molar susceptibility of the $\text{Tl Org}_{2} \ X_2^{-}$ compounds knowing the anionic contribution). Column 3 shows the calculated susceptibility of the $\text{Tl Crg}_{2} \ X_2^{-}$ cation with full halogen contribution the mean of the previous two tables. Column 5 gives a calculated cationic susceptibility value with no halogen contribution i.e. merely the sum of the Pascal organic constants and the value for thallium (I) which assumes that the halogen contribution is entirely quenched by the effect of the large organic ligands. Columns 4 and 6 represent the difference in each case of

<table>
<thead>
<tr>
<th>Cation</th>
<th>Exptl. $\chi_{M}$</th>
<th>$\text{Tl Org}_{2} \ X_2^{-}$ calc.</th>
<th>$\Delta \chi_{calc} \ Exptl.$</th>
<th>$\text{Tl Org}_{2} \ X_2^{-}$ calc.</th>
<th>$\Delta \chi_{calc} \ Tl Org_{2} \ X_2^{-} \ Exptl.$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Tl Bipy}_{2} \text{Cl}_2)^{+}$</td>
<td>231.0</td>
<td>260.1</td>
<td>29.0</td>
<td>219.8</td>
<td>-11.2</td>
</tr>
<tr>
<td>$(\text{Tl Bipy}_{2} \text{Br}_2)^{+}$</td>
<td>233.9</td>
<td>261.1</td>
<td>47.2</td>
<td>219.8</td>
<td>-14.1</td>
</tr>
<tr>
<td>$(\text{Tl Bipy}_{2} \text{I}_2)^{+}$ red</td>
<td>234.3</td>
<td>310.4</td>
<td>76.1</td>
<td>219.8</td>
<td>-14.5</td>
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<tr>
<td>$(\text{Tl Bipy}_{2} \text{I}_2)^{+}$ yellow</td>
<td>240.6</td>
<td>310.4</td>
<td>69.8</td>
<td>219.8</td>
<td>-20.8</td>
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<tr>
<td>$(\text{Tl Bipy}_{2} \text{I}_2)^{+}$</td>
<td>238.1</td>
<td>310.4</td>
<td>72.3</td>
<td>219.8</td>
<td>-18.3</td>
</tr>
<tr>
<td>$(\text{Tl Phen}_{2} \text{Cl}_2)^{+}$</td>
<td>261.5</td>
<td>281.3</td>
<td>19.8</td>
<td>267.9</td>
<td>+ 6.4</td>
</tr>
<tr>
<td>$(\text{Tl Phen}_{2} \text{Br}_2)^{+}$</td>
<td>264.5</td>
<td>302.3</td>
<td>37.8</td>
<td>267.9</td>
<td>+ 3.4</td>
</tr>
<tr>
<td>$(\text{Tl Phen}_{2} \text{I}_2)^{+}$</td>
<td>265.2</td>
<td>332.1</td>
<td>66.9</td>
<td>267.9</td>
<td>+ 2.7</td>
</tr>
<tr>
<td>$(\text{Tl Phen}_{2} \text{I}_2)^{+}$</td>
<td>265.9</td>
<td>332.1</td>
<td>66.2</td>
<td>267.9</td>
<td>+ 2.0</td>
</tr>
</tbody>
</table>
the experimental from these calculated values. It is observed that while the full calculated values are higher than the experimental ones (column 4) there is a difference in behaviour in the two series of compounds shown in column 6. The bipyridine complexes show an experimental susceptibility appreciably greater than the 'quenched' theoretical figure but very much below the full theoretical figure. The 1:10 phenanthroline complexes give an experimental susceptibility which is however lower than the 'quenched' calculated one.

These relationships are shown more clearly by a graphical plot in graphs (20) and (21). They may be interpreted by considering the 1:10 phenanthroline complexes with the larger organic ligand first. Here it appears that there is an almost total quenching of the halogen contribution and in addition a ligand-lowering effect. The combined effect of these two factors brings the experimental cation susceptibility some few susceptibility units below the calculated figure without allowance for the halogen. As there are two factors here it is not possible to assess a ligand lowering constant from the present data.

The results in the case of the 2-2' bipyridine series can be explained by a large though not complete, residual halogen contribution to the susceptibility together with
Graph (20)

(a) Experimental magnetic susceptibilities of [TePhen$_2$X$_2$]$^+$
(b) Calculated
(c)
GRAPH (21)

(a) EXPERIMENTAL MAGNETIC SUSCEPTIBILITIES OF [(TEB)py₂X₂]⁺
(b) CALCULATED  "  "  "  "
(c) "  "  "  " [(TEB)py₂]⁺

-10⁻⁶ \chi_M

2 x ATOMIC NUMBER OF HALOGENS
a bond lowering effect which is not sufficient to bring the experimental susceptibility below the calculated one.

It was seen before (Page 147) that the increment obtained on passing from bipyridine complexes to the corresponding phenanthroline ones was almost constant throughout the series and thus it is reasonable to assume that the organic ligands have a constant ligand lowering effect in the chloro, bromo and iodo complexes. Any variation therefore in the difference between calculated and experimental susceptibilities from one halide complex to another can be ascribed to the halogen ligands alone. From the results in columns 3 and 4 it is indicated that this effect is present in the complexes in the following order:

\[ \text{iodo} > \text{bromo} > \text{chloro}. \]

This susceptibility lowering effect appears to be in the same order as that of the relative co-ordinating affinities of ligand atoms from group VII to class (b) metals acting as acceptors as outlined by Ahrland, Chatt and Davies (77). In considering complexes of thallium, these authors have pointed out that thallium like lead and bismuth in the same periodic series is likely to be borderline in its acceptor character towards various ligands. The available data for thallium-halogen ligand affinity constants shows however that thallium (I) and thallium (III)
are both class (b) acceptors towards atoms of group VII but that thallium (III) has a far stronger class (b) character. Stability constants for the various halocomplexes of thallium (III) as obtained by different authors are listed in table (35).

<table>
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<tr>
<th>Complex &amp; X=Cl (13)</th>
<th>x=Br (13)</th>
<th>x=Cl (14)</th>
<th>x=Br (14)</th>
<th>x=I (24)</th>
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<td>TlX$^2+$</td>
<td>8.1</td>
<td>9.7</td>
<td>6.25</td>
<td>8.9</td>
</tr>
<tr>
<td>TlX$^-$</td>
<td>5.5</td>
<td>6.9</td>
<td>5.15</td>
<td>7.5</td>
</tr>
<tr>
<td>TlX$^{-}$</td>
<td>2.2</td>
<td>4.6</td>
<td>3.10</td>
<td>5.7</td>
</tr>
<tr>
<td>TlX$_4^-$</td>
<td>2.6</td>
<td>2.7</td>
<td>2.5</td>
<td>4.0</td>
</tr>
<tr>
<td>TlX$_5^{2-}$</td>
<td></td>
<td></td>
<td>1.8</td>
<td>3.1</td>
</tr>
<tr>
<td>TlX$_6^{3-}$</td>
<td></td>
<td></td>
<td></td>
<td>2.4</td>
</tr>
</tbody>
</table>

Acceptors metals of class (b) thus show ligand affinity constants for halide ions in the sequence $I > Br > Cl > F$; those of class (a) on the other hand show the reverse sequence $F > Cl > Br > I$. The above lowering of susceptibility which is related to the strength of the metal-ligand bond, appears to give interesting support to the relative ligand affinity assignment for thallium (III) halide complexes since it follows the same sequence $I > Br > Cl$. 
Conductivity Measurements

In the previous section it was shown that the magnetic results on the solid complexes of thallium (III) halides with 2-2' bipyridine and 1:10 phenanthroline, give evidence for the dimeric structure $\text{Tl Org}_2 \text{X}_2 \cdot \text{Tl X}_4$. It is however of interest to study their behaviour in solution.

The above complexes are only sparingly soluble in water. By using non-aqueous solvents, such as nitrobenzene, nitromethane and acetone, it is possible however to study their behaviour in these media. By measuring the electrical conductivity of the complexes in the above solvents, the number of ions formed on dissociation can be determined. Sutton carried out conductance measurements in nitrobenzene for these complexes and found molar conductances of the order $18.1 - 22.1 \Omega^{-1} \text{cm}^2$ for concentrations ranging between $1.56 \times 10^{-2}$ and $1.1 \times 10^{-3} \text{M}$. Conductance measurements in nitrobenzene were repeated for this solvent as a check.

Kabesh and Nyholm (38), Harris and McKenzie (112), Reynolds and Kraus (113), and many others have shown that univalent electrolytes in nitrobenzene, nitromethane and acetone solutions give molar conductances respectively of the following orders: $15.35 \Omega^{-1} \text{cm}^2$, $70 - 110 \Omega^{-1} \text{cm}^2$ and $150 - 170 \Omega^{-1} \text{cm}^2$. The range of concentration being $2 \times 10^{-2} - 1 \times 10^{-4} \text{M}$. 
Table (36) shows the experimental conductances in these solvents obtained for the 2-2' bipyridine and 1:10 phenanthroline complexes of thallium (III) halides.

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>[TlBipy₂Cl₂][TlCl₄]</td>
<td>0.0012</td>
<td>15</td>
<td>0.0011</td>
<td>73</td>
<td>0.0012</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>0.0002</td>
<td>16</td>
<td>0.0002</td>
<td>74</td>
<td>0.0003</td>
<td>158</td>
</tr>
<tr>
<td>[TlBipy₂Br₂][TlBr₄]</td>
<td>0.0013</td>
<td>16</td>
<td>0.0012</td>
<td>74</td>
<td>0.0013</td>
<td>158</td>
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<tr>
<td></td>
<td>0.0004</td>
<td>16</td>
<td>0.0001</td>
<td>74</td>
<td>0.0002</td>
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<td>[TlBipy₂I₂][TlI₄]</td>
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<td>77</td>
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<td>[TlBipy₂I₂][TlCl₄]</td>
<td>0.0010</td>
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<tr>
<td>[TlBipy₂][TlI₄]</td>
<td>0.0011</td>
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<tr>
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<td>[TlBipy₂][TlBr₄]</td>
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<td>19</td>
<td>0.0002</td>
<td>77</td>
<td>0.0001</td>
<td>162</td>
</tr>
</tbody>
</table>

As stated above the magnetic evidence supports the dimeric structure \([\text{Tl Org}_2 X_2 - \text{Tl X}_4]\) for these complexes. On this basis, if only a simple dissociation occurs in the solvents used two ions would be expected to be formed:

\[
[\text{Tl Org}_2 X_2 - \text{Tl X}_4] \rightarrow [\text{Tl Org}_2 X_2]^+ + \text{Tl X}_4^-
\]

the observed conductances all agree well with the expected range for uni-univalent electrolytes.

A comparison of Sutton's results (23) for these
complexes in nitrobenzene with the present results, show that slightly lower values are obtained here. This may be due to a difference in the purity of the solvent. Table (36) shows further that molar conductances increase on passing from the chloro to the bromo to the iodo complexes. There appears also to be a small increase in the molar conductances on dilution, but measurements were not carried out under conditions to give an accurate figure for the molar conductance at infinite dilution.

Another point of interest is the slightly higher value for the molar conductance obtained for the red $\text{[Tl Bipy}_2 \text{I}_2\text{I}_4$ as compared to that found for the analogous yellow complex. This supports further the suggestion that the yellow and red iodo complexes might be two geometrical isomers, since Carassiti's results (78) on the mobilities of some cis and trans isomers showed that the mobility of the cis and trans isomers differed. The trans always has the greater mobility. This difference has been attributed to the larger dipole of the cis-compound leading to a higher hydration number and a smaller mobility.
Infra Red Spectra in the 4000 - 500cm\(^{-1}\) region

Schilt and Taylor (79) were the first authors to attempt investigations and correlations on the infra-red spectra of several 2-2' bipyridine and 1:10 phenanthroline metal complexes. Since then several papers have been published by other authors (80)(81) dealing with the infra-red spectra of transition and rare earth complexes containing the above ligands. No study of similar thallium (111) complexes has been previously made.

The vibrational frequencies observed in this region arise exclusively in the ligand (2-2' bipyridine or 1:10 phenanthroline) part of the complex, the metal ligand frequencies falling outside the range of the instrument used. According to Bellamy (82) there is a reasonable close analogy between the ring vibrations of benzene and those of other heterocyclic compounds such as pyridine and quinoline. It has further been observed, that although there are considerable differences in the hydrogen deformation vibrations, the out-of-plane hydrogen deformation vibrations appear to be like those of benzene compounds containing an additional substituent. For such compounds composed of a substituent and an aromatic ring Katritsky (83) divides the normal vibrations of a hetero-aromatic ring into (a) those in which hydrogen atoms move relatively to the heavy skeleton and (b) those in which each CH or NH group moves as a unit. Because of the similar masses involved,
substitution of \( \text{N} \) for \( \text{CH} \) would be expected to have relatively little effect upon the normal vibrations of class (b). In general it has been found that if \( n \) hydrogen atoms are attached to a planar ring, there will be \( 3n \) \( \text{CH} \) type modes and that in each group the \( n \) modes will be coupled. The fundamental absorption bands corresponding to the three classes occur in different parts of the spectrum: \( \text{CH} \) stretching near 3000 cm\(^{-1}\), in-plane \( \text{CH} \) bending at ca. 1300-1000 cm\(^{-1}\) and out-of-plane \( \text{CH} \) bending in the 1000 - 700 cm\(^{-1}\) region.

The I.R. spectra of the various 2-2' bipyridine and 1:10 phenanthroline thallium (III) complexes were thus studied in the region 3000 - 600 cm\(^{-1}\).

**Halogeno Complexes**

(a) 2-2' Bipyridine Complexes

The positions and intensities of the infra-red bands in the spectra (4000 - 500 cm\(^{-1}\)) of 2-2' bipyridine and its complexes are given in Table (37) and graph (22) represents these spectra. The respective assignments of the various bands are shown in the last column of the same table. The latter has been made by a straight-forward comparison between the spectrum of the free base and that of co-ordinated 2-2' bipyridine. A comparison of the results obtained here for the free ligand with those of Schilt and Taylor (79) and Sinha (81) was made. The agreement between Sinha's work
<table>
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<th>B(1)</th>
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<td>and C-N stretching vibrations</td>
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<td>New band observed on complexing</td>
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B = 2-2' Bipyridine Column (1) R.G. Inskeep (80) Column (2) A.A. Schilt & R.C. Taylor (79) Column (3) S.P. Sinha (81) Column (4) This work.
<table>
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<th>B(3)</th>
<th>B(4)</th>
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<th>TlB$_2$Br$_2$</th>
<th>TlB$_2$I$_2$ yellow</th>
<th>TlB$_2$I$_2$ red</th>
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B = 2-2' Bipyridine
Column (1) R.G. Inskeep (80)
Column (2) A.A. Schilt and R.C. Taylor (79)
Column (3) S.P. Sinha (81)
Column (4) This work.
and the present results is good. Schilt and Taylor's results show, however, certain differences. The band which in the present work appears at $1450\ \text{cm}^{-1}$ is absent in Schilt and Taylor's spectra. It is obvious that Nujol bands prevented the observation of such bands in their spectra, since by using $n$-hexachlorobutadiene as the mulling agent in the present work instead of nujol, it still appears as a strong well characterised band. Apart from some very small differences of a frequency unit$\text{v}$ over the whole spectrum range from Schilt and Taylor's observations, it was noted that two other bands are absent in their work. In the present work they appear at $1200$ and $1210\ \text{cm}^{-1}$ as very weak bands. Schilt and Taylor's $^{79}$ and Sinha's $^{81}$ results are listed in columns 1 and 2 respectively in Table (37).

The $3000\ \text{cm}^{-1}$ region

The CH aromatic stretching vibrations occur in this region. In the case of the free base these CH stretching vibrations produce bands at $3028$ and $2994\ \text{cm}^{-1}$ and a shoulder at $2967\ \text{cm}^{-1}$. In the bis 2-2' bipyridine complexes however, four bands appeared at $3097$, $3056$, $3042$ and $3014\ \text{cm}^{-1}$. Their positions and intensities remaining constant throughout the spectra of the various complexes. As can be seen from Table (37) there is a shift to a higher frequency in going from the free base to co-ordinated 2-2' bipyridine.
The 1600 - 1350 cm\(^{-1}\) region

Bands due to the C = N and C = C vibrations of the pyridine rings occur in this region. In the spectra of the free base there is a group of four strong bands at 1578, 1550, 1450 and 1418 cm\(^{-1}\). On complexing, splittings of some of the bands occurs and new bands of medium to strong intensity are observed. Thus for the tetrachloro, bromo and yellow iodothallate complexes, the band on the high frequency side of the doublet near 1592 cm\(^{-1}\) shows a shoulder close to 1603 cm\(^{-1}\). In the case of the red tetra iodothallate a triplet appears there, the peaks on the high frequency side being of equal intensity. For the iodide complex the triplet still appears but the peaks differ in intensity. The strong band at 1550 cm\(^{-1}\) in the free base, is reproduced with only a minor shift of 8 cm\(^{-1}\) to higher frequency in the spectra of the complexes. There are too, strong bands close to 1484 and 1468 cm\(^{-1}\) in the spectrum of co-ordinated bipyridine, which are absent in that of the free base. The strong band, which in the free base appears at 1418 cm\(^{-1}\) seems to be shifted to 1433 cm\(^{-1}\) in the complexes, the nature of the band remaining the same.

The 1250 - 1000 cm\(^{-1}\) region

In this region heterocyclic compounds show a series of characteristic bands which have been assigned to in-plane CH deformation and ring breathing modes.
The spectrum of the free base here consists of several bands of various intensities. The band at 1248 cm\(^{-1}\) in the free base is faithfully reproduced in all the complexes; the band is however slightly shifted on co-ordination. Between 1176 and 1149 cm\(^{-1}\) new bands appear on complexing and are listed in table (38) for comparative purposes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequency cm(^{-1})</th>
<th>(\Delta I - II)</th>
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</thead>
<tbody>
<tr>
<td>(\text{Tl}bipy_2\text{Cl}_2\text{TlCl}_4)</td>
<td>1172 1156 16</td>
<td></td>
</tr>
<tr>
<td>(\text{Tl}bipy_2\text{Br}_2\text{TlBr}_4)</td>
<td>1175 1152 23</td>
<td></td>
</tr>
<tr>
<td>(\text{Tl}bipy_2\text{I}_2\text{TlI}_4)</td>
<td>1174 1151 23</td>
<td></td>
</tr>
<tr>
<td>Yellow</td>
<td>1171 1151 20</td>
<td></td>
</tr>
<tr>
<td>(\text{Tl}bipy_2\text{I}_2\text{TlI}_4) red</td>
<td>1174 1155 19</td>
<td></td>
</tr>
</tbody>
</table>

The above bands, being absent in the spectrum of the free base are characteristic of the complexes. Whereas in the case of the tetrachlorothallate complex, both bands are of almost the same intensity, in the other complexes the band on the higher frequency side is of much lower intensity than the other.

The band which in the free base is observed at 1135 cm\(^{-1}\) and assigned as a characteristic vibration of the ortho substituted pyridine, appears to be shifted in the complexes to higher frequency as can be seen in Table (39) below.
A new band, not present in the spectrum of the free base appears in the complexes at about 1099 cm\(^{-1}\) and is almost identical both in position and intensity in all the complexes.

The band which in the spectrum of 2-2' bipyridine appears at 1083 cm\(^{-1}\) seems to disappear on complexing. However, a new band of medium intensity appears in the complexes, at about 1070 cm\(^{-1}\) whilst that band which in the free base appears at 1060 cm\(^{-1}\) is reproduced, but only shifted slightly in the complexes as shown in Table (40).

## TABLE 39

<table>
<thead>
<tr>
<th>Compound</th>
<th>Shift cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{Cl}_2\text{-TlCl}_4)</td>
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<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{Br}_2\text{-TlBr}_4)</td>
<td>17</td>
</tr>
<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{I}_2\text{-TlI}_4) (Yellow)</td>
<td>16</td>
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<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{I}_2\text{-TlI}_4) (Red)</td>
<td>16</td>
</tr>
<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{Cl}_2\text{-TlI}_4)</td>
<td>20</td>
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</tbody>
</table>

## TABLE 40

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequency cm(^{-1})</th>
<th>(\Delta) III - IV</th>
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<tr>
<td>Band III</td>
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<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{Cl}_2\text{-TlCl}_4)</td>
<td>1072</td>
<td>1062</td>
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<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{Br}_2\text{-TlBr}_4)</td>
<td>1071</td>
<td>1062</td>
</tr>
<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{I}_2\text{-TlI}_4) Yellow</td>
<td>1070</td>
<td>1062</td>
</tr>
<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{I}_2\text{-TlI}_4) Red</td>
<td>1070</td>
<td>1059</td>
</tr>
<tr>
<td>(\text{Tl}b\text{i}p\text{y}_2\text{I}_2\text{-TlI}_4)</td>
<td>1071</td>
<td>1062</td>
</tr>
</tbody>
</table>
Between 1053 and 1000 cm\(^{-1}\) only one strong band is observed in the free base at 1038 cm\(^{-1}\) and this appears as a very weak band in all the complexes.

The 1000 - 600 cm\(^{-1}\) region

Out-of-plane CH deformation and in-plane ring deformations could cause absorption in this region.

In the spectrum of the free base several bands are observed: a sharp and strong band at 990 cm\(^{-1}\) and a weak one at 890 cm\(^{-1}\). In the complexes the band on the high frequency side seems to be slightly shifted and this shift is shown in table (41) for the various complexes considered. The 890 cm\(^{-1}\) band on the other hand remains fairly constant.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band V</th>
<th>Shift cm(^{-1})</th>
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</thead>
<tbody>
<tr>
<td>([\text{Tl}bipy_2\text{Cl}_2\text{-TlCl}_4])</td>
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<tr>
<td>([\text{Tl}bipy_2\text{Br}_2\text{-TlBr}_4])</td>
<td>976</td>
<td>14</td>
</tr>
<tr>
<td>([\text{Tl}bipy_2\text{I}_2\text{-TlI}_4\text{ (Yellow)}])</td>
<td>971</td>
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<tr>
<td>([\text{Tl}bipy_2\text{I}_2\text{-TlI}_4\text{ (Red)}])</td>
<td>972</td>
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</tr>
<tr>
<td>([\text{Tl}bipy_2\text{I}_2\text{-Tl}])</td>
<td>972</td>
<td>18</td>
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</tbody>
</table>

In the spectrum of the free ligand, the vibration ascribed to the CH out-of-plane in-phase bending modes appears as a strong and sharp peak at 755 cm\(^{-1}\), this is as expected for two identical groups of four hydrogen atoms in each ring. This peak shows a satellite on its low frequency side, which on co-ordination appears as a fairly strong band at a lower frequency, the strong peak at 755 cm\(^{-1}\)
being shifted towards the higher frequency region. A conspicuous split of the latter is observed for the yellow tetraiodothallate complex. Martin, McWhinnie and Waind have suggested that this splitting, observed for some rhodium-2-2'-bipyridine complexes may possibly be due to a cis-configuration of the 2-2' bipyridine ligands. Later Beck and co-workers observed a similar splitting for the compound Fe(II) bipy$_2$ (NCO)$_2$ but evidence was not supplied as to which form was being studied. Murray on the other hand investigating the trans diaquo bis 2-2' bipyridine chromium (III) nitrate reported the absence of a splitting of this mode. This was also found to be the case by McWhinnie for the trans-bis 2-2' bipyridine nickel (II) nitrate and the trans dichloro bis-2-2' bipyridine cobalt (III) chloride. In view of these assignments, it appears that the splitting of the above band observed in the present work for the yellow bipyridine complex is indicative of a cis configuration of the 2-2' bipyridine ring. The red compound on the other hand fails to give complexity in this region of the spectrum and thus must be the trans form. By analogy then, all the other 2-2' bipyridine thallium (III) halogeno complexes studied in this section would be expected to have a trans coplanar arrangement.

Shifts of the above bands and distances of separation for the different complexes are shown in table (41).
In the spectrum of the free 2-2' bipyridine, two bands of broad and medium intensity are observed at 652 and 617 cm$^{-1}$. The 652 cm$^{-1}$ band can here be assigned as an in-plane ring deformation vibration. This follows the assignment of this band by Kleine and co-workers (88) to the $\gamma_4$ ring vibration mode of the pyridine ring on the basis of their calculations and an observed experimental band in this position, at 652 cm$^{-1}$ in the pyridine molecule. This ring deformation mode appears also in all the complexes studied with very little shift from the original position, i.e. about 7 cm$^{-1}$. No assignment has been found for the accompanying band at 617 cm$^{-1}$ in the free base. This appears in all the complexes with a more marked shift of about 14 cm$^{-1}$.

Table (43) shows the shifts of the above bands and the distances of separation for the various complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>755 cm$^{-1}$ band VI</th>
<th>736 cm$^{-1}$ band VII</th>
<th>$\Delta$(VI-VII)</th>
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<tr>
<td>Tlbipy$_2$Cl$_2$TlCl$_4$</td>
<td>769</td>
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<td>Tlbipy$_2$Br$_2$TlBr$_4$</td>
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<td>38</td>
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<tr>
<td>Tlbipy$_2$I$_2$TlI$_4$Yellow</td>
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<td>Tlbipy$_2$I$_2$TlI$_4$Red</td>
<td>760</td>
<td>725</td>
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<tr>
<td>Tlbipy$_2$I$_2$I</td>
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<td>725</td>
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**TABLE 42**
TABLE 4.3

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<th>Compound</th>
<th>(652\text{cm}^{-1}\text{ band VIII})</th>
<th>(617\text{cm}^{-1}\text{ band IX})</th>
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<td>(\text{Tlbipy}_2\text{l}_2\text{-TlI}_4\text{Yellow})</td>
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<td>631</td>
<td>14</td>
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<tr>
<td>(\text{Tlbipy}_2\text{l}_2\text{-TlI}_4\text{Red})</td>
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<td>632</td>
<td>13</td>
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<tr>
<td>(\text{Tlbipy}_2\text{l}_2\text{-TlI})</td>
<td>645</td>
<td>632</td>
<td>13</td>
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</table>

(b) 1:10 Phenanthroline Complexes

Table (44) shows the positions and intensities of the infra-red bands in the spectra (4000-500\text{cm}^{-1}) of 1:10 phenanthroline, its hydrate and the complexes with thallium (III) halides. A comparison of the spectrum of the free base and hydrate obtained in the present work shows good agreement with results of previous workers (79,80), variations when they occur being only two or three cm\(^{-1}\). Some Nujol bands apparent in Schilt and Taylor's spectra are not observed in the present work, as n-hexachlorobutadiene was used here as mulling agent in the range 2000-1250 cm\(^{-1}\). The last column in the above table shows the assignment for the various bands.

The 3000 cm\(^{-1}\) region

Here the CH aromatic stretching vibrations are expected. In the spectrum of the free base a sharp band appears at 3020 cm\(^{-1}\) with a shoulder at 2997 cm\(^{-1}\). In the spectrum of the hydrate a broad peak, due to the anti-symmetric and symmetric C-H stretching modes appear at
<table>
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<th>PH$_2$O</th>
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<th>TlP$_2$Br$_2$ TlBr$_4$</th>
<th>TlP$_2$I$_2$ TlI$_4$</th>
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<td>3042(m)</td>
<td>3042(m)</td>
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<td>1585(s)</td>
<td>1585(sh)</td>
<td>1565(vs)</td>
<td>1565(vs)</td>
<td>1563(vs)</td>
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<td>1563(vs)</td>
<td>1565(s)</td>
<td>1515(vs)</td>
<td>1508(m)</td>
<td>1495(m)</td>
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<td>1425(vs)</td>
<td>1425(vs)</td>
<td>1431(vs)</td>
<td>1431(vs)</td>
<td>1429(vs)</td>
<td>1414(s)</td>
<td>C=C stretching vibrations</td>
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<td>1344(m)</td>
<td>1337(m)</td>
<td>1337(m)</td>
<td>1335(w)</td>
<td>1335(w)</td>
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<td>1227(m)</td>
<td>1221(m)</td>
<td>1220(m)</td>
<td>1220(m)</td>
<td>New bands observed on complexing</td>
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<td>1135(m)</td>
<td>1139(s)</td>
<td>1139(s)</td>
<td>1138(m)</td>
<td>1138(s)</td>
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<td>1091(m)</td>
<td>1094(m)</td>
<td>1099(s)</td>
<td>1098(s)</td>
<td>1096(s)</td>
<td>ring vibrations</td>
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<td>( \text{PH}_2\text{O} )</td>
<td>( \text{Tp}_2\text{Cl}_2\text{TlCl}_4 )</td>
<td>( \text{Tp}_2\text{Br}_2\text{TlBr}_4 )</td>
<td>( \text{Tp}_2\text{I}_2\text{TlI}_4 )</td>
<td>( \text{Tp}_2\text{I}_2\text{I} )</td>
<td>ASSIGNMENTS</td>
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</tr>
<tr>
<td>1075(w)</td>
<td>1077(sh)</td>
<td>1047(w)</td>
<td>1032(w)</td>
<td>1031(w)</td>
<td>1076(sh)</td>
<td>Ring breathing modes</td>
</tr>
<tr>
<td>1029(w)</td>
<td>1033(w)</td>
<td>995(w)</td>
<td>989(w)</td>
<td>986(w)</td>
<td>1030(w)</td>
<td></td>
</tr>
<tr>
<td>993(m)</td>
<td>987(m)</td>
<td>961(w)</td>
<td>960(w)</td>
<td>952(w)</td>
<td>976(w)</td>
<td></td>
</tr>
<tr>
<td>876(w)</td>
<td>883(w)</td>
<td>902(w)</td>
<td>897(w)</td>
<td>893(w)</td>
<td>893(w)</td>
<td></td>
</tr>
<tr>
<td>854(sh)</td>
<td></td>
<td>864(sh)</td>
<td>859(s)</td>
<td>861(m)</td>
<td>861(w)</td>
<td></td>
</tr>
<tr>
<td>843(vs)</td>
<td>852(vs)</td>
<td>853(vs)</td>
<td>846(vs)</td>
<td>845(vs)</td>
<td>840(vs)</td>
<td>Out-of-plane motion of the hydrogen atoms on the centre ring</td>
</tr>
<tr>
<td>814(w)</td>
<td></td>
<td>806(w)</td>
<td>801(w)</td>
<td>800(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>797(w)</td>
<td></td>
<td>787(m)</td>
<td>785(m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>783(w)</td>
<td>776(s)</td>
<td>782(s)</td>
<td>775(sh)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>766(s)</td>
<td></td>
<td>775(sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>744(sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>734(vs)</td>
<td>738(vs)</td>
<td>732(sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>722(sh)</td>
<td>723(m)</td>
<td>723(sh)</td>
<td>749(w)</td>
<td>723(sh)</td>
<td>723(vs)</td>
<td>Out-of-plane motion of the hydrogen atoms on the heterocyclic rings</td>
</tr>
<tr>
<td>704(w)</td>
<td>707(sh)</td>
<td>719(vs)</td>
<td></td>
<td>718(vs)</td>
<td>718(vs)</td>
<td></td>
</tr>
<tr>
<td>695(sh)</td>
<td>690(m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>664(w)</td>
<td></td>
<td>641(m)</td>
<td>639(m)</td>
<td>639(m)</td>
<td>637(m)</td>
<td>In-plane ring deformation vibration</td>
</tr>
<tr>
<td>620(m)</td>
<td>622(s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( P = 1:10 \) Phenanthroline
\( P_{\text{H}_2\text{O}} = 1:10 \) Phenanthroline hydrate
GRAPH (23)

MOPHENANTHROLINE

TLPHENCL TLCL 2 2 4

TLPHENBrTLBr 2 2 4

TLPHENITrI 22 4

TLPHENII 22

HOPHENANTHROLINE HYDRATE
The C–H aromatic vibration is observed at 3301 cm\(^{-1}\) (89). The C–H aromatic vibration is observed at 3040 cm\(^{-1}\) as a sharp band of medium intensity with a satellite on its lower frequency side at 3014 cm\(^{-1}\). In the case of the complexes the band appears at 3042 cm\(^{-1}\) and a very weak peak is observed at 3018 cm\(^{-1}\). These positions and the intensities remain constant for the various complexes. A shift of the 1:10 phenanthroline bands towards higher frequencies on co-ordination does occur, but as can be observed is smaller than in the case of the 2-2′ bipyridine complexes in the previous section. The 1600 – 1350 cm\(^{-1}\) region

The C=N and C=C vibration frequencies occur in this region. In the spectra of the free base a group of four bands is observed, their positions being 1615, 1590, 1556 and 1425 cm\(^{-1}\). These vary in intensity. On hydration a new band appears at 1645 cm\(^{-1}\) (due to the C–H anti-symmetric and symmetric vibrations) and some shift of the other bands also takes place. On co-ordination splitting and shift of some of the bands in this region takes place. Some additional bands also appear.

It is observed that the bands which are attributed to the C=C bonds are shifted in the complexes to higher frequencies, thus indicating that complexing leads to increased localisation of the electrons in the aromatic ligand (90). This is also the explanation of the shift
involving the C=C bonds in the bipyridine complexes.

The $1250 - 1000 \, \text{cm}^{-1}$ region

The bands which appear in this region have been assigned to in-plane CH aromatic deformation and ring breathing modes. The spectrum of the free base here consists of five bands of medium intensity. In the spectrum of its hydrate the same five bands appear, some of them only slightly shifted. Apart from two weak bands at 1208 and 1203 cm$^{-1}$, which appear in the tetrachloride and tetrabromide complexes, the bands in this region are very similar in all the complexes. The slight shifts which occur in these bands are in the order:

$\langle \text{TlPhen}_2\text{Cl}_2-\text{TlCl}_4 \rangle > \langle \text{TlPhen}_2\text{Br}_2-\text{TlBr}_4 \rangle > \langle \text{TlPhen}_2\text{I}_2-\text{TlI}_4 \rangle$

They are listed in Table (45).

<table>
<thead>
<tr>
<th>Compound</th>
<th>cm$^{-1}$</th>
<th>cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10Phenanthroline</td>
<td>1092</td>
<td>1029</td>
</tr>
<tr>
<td>1:10 Phenanthroline hydrate</td>
<td>1091</td>
<td>1033</td>
</tr>
<tr>
<td>$\langle \text{TlPhen}_2\text{Cl}_2-\text{TlCl}_4 \rangle$</td>
<td>1103</td>
<td>1047</td>
</tr>
<tr>
<td>$\langle \text{TlPhen}_2\text{Br}_2-\text{TlBr}_4 \rangle$</td>
<td>1099</td>
<td>1032</td>
</tr>
<tr>
<td>$\langle \text{TlPhen}_2\text{I}_2-\text{TlI}_4 \rangle$</td>
<td>1098</td>
<td>1031</td>
</tr>
<tr>
<td>$\langle \text{TlPhen}_2\text{I}_2-\text{I} \rangle$</td>
<td>1096</td>
<td>1030</td>
</tr>
</tbody>
</table>

The 1000–600 cm$^{-1}$ region

Out-of-plane C-H deformation and in-plane ring deformations cause absorption in this region. The
The correlation between the number of adjacent hydrogen atoms and the frequency of the corresponding absorption band for in-phase-out-of-plane C-H deformation is well established for benzene with various substituents \(^{(82)}\) and for fused ring aromatic compounds \(^{(91)}\). The infra-red spectra of hetero aromatics such as pyridine, quinoline and their derivatives likewise show the above correlation \(^{(92)}\).

Table (46) lists the frequencies of the absorption bands observed between 900 - 650 cm\(^{-1}\) in the various spectra. Possibilities of the vibration involving one hydrogen atom or two and three adjacent hydrogen atoms arise. The corresponding regions of absorption \(^{(*)}\) are inserted in the column headings of the same table (46).

<table>
<thead>
<tr>
<th>Compound</th>
<th>900-850 cm(^{-1})</th>
<th>860-800 cm(^{-1})</th>
<th>810-700 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One H atom</td>
<td>Two adj. H atoms</td>
<td>Three adj. H atoms</td>
</tr>
<tr>
<td>1:10 Phenanthroline</td>
<td>876 (w)</td>
<td>854 (sh), 843 (s)</td>
<td>783 (w) 766 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>814 (w)</td>
<td>744 (sh) 734 (vs)</td>
</tr>
<tr>
<td>1:10 Phenanthroline hydrate</td>
<td>883 (w)</td>
<td>852 (vs)</td>
<td>722 (sh) 704 (w)</td>
</tr>
<tr>
<td>(\text{TlPhen}_2\text{Cl}_2_\text{TlCl}_4)</td>
<td>902 (w)</td>
<td>864 (sh) 853 (vs)</td>
<td>775 (s) 758 (vs)</td>
</tr>
<tr>
<td>(\text{TlPhen}_2\text{Br}_2_\text{TlBr}_4)</td>
<td>897 (w)</td>
<td>859 (s) 846 (vs)</td>
<td>719 (vs)</td>
</tr>
</tbody>
</table>
In phenanthroline, its hydrate and its complexes two strong bands appear at about 850 and 720 cm\(^{-1}\) as expected for one group of two and two groups of three adjacent hydrogen atoms, in the ring system. The 850 cm\(^{-1}\) band has thus been assigned to the out of plane motion of the hydrogen atoms on the centre ring and the 720 cm\(^{-1}\) band to the hydrogens on the heterocyclic rings. Several weak features are also observed in the range 900-700 cm\(^{-1}\) both in the spectrum of the free base, of its hydrate and that of its complexes. These bands probably result among other factors from out-of-phase motions of the ring hydrogen atoms.

In the 700-600 cm\(^{-1}\) region, the spectra of the free base shows a weak band at 664 cm\(^{-1}\) and a band of medium intensity at 620 cm\(^{-1}\). In the case of the hydrated base two bands still appear. The 664 cm\(^{-1}\) band is shifted to 690 cm\(^{-1}\) while the 620 cm\(^{-1}\) band remains quite constant at 622 cm\(^{-1}\). By analogy with the bipyridine complexes of the previous section the 664 cm\(^{-1}\) band can similarly be assigned as an in-plane ring deformation vibration of the pyridine ring \(83\). On complexing, however, this assignment does not appear to
be certain because of the appearance of only one band in this region, namely about 639 cm\(^{-1}\), coming intermediate between the above two frequencies.

**Nitrate Complexes**

For the purpose of comparison various 2-2' bipyridine and 1:10 phenanthroline complexes of thallium (III) nitrate were prepared and their infra-red spectra recorded. The latter are shown in graphs (24, 25) and the infra-red frequencies together with the assignments are indicated in tables (48, 49). The compounds and their molar conductivities are listed in table (47).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
<th>Conductance Mho/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>TlBipy(H(_2)O)(_2)(NO(_3))(_3)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>TlBipy(_2)(NO(_3))(_3)</td>
<td>1 \times 10(^{-3})</td>
<td>370</td>
</tr>
<tr>
<td>TlBipy(_3)(NO(_3))(_3)</td>
<td>1 \times 10(^{-3})</td>
<td>362</td>
</tr>
<tr>
<td>TlPhen(H(_2)O)(_2)(NO(_3))(_3)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>TlPhen(_2)(NO(_3))(_3)</td>
<td>1 \times 10(^{-3})</td>
<td>382</td>
</tr>
<tr>
<td>TlPhen(_3)(NO(_3))(_3)</td>
<td>1 \times 10(^{-3})</td>
<td>358</td>
</tr>
</tbody>
</table>

The conductance results are in agreement with those of Kul'ba and Mironov (24) and indicate the presence of univalent electrolytes. These compounds however hydrolyse in the following order Tl Crg\(^{+++}\) > Tl Crg\(^{++}\) > Tl Crg\(^{+}\) (where Crg = 2:2' Bipyridine or 1:10 phenanthroline) with the formation of the brown thallium (III) hydroxide. The
GRAPH (a5)

TLPHEN(H₂O)(NO)

TLPHEN(NO)

TLPHEN(NO)

2 2 3 3

2 3 3

3 3 3

25 275 30 325 35 375 40 45

5 6 7 8 9 10 11 12 13 14 15 16 17
<table>
<thead>
<tr>
<th>B</th>
<th>$\text{TlB}(\text{H}_2\text{O})(\text{NO}_3)_3$</th>
<th>$\text{TlB}_2(\text{NO}_3)_3$</th>
<th>$\text{TlB}_3(\text{NO}_3)_3$</th>
<th>ASSIGNMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3028(m)</td>
<td>3300(s)</td>
<td>3097(m)</td>
<td>3096(s)</td>
<td>Antisymmetric and symmetric O-H stretching modes</td>
</tr>
<tr>
<td>2994(w)</td>
<td>3097(s)</td>
<td>3056(w)</td>
<td>3049(s)</td>
<td>CH stretching vibrations</td>
</tr>
<tr>
<td>2967(sh)</td>
<td>3042(m)</td>
<td>3042(m)</td>
<td>3014(w)</td>
<td>H-O-H bending mode</td>
</tr>
<tr>
<td>1578(s)</td>
<td>1626(sh)</td>
<td>1600(sh)</td>
<td>1605(m)</td>
<td>$\gamma_4$ of nitrato group</td>
</tr>
<tr>
<td>1550(s)</td>
<td>1558(v.s.)</td>
<td>1558(v.s.)</td>
<td>1575(sh)</td>
<td>$\gamma_3$ of the nitrate ion</td>
</tr>
<tr>
<td>1511(sh)</td>
<td>1486(s)</td>
<td>1488(s)</td>
<td>1487(s)</td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1450(s)</td>
<td>1441(s)</td>
<td>1429(vs)</td>
<td>1441(s)</td>
<td>0-substituted pyridine vibration</td>
</tr>
<tr>
<td>1418(s)</td>
<td>1368(s)</td>
<td>1364(s)</td>
<td>1364(s)</td>
<td></td>
</tr>
<tr>
<td>1321(s)</td>
<td>1321(s)</td>
<td>1332(s)</td>
<td>1330(s)</td>
<td></td>
</tr>
<tr>
<td>1305(s)</td>
<td>1296(sh)</td>
<td>1289(sh)</td>
<td>1289(sh)</td>
<td></td>
</tr>
<tr>
<td>1268(w)</td>
<td>1263(s)</td>
<td>1263(s)</td>
<td>1263(s)</td>
<td></td>
</tr>
<tr>
<td>1248(m)</td>
<td>1232(sh)</td>
<td>1248(s)</td>
<td>1250(s)</td>
<td></td>
</tr>
<tr>
<td>1210(w)</td>
<td>1179(m)</td>
<td>1211(w)</td>
<td>1220(s)</td>
<td></td>
</tr>
<tr>
<td>1135(s)</td>
<td>1124(w)</td>
<td>1116(w)</td>
<td>1119(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1100(m)</td>
<td></td>
</tr>
</tbody>
</table>
\[
\begin{array}{|c|c|c|c|c|c|}
\hline
B & T1B(H_2O)(NO_3)_3 & T1B_2(NO_3)_3 & T1B_3(NO_3)_3 & ASSIGNMENTS \\
\hline
1085(s) & 1073(m) & 1098(w) & 1075(w) & 0-Substituted pyridine vibration \\
1060 & 1063(m) & 1068(w) & 1060(m) & \\
1038(s) & 1037(sh) & 1035(w) & 1033(s) & \gamma_2 \text{ mode of the nitrato group} \\
 & 1022(sh) & & 1019(s) & \\
 & 1016(sh) & 1014(s) & & \\
 & 1000(v.s.) & & & \\
990 & 933(w) & 976(w) & 976(w) & \gamma_6 \text{ of nitrato group} \\
890(w) & 810(sh) & 905(w) & 933(w) & \\
 & 799(s) & & 913(m) & \\
 & 782(m) & & & \\
755(vs) & 769(v.s.) & 769(v.s.) & 776(v.s.) & Out-of-plane bending of ring hydrogens \\
736(m) & 747(m) & 741(w) & 763(m) & \\
 & 725(s) & 727(w) & 742(w) & \\
 & 712(w) & 727(s) & 727(s) & Out-of-plane bending of ring hydrogens \\
652(m) & 657(w) & 646(m) & & In-plane ring deformation vibration \\
617(m) & 647(w) & 629(w) & & \\
& 637(w) & 629(w) & & \\
\hline
\end{array}
\]

\(B = 2,2'\) Bipyridine
**TABLE 49**

<table>
<thead>
<tr>
<th>P (2)</th>
<th>$\text{PH}_2\text{O}(2)$</th>
<th>$\text{TLP}(\text{H}_2\text{O})_2(\text{NO}_3)_3$</th>
<th>$\text{TLP}_2(\text{NO}_3)_3$</th>
<th>$\text{TLP}_3(\text{NO}_3)_3$</th>
<th>ASSIGNMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3333-3040 (s, bd)</td>
<td>3030 (s)</td>
<td>3030 (s)</td>
<td>Antisym. synn. stretching mode</td>
</tr>
<tr>
<td>3020 (s)</td>
<td>3301 (s)</td>
<td>3014 (w)</td>
<td>2994 (sh)</td>
<td>2994 (sh)</td>
<td>CH stretching vibrations</td>
</tr>
<tr>
<td>2997 (sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH stretching vibrations</td>
</tr>
<tr>
<td>2997 (sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH stretching vibrations</td>
</tr>
<tr>
<td>2997 (sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH stretching vibrations</td>
</tr>
<tr>
<td>1615 (m)</td>
<td>1642 (m)</td>
<td>1653 (sh)</td>
<td>1608 (m)</td>
<td></td>
<td>H-O-H bending mode</td>
</tr>
<tr>
<td>1615 (m)</td>
<td>1621 (m)</td>
<td>1610 (m)</td>
<td></td>
<td></td>
<td>H-O-H bending mode</td>
</tr>
<tr>
<td>1590 (s)</td>
<td>1585 (s)</td>
<td>1595 (m)</td>
<td></td>
<td></td>
<td>H-O-H bending mode</td>
</tr>
<tr>
<td>1556 (s)</td>
<td>1563 (v.s.)</td>
<td>1560 (s)</td>
<td>1558 (s)</td>
<td></td>
<td>C=O stretching vibrations</td>
</tr>
<tr>
<td>1556 (s)</td>
<td>1508 (s)</td>
<td>1481 (v.s., bd)</td>
<td>1497 (m)</td>
<td></td>
<td>$\gamma_4$ of nitrato group</td>
</tr>
<tr>
<td>1425 (v.s.)</td>
<td>1425 (v.s.)</td>
<td>1429 (s)</td>
<td>1479 (sh)</td>
<td>1451 (w)</td>
<td>$\gamma_3$ of the nitrate ion</td>
</tr>
<tr>
<td>1346 (s)</td>
<td>1344 (m)</td>
<td>1342 (s)</td>
<td>1349 (v.s.)</td>
<td>1328 (v.s.)</td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1346 (s)</td>
<td>1307 (sh)</td>
<td>1307 (sh)</td>
<td>1307 (sh)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1297 (w)</td>
<td>1266 (s, bd)</td>
<td>1269 (sh)</td>
<td>1269 (sh)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1297 (w)</td>
<td>1244 (sh)</td>
<td>1242 (w)</td>
<td>1242 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1217 (w)</td>
<td>1219 (s)</td>
<td>1218 (w)</td>
<td>1218 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1217 (w)</td>
<td>1200 (w)</td>
<td>1202 (w)</td>
<td>1202 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1135 (m)</td>
<td>1135 (m)</td>
<td>1147 (s)</td>
<td>1129 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1135 (m)</td>
<td>1101 (s)</td>
<td>1101 (s)</td>
<td>1101 (s)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1092 (m)</td>
<td>1091 (m)</td>
<td>1089 (sh)</td>
<td>1096 (m)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1075 (w)</td>
<td>1077 (sh)</td>
<td>1055 (w)</td>
<td>1086 (sh)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1029 (w)</td>
<td>1033 (w)</td>
<td>1029 (w)</td>
<td>1050 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1029 (w)</td>
<td>1033 (w)</td>
<td>1029 (w)</td>
<td>1050 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1029 (w)</td>
<td>1033 (w)</td>
<td>1029 (w)</td>
<td>1050 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1029 (w)</td>
<td>1033 (w)</td>
<td>1029 (w)</td>
<td>1050 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
<tr>
<td>1029 (w)</td>
<td>1033 (w)</td>
<td>1029 (w)</td>
<td>1050 (w)</td>
<td></td>
<td>$\gamma_1$ mode of the nitrato group</td>
</tr>
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<td>1029 (w)</td>
<td>1033 (w)</td>
<td>1029 (w)</td>
<td>1050 (w)</td>
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<td>$\gamma_1$ mode of the nitrato group</td>
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<td>1029 (w)</td>
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<td>1029 (w)</td>
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<td>1029 (w)</td>
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<tr>
<td>P (2)</td>
<td>PH₂O(2)</td>
<td>Tl₂P₂(NO₃)₃</td>
<td>Tl₃P₃(NO₃)₃</td>
<td>ASSIGNMENTS</td>
<td></td>
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<tr>
<td>993(w)</td>
<td>987(m)</td>
<td>1004(s)</td>
<td>1002(sh)</td>
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<td>883(w)</td>
<td>902(w)</td>
<td>971(w)</td>
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<tr>
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<td>856(s)</td>
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<td>829(sh)</td>
<td>792(w)</td>
<td>In-plane ring deformation vibration</td>
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<td>766(s)</td>
<td>776(s)</td>
<td>776(m)</td>
<td>773(w)</td>
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<tr>
<td>744(sh)</td>
<td>738(v.s.)</td>
<td>743(w)</td>
<td>789(w)</td>
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<tr>
<td>734(v.s.)</td>
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<tr>
<td>718(v.s.)</td>
<td>717(v.s.)</td>
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<tr>
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<td>707(sh)</td>
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<td>695(sh)</td>
<td>690(m)</td>
<td>690(m)</td>
<td>756(w)</td>
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<tr>
<td>620(w)</td>
<td>622(s)</td>
<td>671(w)</td>
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</table>

P = 1:10 Phenanthroline
P₂H₂O = 1:10 Phenanthroline hydrate
mono 2'-2' bipyridine and 1:10 phenanthroline complexes hydrolyse very readily and thus it was not possible to measure their conductivities at the concentration studied. Attempts to employ other solvents such as nitrobenzene, nitromethane, dimethylformamide, etc. failed because of the insolubility of these complexes in them. It was noted that the solubility of the 1:10 phenanthroline thallium (III) nitrate complexes in water was greater than that of the corresponding 2-2' bipyridine ones.

The general feature of the infra-red spectra of all the nitrate complexes are similar in nature to that of the halogeno complexes studied in the previous section. A few more peaks due to the nitrate vibrations and, in the case of the aquo complexes, to the C-H vibrations are observed. Overlapping of nitrate frequencies with those of the complexes are also apparent. Their spectra are shown in graphs (24) and (25); the positions, intensities and assignment of the bands are given in tables (48) and (49).

The 3000 cm\(^{-1}\) region

Certain differences are observed here in the spectra of the various complexes. In the spectra of both the TlBipy(H\(_2\)O)\(_2\)(NO\(_3\))\(_3\) and TlPhen(H\(_2\)O)\(_2\)(NO\(_3\))\(_3\) a broad peak, due to the C-H antisymmetric and symmetric stretching vibrations (89), appears. For the bipyridine complex
two peaks due to the CH stretching vibrations are apparent but are not evident in the phenanthroline complex. In the spectrum of the bis-2-2'-bipyridine complex \( \text{TlBipy}_2(\text{NO}_3)_3 \) few peaks appear in this region, as in the case of the bis halogeno complexes of the previous section. The tris complex, \( \text{TlBipy}_3(\text{NO}_3)_3 \), is however characterised by only two peaks. The spectra of the bis and tris 1:10 phenanthroline nitrate complexes both show a peak at 3030 cm\(^{-1}\) with a shoulder on its lower frequency side. The spectra of the bis and tris 1:10 phenanthroline nitrate complexes are thus similar in this region while the bipyridine complexes differ.

**The 1600 - 1350 cm\(^{-1}\) region**

The H-O-H bending mode of the water molecules causes absorption at 1626 and 1653 cm\(^{-1}\) (97) in the spectrum of the 2-2' bipyridine and 1:10 phenanthroline aquo complexes respectively. As was noted in the previous section the spectrum of the ligands contained fairly weak features between 1250 and 1350 cm\(^{-1}\) and it is in this range that intense bands indicative of ionic nitrate (1330 cm\(^{-1}\)) and the covalent nitrate group (1280 cm\(^{-1}\)) are expected to occur. In the mono bipyridine and 1:10 phenanthroline complexes the appearance of a very strong peak around 1500 cm\(^{-1}\) is also an indication of a coordinated nitrate-group (93). According to Gatehouse and co-workers (93) the
absorption occurring in the region 1531 - 1481 cm\(^{-1}\) (the \(\gamma_4\) mode of the nitrato group or asymmetric NO\(_2\) stretching mode) and 1290 - 1251 cm\(^{-1}\) (the \(\gamma_1\) mode of the nitrato group or NO\(_2\) stretching mode) do not occur in ionic nitrates where all the N-O bonds are equivalent; whereas characteristic vibrations of O-NO\(_2\) (\(\gamma_4\) and \(\gamma_1\)) are possible when one of the oxygen atoms is covalently bonded to another atom. Peaks in the region near 1050 cm\(^{-1}\) have furthermore been assigned to the N-O stretching frequencies (the \(\gamma_2\) mode of the nitrate group). In both the mono complexes studied an intense band is observed at 1266 (for the 1:10 \(\text{phenanthroline complex}\)) and at 1263 (for the 2;2' \(\text{bipyridine complex}\)); thus nitrato groups are indicated. The bis and tris complexes of both 2;2' bipyridine and 1:10 \(\text{phenanthroline}\), on the other hand show peaks around 1350 cm\(^{-1}\) indicating that the nitrate group is ionic. The infra red results are thus consistent with the conductivity measurements. Strong peaks in the region 970 - 1034 cm\(^{-1}\), in the spectra of the mono complexes, possibly correspond to the N-O stretching frequency (the \(\gamma_2\) mode of the nitrate group). In the case of the trigonally symmetric NO\(_2^-\) ion the absorption at 1050 cm\(^{-1}\) is infra red inactive but appears as a strong absorption in the nitrato complexes due to reduction of symmetry. Gatehouse and co-workers (93) observed that
this forbidden vibration appeared weakly in the region of 1050 cm
in the complexes containing the free nitrate ion. This is seen to be the case here with the bis and tris complexes. Another peak, only observed in the spectra of the mono complexes is that near 799 cm
corresponding to the \( \gamma_6 \) mode of the nitrato group, namely, the out-of-plane rocking vibration. In addition the appearance of strong bands near 1382 and 1300 cm
in the spectra of both mono complexes must also be considered. These bands indicate characteristic nitrate ion frequencies.

From these infra red results, the structures of the mono complexes seem to contain both covalent and ionic nitrate. The presence of coordinated bonds between thallium and the water molecules should give rise to new modes of vibration (i.e. the wagging, twisting and rocking modes) of the water bonded to the thallium atom. However, these bands are expected in the 1000 - 714 cm
region (94) and here the presence of other strong absorptions prevents their observation, if present.

From the evidence here obtained, the mono complexes may be tentatively formulated as:

\[ \text{L}_{\text{Tl}} \text{Bipy (NO}_3\text{)}_2 \text{NO}_3 \text{ and L}_{\text{Tl}} \text{Phen (NO}_3\text{)}_2 \text{NO}_3. \]

The bis and tris complexes on the other hand contained only ionic nitrate and their structures must therefore be as follows:
Further work is however needed to confirm this suggestion.

For the nitrato complexes there is the same strong shift of the band attributable to C=C vibrations (from the position in the free ligands) towards higher frequencies on coordination. This effect originally noted for the tris 2-2' bipyridine and 1:10 phenanthroline iron (II) complexes by Bush and co-workers (90) has already been explained as an increase in localisation of the electrons in the aromatic ligand.

Metal-ligand stretching frequencies (in this case M-N) are of particular interest since they provide direct information about the coordinate bond. Because of the relatively heavy mass of the thallium atom and the low bond order of the coordinate bond the M-N stretching vibration would be expected in the low frequency region below 600 cm⁻¹. A comparison of the values found for other metal-ligand bonds (such as M-C in cyanides (95) (500 cm⁻¹); M-F in complex fluorides (96) (400 cm⁻¹); Pt-N in amines (97) (540 cm⁻¹); Co-N in Co(NH₂)₆³⁺ (98) (575 cm⁻¹)) gives in general an idea of the expected range for the M-N frequencies. More valuable information can however be obtained from Inkeep's (80) work on the infra-red spectra of some 2-2' bipyridine and 1:10 phenanthroline divalent
metal complexes in the region below 600 cm\(^{-1}\). With the exception of the iron (II) complexes for which he assigned the Fe-N stretching frequencies at 423 cm\(^{-1}\) (for the 2-2' bipyridine complex) and 530 cm\(^{-1}\) (for the 1:10 phenanthroline complex), the M-N stretching frequencies for the other complexes (Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\)) appeared in the range 260-300 cm\(^{-1}\). He attributed this difference between the iron (II) complexes and the other divalent metal complexes, as a difference in bonding in the former from that in the latter.

Nyholm (qq) following the original suggestion of Pauling (100), has furthermore proposed that the major factor responsible for electron pairing and strong covalent binding in many of the 2-2' bipyridine and 1:10 phenanthroline complexes, is the formation of double bonds and suggested the structures I and II contributing to a resonance hybrid:

\[
\text{I} \quad \leftrightarrow \quad \text{II}
\]

Double bonding of this type would be expected to strengthen the Ti-N bonds, but if present, it does not appear to strengthen them sufficiently to bring the infra-red peaks above 400 cm\(^{-1}\), as no indication was found with the
instrument (Grubb-Parsons DB' model) whose extreme range was 550cm$^{-1}$. It is however expected from the correlation with other M-N frequencies that the Tl-N band is likely to be in the range 200–250cm$^{-1}$. 
Ultra-Violet Absorption Spectra

The ultra-violet absorption spectra of 2-2' bipyridine and 1:10 phenanthroline and those of their complexes with thallium (III) halides were measured in ethanol using an Unicam SP700 Spectrophotometer. Small path length silica cells (0.1 - 0.2 cm) were employed in order to eliminate any solvent absorption in this region of the spectrum. The solutions used were of the order of $10^{-5} M$.

Graphs (26) and (27) show the spectra of 2-2' bipyridine and 1:10 phenanthroline respectively in the region 48,000 - 32,000 cm$^{-1}$ (208 - 313 m$\mu$). The spectra for complexes of the type $\text{TlOrg}_2X_2\text{TLX}_4$ and $\text{TlOrg}_2X_2\text{TX}'$ (where Org = 2-2' bipyridine or 1:10 phenanthroline and X = Cl, Br or I and X' = I) are shown in graphs (28) and (29). The positions of the absorption maxima and extinction coefficients for both ligands and those for their complexes are listed in table (50).

As can be observed from graphs (26) and (27), the spectra of the free ligands consist of two bands at 35,200 cm$^{-1}$ (284 m$\mu$) and 42,194 cm$^{-1}$ (237 m$\mu$) (for 2-2' bipyridine and at 37,700 cm$^{-1}$ (265 m$\mu$) and 43,400 cm$^{-1}$ (235 m$\mu$) (for 1:10 phenanthroline). The spectra of 2-2' bipyridine in ethanol shows an additional shoulder at 41,000 cm$^{-1}$ (243 m$\mu$). These band positions and their
GRAPH (26)
ULTRA VIOLET ABSORPTION SPECTRUM OF
1:10 PHENANTHROLINE IN ETHANOL.

GRAPH (27)
ULTRA VIOLET ABSORPTION SPECTRUM OF
2-2' BIPYRIDINE IN ETHANOL.
GRAPH (28)
ULTRA VIOLET ABSORPTION SPECTRA
(a) [TEBI2Cl4]TeCl4  (b) [TEBI2Br4]TeBr4
(c) [TEBI2I4]TeI4 (RED)  (d) [TEBI2I4]TeI4 (YELLOW)
(e) [TEBI2I4]I
GRAPH (a)
ULTRA VIOLET ABSORPTION SPECTRA OF
(a) [Tetphen₂Cl₂]⁴⁺ (b) [Tetphen₂Br₂]⁴⁺ (c) [Tetphen₂I₂]⁴⁺ (d) [Tetphen₂I₁]⁺
<table>
<thead>
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<th>Compound</th>
<th>Ultra-Violet Absorption Spectra of 2-2' Bipyridine and 1:10 Phenanthroline Complexes</th>
</tr>
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<tr>
<td></td>
<td>cm⁻¹ (μ)</td>
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<tr>
<td>2-2' Bipyridine</td>
<td>35,200 (284.0)</td>
</tr>
<tr>
<td>(TLBipy₂Cl₂)TLCl₄</td>
<td>35,500 (281.7)</td>
</tr>
<tr>
<td>(TLBipy₂Br₂)TLBr₄</td>
<td>35,700 (280.1)</td>
</tr>
<tr>
<td>(TLBipy₂I₂)TLI₄ (red)</td>
<td>35,600 (280.9)</td>
</tr>
<tr>
<td>(TLBipy₂I₂)TLI₄ (yellow)</td>
<td>35,600 (280.9)</td>
</tr>
<tr>
<td>1:10 Phenanthline</td>
<td>37,700 (265.3)</td>
</tr>
<tr>
<td>(TLPhen₂Cl₂)TLCl₄</td>
<td>36,700 (265.3)</td>
</tr>
<tr>
<td>(TLPhen₂Br₂)TLBr₄</td>
<td>37,000 (270.3)</td>
</tr>
<tr>
<td>(TLPhen₂I₂)TLI₄</td>
<td>37,000 (270.3)</td>
</tr>
<tr>
<td>(TLPhen₂I₂)I</td>
<td>36,700 (272.5)</td>
</tr>
</tbody>
</table>
extinction coefficients are in good agreement with those reported in the literature (102, 103).

The spectra of the various complexes of thallium (III) halides with the above ligands are found to be very similar for each series. In each case the intense ligand bands are observed, only minor shifts occurring. The extinction coefficients however differ from complex to complex. These are of the order of $3.6 \times 10^{-4}$ - $6.4 \times 10^{-4}$ and $4.8 \times 10^{-4}$ - $10 \times 10^{-4}$ for the 2-2' bipyridine and 1:10 phenanthroline complexes respectively. The chloro complexes have the lower extinction coefficients whilst the corresponding bromo complexes have the higher ones. The disappearance on coordination of the shoulder (at 41,000 cm$^{-1}$) indicated above in the spectrum of the free 2-2' bipyridine must be noted. Additional shoulders appear however in both the 2-2' bipyridine (at $33,000$ cm$^{-1}$ (303 m$\mu$)) and the 1:10 phenanthroline (at $34,000$ cm$^{-1}$ (294 m$\mu$)) complexes. These shoulders, which are absent in the spectra of the free ligands, thus seem characteristic of the complex compounds.

If the simple dissociation of these complexes is considered:

$$\begin{align*}
\text{Tl}\text{O}_6\text{X}_2^-\text{TLX}_4^- & \rightleftharpoons \text{Tl}\text{O}_6\text{X}_2^- + \text{TLX}_4^- \\
\text{the appearance of the TlCl}_4^- & \text{bands (at 40,600 cm}^{-1}(246.3 \text{m} \mu)\text{) and TlBr}_4^- \text{bands (at 36,300 cm}^{-1}(275.4 \text{m} \mu)\text{).} 
\end{align*}$$


be indicated in the spectra of these complexes. No such bands are however indicated in the above spectra and thus a comparison of the intensities of the tetrahalothallate bands with those of the organic ligand is necessary. The results show that the latter bands are quite intense.

The maximum extinction coefficients for the 2-2' bipyridine bands are $1.0 \times 10^4$ and $1.8 \times 10^3$ whilst those for the 1:10 phenanthroline ones are $2.9 \times 10^4$ and $4.1 \times 10^4$. In the case of these coordination compounds containing two molecules of 2-2' bipyridine and 1:10 phenanthroline, the ligand bands must furthermore increase in intensity giving rise to still higher extinction coefficients (table (50)). It is thus expected, as already noted in the spectra of the intermediate compounds (section (VI)), that the tetrahalogeno bands must be submerged under the highly intense bands arising in this case from the organic ligands. Contribution from the $\text{TlX}_4^-$ bands towards the total intensity of the system must however arise. The situation for the two iodide complexes, namely $\text{TlOg}_2\text{I}_2^-\text{I}$ must be analogous and the characteristic iodide bands, which are of lower intensity than those from the organic ligands, are also masked by the latter bands.

A further point of interest arises when the spectra of the two forms of the iodothallate complexes of 2-2' bipyridine are considered i.e. the yellow and red forms.
The infra-red spectra results for these compounds indicated a cis configuration of the bipyridine rings in the yellow compound whilst a trans configuration was ascribed for the red compound. The ultra-violet absorption spectra for these compounds (graph (23)) show however that their bands are coincident in position and intensity in the ultra-violet region. In view of these facts it must be inferred that although the cis configuration exists in the solid state, on passing into solution, this compound undergoes a change to the trans configuration.

The visible spectra of the coloured $[\text{TlCr}_{2}I_{2}]I_{4}$ and $[\text{TlCr}_{2}I_{2}]I$ compounds were measured in the solid state (reflectance spectra) and in ethanol solutions $(10^{-4}\text{M})$. The spectra of these solutions showed a band at $25,000\text{cm}^{-1}$ $(400\text{m} \mu \text{and } \epsilon_{\text{max}} = 10 \times 10^{5})$ which is the same band obtained for the tetralkyl ammonium iodothallate compound. This is shown in graph (11) (page 104). The solid state spectra for the $[\text{TlCr}_{2}I_{2}]I_{4}$ and $[\text{TlCr}_{2}I_{2}]I$ were also measured. A very broad band ranging from $28,571 - 20,833\text{cm}^{-1}$ $(350 - 480\text{m} \mu )$ was observed in each case with an approximate maximum at $25,000\text{cm}^{-1}$ $(400\text{m} \mu )$. The range covered by these bands was found to be in agreement with that for the absorption band $(33,330 - 21,759\text{cm}^{-1}$ or $300 - 460\text{m} \mu )$ observed by Hilsch and Pohle (104) for solid iodine. A detailed interpretation of these bands
could not however be made because the reflectance spectra measured in the present work were entirely in the undiluted state.
In the previous section, the 2-2' bipyridine and 1:10 phenanthroline complexes of thallium (III) halides were studied both conductimetrically and spectrophotometrically in organic solvents. These measurements indicated the presence of the complexation species in the solutions but they did not lead to any quantitative evidence of the extent of dissociation of such species. Measurements of the stability constants are the usual methods for determining the effect of solvent interactions on complex ionic species.

Various experimental methods such as conductance, potentiometric, distribution, optical and many others are available for investigating the stability of complex ionic species in solution. A comprehensive and thorough treatment of the theory and measurement of stability constants is to be found in the book of Rossotti and Rossotti (105).

In the case of the complexes of thallium (III) it has already been shown that the simple halide complexes have been studied by potentiometric, spectrophotometric and distribution methods by several workers (316). Little work of this kind appears to have been done on other complex compounds of thallium (III). Apart from an approximate instability constant determination for TlBipy$_3^{3+}$ and a
potentiometric study for $\text{TlPhen}^3+$, $\text{TlPhen}_2^3+$ and $\text{TlPhen}_3^3+$, by Kul'ba and co-workers (24), no other stability constants determination appeared to have been made.

A study of various methods suggested that the distribution method might be suitable for investigating the stability of these complexes, as used by Koltoff in the study of zinc:1:10 phenanthroline complexes (106). An attempt was made to apply this method to the thallium (III):1:10 phenanthroline perchlorate (or nitrate) system using chloroform/water, carbon tetrachloride/water and n-hexane/water as solvents. The perchlorate and nitrate are the most soluble of the thallium (III):1:10 phenanthroline complexes but their solubility was still too low for accurate results to be obtained. When relatively higher concentrations in the organic solvent were employed, precipitates of $\text{TlPhen}_2^-(\text{ClO}_4)_3^-$ and $\text{TlPhen}_2^-(\text{NO}_3)_3^-$ were obtained on mixing with water. This method was thus not developed.

**Method of competitive reactions**

Koltoff in addition to the distribution method, successfully employed the competitive reaction method to find the instability constants of the zinc:1:10 phenanthroline nitrate (106) complexes. Several metal complexes have been studied by this method (105) using various analytical techniques. In this method a spectrophotometric measurement with a Unicam Sp 500 Spectrophotometer can be used.
If $M$ and $M'$ represent two central metal species each of which can form a complex with a ligand $L$, two series of complexes $M_L^n$ and $M'L^n_*$ will tend to be formed with stability constants $\beta_n$ and $\beta'_n$ respectively. An auxiliary metal cation is introduced which competes with that being studied for the complexing agent. Knowledge of the stability constants of the complexes of one of the central metals (i.e. the auxiliary metal) is used to determine the stability of complexes of the other metal. Various simplifications are introduced, any hydrolytic interactions due to acid-base equilibria being ignored in the simple treatment. Iron (II) was used in Koltoff's studies (106) as an auxiliary cation since it gives complexes which generally absorb at longer wavelengths than those of other metal ions. In the current investigation iron (II) was used in competition with the thallium (III) cation. The stability constants for the ferrous tris and mono phenanthroline complexes are well established. It was previously shown by Koltoff (107) in his study of the iron (II):1:10 phenanthroline system that only the $[\text{FePhen}^{++}]$ and $[\text{FePhen}_3^{++}]$ species need to be considered under the conditions of the experiment and the concentration of the latter could be found directly from $[\text{FePhen}_3^{++}] = \text{optical density}/1.07 \times 10^{-4}$ (where $1.07 \times 10^{-4}$ is the molar extinction coefficient of this complex). The
concentration of the mono-phenanthroline iron (II) ion can be obtained by calculation, details of which will be given later.

Following Koltoff's procedure, appropriate concentrations of thallium (III) and iron (II) were used, and the two metals allowed to compete for a limited amount of 1:10 phenanthroline. The solutions were allowed to attain equilibrium and the equilibrium concentrations of tris-phenanthroline ferrous ion (ferroin) was measured spectrophotometrically. The molar concentration of 1:10 phenanthroline present as thallium (III) complexes in solutions containing thallium (III), iron (II) and 1:10 phenanthroline will be given by

\[ y = C_{\text{Phen}} - 3[FePhen]^3+ - [FePhen]^+ \]  \hspace{1cm} (1)

where \( C_{\text{Phen}} \) is the total concentration of 1:10 phenanthroline and brackets are the actual concentrations. Since both \( [FePhen]^3+ \) and \( [FePhen]^+ \) can be determined and \( C_{\text{Phen}} \) is known \( y \) can be obtained.

**Determination of the concentration of \( [FePhen]^+ \)**

The concentration of the mono-phenanthroline complex of iron (II) is obtained in the following way. Consider the stability constants for the mono \( (K_1) \) and tris \( (K_3) \) 1:10 phenanthroline complexes of iron (II), which are given by
\[ K_1 = \frac{\text{Fe}^{++} / \text{Phen}^{2-}}{\text{Fe Phen}^{++}} \quad (2) \text{ and } K_3 = \frac{\text{Fe}^{++} / \text{Phen}^{3-}}{\text{Fe Phen}^{++}} \quad (3) \]

From equation (3)

\[ \overline{\text{Phen}}^{-} = \frac{K_3^2 \overline{\text{Fe Phen}^{++}}^{1/3}}{\overline{\text{Fe}^{++}}^{1/3}} \quad (4) \]

Substituting (4) in equation (2)

\[ K_1 = \frac{\overline{\text{Fe}^{++}} \overline{\text{Phen}^{+}}^{2/3} \overline{\text{Fe Phen}^{++}}^{1/3}}{\overline{\text{Fe}^{++}}^{1/3} \overline{\text{Fe Phen}^{++}}^{1/3}} \]

\[ \overline{\text{Fe Phen}^{++}} = \frac{K_3^3}{K_1} \overline{\text{Fe Phen}^{++}}^{1/3} \overline{\text{Fe}^{++}}^{2/3} \]

but \[ \overline{\text{Fe}^{++}}^{2/3} = \left\{ \frac{C_{\text{Fe}} - \overline{\text{Fe Phen}^{++}} - \overline{\text{Fe Phen}^{+}}}{\overline{\text{Fe Phen}^{++}}} \right\}^{2/3} \]

\[ \overline{\text{Fe Phen}^{++}} = \frac{K_3^3}{K_1} \overline{\text{Fe Phen}^{++}}^{1/3} \left\{ \frac{C_{\text{Fe}} - \overline{\text{Fe Phen}^{++}} - \overline{\text{Fe Phen}^{+}}}{\overline{\text{Fe Phen}^{++}}} \right\}^{2/3} \]

Let \( \overline{\text{Fe Phen}^{++}} = x \) and \( \overline{\text{Fe Phen}^{+}} = p \) and \( \frac{K_3^3}{K_1} = q \)

\[ x = q^{1/3} (C_{\text{Fe}} - p - x)^{2/3} \]

\[ x = q^{1/3} (C_{\text{Fe}} - p)^{2/3} \left[ 1 - \frac{x}{C_{\text{Fe}} - p} \right]^{2/3} \quad (5) \]

An expansion of the term \( \left[ 1 - \frac{x}{C_{\text{Fe}} - p} \right]^{2/3} \) seems justified, neglecting terms higher than \( x^2 \). This is reasonable as \( x \) is of the order \( 10^{-6} \) and \( C_{\text{Fe}} - p \) of the order \( 10^{-4} \) so that \( \frac{x}{C_{\text{Fe}} - p} \) has the order \( 10^{-2} \) and \( \left( \frac{x^3}{C_{\text{Fe}} - p} \right)^3 \) has the order \( 10^{-6} \) which would be negligible compared to the first three terms \( (1, x, x^2) \). This method gives rise to a quadratic equation in \( x \) which can be solved in a general form so that individual results may easily be calculated. Koitoff has suggested a
solution of the problem in the case of zinc complexes by the method of successive approximations. This was in fact applied to one set of the present results and did not give rise to appreciably greater accuracy. It also needs to be repeated for each individual result, so complicating the work considerably.

Therefore expanding equation (5)

\[ x = q^3 \left( C_{Fe} - p \right)^2 \left[ 1 - \frac{2x}{5(C_{Fe} - p)} - \frac{x^2}{9(C_{Fe} - p)^2} \right] \]

\[ x = q^3 \left[ \left( C_{Fe} - p \right)^2 - \frac{2x}{5(C_{Fe} - p)^3} - \frac{x^2}{9(C_{Fe} - p)^4/3} \right] \]

\[ \frac{x^2}{9(C_{Fe} - p)^{4/3}} + \frac{2x}{5(C_{Fe} - p)^3} + \frac{x}{q^3} - \left( C_{Fe} - p \right)^2 = 0 \]

\[ x^2 + x \left[ 6(C_{Fe} - p) + \frac{9(C_{Fe} - p)^{4/3}}{q^3} \right] - 9(C_{Fe} - p)^2 = 0 \]

\[ x^2 + (C_{Fe} - p) x \left[ 6 + \frac{9(C_{Fe} - p)^{1/3}}{q^3} \right] - 9(C_{Fe} - p)^2 = 0 \]

\[ 2x - (C_{Fe} - p) \left[ 6 + \frac{9(C_{Fe} - p)^{1/3}}{q^3} \right] + \left\{ \frac{9(C_{Fe} - p)^{3/2}}{q^3} \right\} \left( C_{Fe} - p \right)^2 + 36(C_{Fe} - p)^2 \]

\[ 2x - (C_{Fe} - p) \left[ 6 + \frac{9(C_{Fe} - p)^{3/2}}{q^3} \right] + (C_{Fe} - p) \left[ \frac{36 + 108(C_{Fe} - p)^{3/2}}{q^3} \right] + \frac{81(C_{Fe} - p)^{3/2}}{q^2} + \frac{36}{q^3} \]

\[ 2x = (C_{Fe} - p) \left[ -9 \left( 6 + \frac{9(C_{Fe} - p)^{1/3}}{q^3} \right) \right] + 3 \left( \frac{12(C_{Fe} - p)^{3/2}}{q^3} + \frac{9(C_{Fe} - p)^{3/2}}{q^2} \right) \]

Let \( \frac{(C_{Fe} - p)^{1/3}}{q^3} = r \)
X = \frac{(C_{Fe} - p)}{2} \left[ - (6 + 9r) + 3 \sqrt{8 + 12r + 9r^2} \right]

x = q_p^{\frac{3}{2}} \left( \frac{(C_{Fe} - p)}{2} \right)^{\frac{3}{2}} \left[ 1 - \frac{x}{C_{Fe} - p} \right]^{\frac{3}{2}}

gives approximately

x = \frac{3(C_{Fe} - p)}{2} \left[ \sqrt{8 + 12r + 9r^2} - (2 + 3r) \right] \quad (6)

where \( r = \frac{(C_{Fe} - p)^{\frac{1}{2}}}{q_p^{\frac{3}{2}}} \)

and thus since \( x = \sqrt[3]{FePhen^{++}} \), the concentration of the mono phenanthroline iron (II) ion can be obtained by means of equation (6).

**Determination of the instability constants of thallium (III): 1:10 Phenanthroline complexes**

Consider the system:

\[ TlPhen_{n}^{+++} \rightleftharpoons Tl^{+++} + n \text{ Phen} \]

where \( n = 1, 2 \) or 3. If one assumes that only one complex is present, the instability constant of the mono complex is given by

\[ K'_1 = \frac{\sqrt{Tl^{+++}}}{\sqrt{TlPhen^{+++}}} \frac{\sqrt{TlPhen^{+++}}}{\sqrt{TlPhen^{+++}}} \quad (7) \]

The concentration of \( TlPhen^{+++} \) is thus determined by \( y \) i.e. the concentration of 1:10 phenanthroline present as thallium (III) complexes in solution.

\[ \sqrt{TlPhen^{+++}} = y \quad (8) \quad \text{and} \quad \sqrt{Tl^{+++}} = C_{Tl} - y \quad (9) \]

Substituting (8) and (9) in equation (7)
\[ K_1' = \frac{(C_{\text{Tl}} - y)}{y} \langle \text{ Phen} \rangle \]

\[ K_2' = \frac{C_{\text{Tl}}}{y} - 1 \langle \text{ Phen} \rangle \]

The concentration of unco-ordinated 1:10 phenanthroline \( \langle \text{ Phen} \rangle \) in equation (7) can be obtained from the expression for \( K_3 \) of the tris 1:10 phenanthroline iron (II) complex

\[ K_3 = \frac{\langle \text{ Fe}^{3+} \rangle}{\langle \text{ Phen} \rangle} \]

\[ \langle \text{ Phen} \rangle = \left[ \frac{K_3 \langle \text{ FePhen}_{3}^{3+} \rangle}{\langle \text{ Fe}^{3+} \rangle} \right]^\frac{1}{2} \]

\[ K_1' = \left( \frac{C_{\text{Tl}}}{y} - 1 \right) \left( \frac{K_3 \langle \text{ FePhen}_{3}^{3+} \rangle}{\langle \text{ Fe}^{3+} \rangle} \right)^\frac{1}{2} \]

Now \( \langle \text{ Fe}^{3+} \rangle = C_{\text{Fe}} - \langle \text{ FePhen}_{3}^{3+} \rangle - \langle \text{ FePhen}^{3+} \rangle \)

\[ K_1' = \frac{1}{y} \left( C_{\text{Tl}} - y \right) \left( \frac{K_3 \langle \text{ FePhen}_{3}^{3+} \rangle}{C_{\text{Fe}} - \langle \text{ FePhen}_{3}^{3+} \rangle - \langle \text{ FePhen}^{3+} \rangle} \right)^\frac{1}{2} \] (10)

Following the same procedure for the bis-phenanthroline thallium (III) ion

\[ K_2' = \frac{\langle \text{ TlPhen}_{2}^{3+} \rangle}{\langle \text{ TlPhen}_{2}^{3+} \rangle} \]

the concentration of \( \langle \text{TlPhen}_{2}^{3+} \rangle \) will be determined by one half the concentration of 1:10 phenanthroline present as thallium (III) complexes in solution.

\[ \langle \text{TlPhen}_{2}^{3+} \rangle = \frac{1}{2} y \text{ and } \langle \text{Tl}^{3+} \rangle = C_{\text{Tl}} - \frac{1}{2} y \]

\[ K_2' = \frac{(C_{\text{Tl}} - \frac{1}{2} y) \langle \text{ Phen} \rangle}{\frac{1}{2} y} \] (12)
and obtaining the concentration of unco-ordinated 1:10 phenanthroline as above one finds

$$K'_2 = \frac{2}{y} \left(C_{\text{Tl}} - \frac{V}{2}\right) \left\{ \frac{K_3 \sqrt[3]{\text{FePhen}^{++7}}}{C_{\text{Fe}} - \sqrt[3]{\text{FePhen}^{++7} - \text{FePhen}^{++7}}} \right\}^{\frac{3}{2}} \tag{13}$$

The instability constant $K'_3$ for the tris 1:10 phenanthroline thallium (III) complex is found similarly and is given by equation (14).

$$K'_3 = \frac{3}{y} \left(C_{\text{Tl}} - \frac{V}{2}\right) \left\{ \frac{K_3 \sqrt[3]{\text{FePhen}^{++7}}}{C_{\text{Fe}} - \sqrt[3]{\text{FePhen}^{++7} - \text{FePhen}^{++7}}} \right\} \tag{14}$$

**Experimental**

(a) **Thallium (III) perchlorate**

Stock solutions of thallium (III) perchlorate were prepared as follows. Thallium (I) acetate ($3g$) was dissolved in water and the solution made alkaline with sodium hydroxide. A 30% solution of hydrogen peroxide was then added slowly to oxidise to thallium (III) until further addition of peroxide produced no vigorous reaction. The resultant hydrous thallium (III) oxide was washed by decantation, filtered, washed, dried at $115^\circ\text{C}$ for two hours and then dissolved in a large excess of perchloric acid. Appropriate weights were taken, dissolved in perchloric acid and made up to the required volume so as to give solutions 0.01M in thallium. The stock solutions were stored in dark bottles as suggested by Biedermann (108) to prevent reduction of
thallium (III) by sunlight. The stock thallium (III) perchlorate solutions were standardised iodimetrically: sodium iodide was added and the liberated iodine was titrated with sodium thiosulphate to a starch end point. From the standardisation data and the weight of thallium (III) oxide used the prepared oxide was calculated to have an empirical formula $\text{Tl}_2\text{O}_3\cdot2\text{H}_2\text{O}$. The excess acid in the thallium (III) perchlorate solution was assayed by addition of excess standard sodium hydroxide, centrifugation of the thallium (III) hydroxide and back titration of the alkali with standard acid.

(b) **1:10 Phenanthroline solution**

1:10 phenanthroline was recrystallised from alcohol until a sharp melting point at 102°C was obtained. Stock solutions were made up by dissolving the appropriate weight of the base in water to the required volume.

(c) **Ferrous ammonium sulphate solution**

Ferrous ammonium sulphate reagent was prepared by dissolving the exact quantity of the analar reagent in 0.01M sulphuric acid to give a $2.04 \times 10^{-3}$M solution. One-tenth of a gram of hydroxylamine hydrochloride was added to the solution to inhibit oxidation.

**Method of competitive reactions using iron (II) as auxillary cation**

**Procedure**

Appropriate concentrations of thallium (III) and of
1:10 phenanthroline were taken into 100 mls. volumetric flasks buffered at pH 5 by means of a sodium acetate-acetic acid buffer (8:2) and made up to the required volume by means of the buffer. Twenty mls. aliquots were transferred into a conical flask which was thermostated at 25°C. Nitrogen gas was bubbled through the solution for several minutes. Two mls. of the ferrous ammonium solution were then added, nitrogen bubbled through and the solution allowed to attain equilibrium at the above temperature. The optical density of the solution was measured by means of an Unicam SP500 spectrophotometer whose cell compartment was thermostated at the same temperature. Matched silica cells (1cm.) were used throughout. Dilutions of the stock solutions, whether for analysis or for actual experiments was most accurately performed either by the use of calibrated pipettes or of an accurate burette.

Results

To illustrate the method of calculation (described on page 210), the following example (Experiment 4, table 51) is calculated in detail.

\[
\begin{align*}
C_{Tl} & = 1.0 \times 10^{-4} \text{M} \\
C_{Fe} & = 1.85 \times 10^{-4} \text{M} \\
C_{Phen} & = 2 \times 10^{-4} \text{M}
\end{align*}
\]

Optical density = 0.406

\[
K_1 = 1.3 \times 10^{-6} \text{ at } 25^\circ \text{C}
\]

\[
K_3 = 5 \times 10^{-22} \text{ at } 25^\circ \text{C}
\]
\[ \left[ \text{FePh}_3^{++} \right] = 0.406/1.07 \times 10^4 = 3.79 \times 10^{-5} = \text{p in equ. (6)} \]

\[ q = \frac{K_2^{\frac{1}{3}}}{K_1} = 0.061055 \]

\[ r = \frac{C_{\text{Fe}} - p}{q p^{\frac{1}{3}}} = \frac{(1.85 \times 10^{-4} - 3.79 \times 10^{-5})^{\frac{1}{3}}}{6.1055 \times 10^{-2} \times (3.79 \times 10^{-5})^{\frac{1}{3}}} \]

\[ r = 86.46 \]

\[ C_{\text{Fe}} - p = 1.471 \times 10^{-4} \]

\[ x = \left[ \text{FePhen}^{++} \right] = \frac{3 \times 1.471 \times 10^{-4}}{2} \left[ \sqrt{8+12x86.46+9x(86.46)^2} \right] \]

\[ -(2+3x86.46) \]

\[ x = 5.5 \times 10^{-6} \]

\[ y = C_{\text{Phen}} - \left[ \text{FePhen}_3^{++} \right] - \left[ \text{FePhen}^{++} \right] \]

\[ y = 2 \times 10^{-4} - 3 \times 3.79 \times 10^{-5} - 5.5 \times 10^{-6} \]

\[ y = 0.81 \times 10^{-4} \]

\[ K_n = \frac{n}{\gamma} \left[ \text{FeTl} \right] - \frac{x}{n} \left[ \text{FePhen}_3^{++} \right] \left( \frac{K_2 \left[ \text{FePhen}_3^{++} \right]}{C_{\text{Fe}} - \left[ \text{FePhen}_3^{++} \right] - \left[ \text{FePhen}^{++} \right]} \right)^{\frac{1}{3}} \]

\[ K_1 = \frac{1}{0.81 \times 10^4} \left[ 1.85 \times 10^{-4} \times 0.81 \times 10^{-4} \right] \left[ \frac{5 \times 10^{-22} \times 3.79 \times 10^{-5}}{1.85 \times 10^{-4} - 3.79 \times 10^{-5} - 5.5 \times 10^{-6}} \right] \]

\[ K_1 = 12.00 \times 10^{-9} \]

Similarly: \( K_2 = 3.84 \times 10^{-15} \) and \( K_3 = 3.62 \times 10^{-22} \)

Preliminary experiments were carried out using varying concentrations of thallium (III) but, without standardising the ionic strength, to test the applicability of the competitive reaction method to this system. Although these preliminary results were found to be reproducible for thallium concentrations ranging from \( 0.5 \times 10^{-4} \) to \( 2 \times 10^{-4} \),
plots of the thallium concentrations versus either \( \left[ \text{FePh}^{+7} \right] \) or \( R \ (R = \frac{\left[ \text{FePhen}_3^{+7} \right]}{\left[ \text{FePhen}^{+7} \right]} ) \), obtained by calculation from the experimental data, gave rather scattered results. It was then thought that by maintaining the ionic strength of the solution at a constant value more consistent results would be found. This in fact was the case, as can be observed from the plots shown in graphs (30) and (31). The first of these graphs shows the thallium concentration plotted versus that of the mono and tris complex calculated by the method in the preceding pages. The points marked \( \circ \cdots \circ \) are those at constant ionic strength and those indicated \( \triangle \cdots \triangle \) are some of the more satisfactory preliminary experiments at one of the extreme concentrations in the range covered. The second graph shows the thallium concentration plotted against \( R \ (R = \frac{\left[ \text{FePhen}_3^{+7} \right]}{\left[ \text{FePhen}^{+7} \right]} ) \) the points being similarly indicated. The graphs thus show a satisfactory distribution about the straight lines indicated, in view of the fact that very small differences in the measured optical density become significantly magnified during the course of the calculations. Table (51) gives the results and experimental data used in these graphs and employed in calculating the instability constants.
Graph (30°)

Graph (31)

Concentration of iron complexes

\[ R = \frac{[\text{FePhen}_3]^{++}}{[\text{FePhen}_2]^{+}} \]
TABLE 5

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$C_{Tl} \times 10^4$</th>
<th>O.D.</th>
<th>$[FePhen^{++}] \times 10^5$</th>
<th>$[FePh_{2}^{++}] \times 10^6$</th>
<th>$y \times 10^4$</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>0.284</td>
<td>2.65</td>
<td>5.5</td>
<td>1.15</td>
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</tr>
<tr>
<td>2</td>
<td>1.3</td>
<td>0.317</td>
<td>2.96</td>
<td>5.4</td>
<td>1.06</td>
<td>5.52</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>0.351</td>
<td>3.28</td>
<td>5.5</td>
<td>0.97</td>
<td>5.99</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0.406</td>
<td>3.79</td>
<td>5.5</td>
<td>0.81</td>
<td>6.80</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>0.441</td>
<td>4.12</td>
<td>5.6</td>
<td>0.72</td>
<td>7.36</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>0.505</td>
<td>4.72</td>
<td>5.6</td>
<td>0.53</td>
<td>8.46</td>
</tr>
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<td>4.83</td>
<td>5.6</td>
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<td>8.51</td>
</tr>
<tr>
<td>8</td>
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<td>5.80</td>
<td>5.7</td>
<td>0.20</td>
<td>10.01</td>
</tr>
<tr>
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<td>0.554</td>
<td>6.11</td>
<td>5.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By using the above results and the equation

$$K = \frac{n}{y} \left( \frac{C_{Tl} - \frac{y}{n}}{\frac{K_{3}[FePhen_{3}^{+++}]}{C_{Fe} - [FePhen_{3}^{+++}] - [FePhen^{++}]} \right)$$

it was possible to determine the instability constants for the mono, bis and tris thallium (III) complexes. These are listed in Table (52).
TABLE S2

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$K_1 \times 10^9$</th>
<th>$K_2 \times 10^{15}$</th>
<th>$K_3 \times 10^{22}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>13.46</td>
<td>3.14</td>
<td>2.52</td>
</tr>
<tr>
<td>2.</td>
<td>10.46</td>
<td>3.10</td>
<td>2.64</td>
</tr>
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<td>3.</td>
<td>6.45</td>
<td>2.94</td>
<td>2.68</td>
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<tr>
<td>4.</td>
<td>12.00</td>
<td>3.84</td>
<td>3.62</td>
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<tr>
<td>5.</td>
<td>5.89</td>
<td>3.43</td>
<td>3.48</td>
</tr>
<tr>
<td>6.</td>
<td>7.45</td>
<td>4.01</td>
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</tr>
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<td>-</td>
<td>3.18</td>
<td>3.49</td>
</tr>
<tr>
<td>8.</td>
<td>-</td>
<td>-</td>
<td>11.26</td>
</tr>
</tbody>
</table>

Mean values of $9.28 \times 10^{-9}$ (for $K_1$), $3.41 \times 10^{-15}$ (for $K_2$) and $3.20 \times 10^{-22}$ (for $K_3$) were obtained from table (51) (Experiments 1 - 6). For the later experiments (7 and 8) when less thallium (III) is present the term $(C_{Tl} - \frac{Y}{n})$ becomes very sensitive to small errors. It is this which makes it impossible to obtain instability constant values from experiments 7 and 8 in the table above.

A further set of experiments using Job's method was employed by Koltoff and co-workers to determine the most abundant species in solution as indicated by the values of the above instability constants. An attempt to apply this method to the present investigation was made.
Method of continuous variations (Job's method)

The experimental procedure was essentially the same as before, except that here the total molar concentration of ligand and metal was maintained constant. The iron (II) concentration is the same as in the earlier experiments but \( C_{Tl} + C_{\text{Phen}} \) was kept constant at \( 2 \times 10^{-4} M \). The optical density of the solution was measured using varying proportions of ligand and metal within this limit. The equilibrium molar concentration of phenanthroline present as thallium (III) complexes (\( y \)), were obtained from the equation \( y = C_{\text{Phen}} - 3(Fe\text{Phen}_{2}^{++}) - (Fe\text{Phen}^{+++}) \) since \( C_{\text{Phen}} \) is known and \( (Fe\text{Phen}_{2}^{++}) \) and \( (Fe\text{Phen}^{+++}) \) are calculated as before. These are listed in column 7 (Table 53).

By making an assumption that only one complex is present it is possible to make an estimate of the concentration of 1:10 phenanthroline which would be present as each of the three complexes individually from the equation:

\[
K_n = \frac{n}{y} \sqrt[3]{C_{Tl} - \frac{y}{n}} \left\{ \frac{K_3 (Fe\text{Phen}_{2}^{++})}{C_{Fe} - (Fe\text{Phen}^{+++})} \right\}^{n/3}
\]

The instability constants from the previous section \( K_{Tl\text{Phen}^{+++}}, K_{Tl\text{Phen}_{2}^{+++}} \) and \( K_{Tl\text{Phen}_{3}^{+++}} \) are then employed to give values of \( y', y'' \) and \( y''' \) which are the concentrations of phenanthroline complexed in the mono, bis and tris thallium-1:10 phenanthroline complex respectively, if only one species is present at a time.
The following table (Table 53) shows the results of these calculations for the range of solutions measured:

**TABLE 53**

\[
R = \frac{C_{Tl}}{C_{Tl} + C_{Phen}}; \quad C_{Fe} = 1.85 \times 10^{-4} M; \quad C_{Tl} + C_{Phen} = 2 \times 10^{-4}
\]

\[\text{[}FePhen++]\] and \[\text{[}FePhen^2++]\] were obtained as before.

<table>
<thead>
<tr>
<th>(C_{Tl} \times 10^4)</th>
<th>(C_{Phen} \times 10^4)</th>
<th>(R)</th>
<th>(O.D.)</th>
<th>(FePhen^+)</th>
<th>(FePhen^{++})</th>
<th>(yx)</th>
<th>(y'x)</th>
<th>(y''x)</th>
<th>(y'''x)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.80</td>
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<td>10^5</td>
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<td>0.9</td>
</tr>
<tr>
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<td>0.560</td>
<td>5.22</td>
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</tr>
<tr>
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<td>0.440</td>
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<td>3.6</td>
</tr>
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<td>0.369</td>
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<td>10^5</td>
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</tr>
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<td>0.495</td>
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<td>0.427</td>
<td>2.78</td>
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<td>4.2</td>
<td>10^5</td>
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<td>1.97</td>
<td>5.9</td>
<td>5.4</td>
<td>10^5</td>
<td>6.6</td>
<td>5.0</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>0.50</td>
<td>0.079</td>
<td>0.74</td>
<td>2.9</td>
<td>7.5</td>
<td>10^5</td>
<td>7.5</td>
<td>3.7</td>
</tr>
<tr>
<td>1.10</td>
<td>0.90</td>
<td>0.55</td>
<td>0.031</td>
<td>0.29</td>
<td>2.7</td>
<td>7.9</td>
<td>10^5</td>
<td>7.6</td>
<td>2.4</td>
</tr>
<tr>
<td>1.50</td>
<td>0.50</td>
<td>0.75</td>
<td>0.000</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

In the cases for thallium concentrations of 0.4x10^{-4} - 0.7x10^{-4} M where two separate results are shown the values were obtained with different sets of solutions, and it was found that in this range the optical density appeared very sensitive to slight experimental variations. As a check of these experimental figures a direct plot of the optical density was made against the thallium (III) concentration. Within the range of concentrations studied the graph appears to be almost linear. From this plot then it is evident...
GRAPH (32)

The curves A, B, and C correspond to the three complete reactions, 
Alkanes (1) and (2), respectively, on which the present study is based. 
The above experimental points give results indicated by (a), in the sense 
where they are obtained, are shown as circled points. 

In the curve A, the calculated values show that in the early part of the 
series with low thallium concentrations there is a preponderance of the 
alkene complex, but at the middle stage (B and C) the thallium more 
difficult tends to form complexes with the alkane and then, with increasing 
thallium concentration, increases the rate of the reaction. 

The graph shows the values of the iron chloride as the point of division over to the curve corresponding to the iron chloride.
that the results which in the table are indicated by (a) fall more nearly on the straight line although still slightly above.

Graph (33) shows a plot of the calculated values of $y'$, $y''$ and $y'''$ against the ratio $C_{\text{Tl}}/C_{\text{Tl}^+ \text{Phen}}$. The curves A, B and C correspond to the three complexes $\text{TlPhen}^{+++}$, $\text{TlPhen}_{2}^{+++}$ and $\text{TlPhen}_{3}^{+++}$ respectively, as predominant species. The above experimental points, using the results indicated by (a), in the cases where duplicate results were obtained, are shown as circles (○—○). A comparison of these experimental results with the curves of the calculated values shows that in the early part of the range with low thallium concentrations there is a preponderance of the tris complex. In the middle range ($R=0.25 - 0.45$) the experimental curve at first tends to follow the lower curves for the mono and bis complexes and then showing signs of an inflexion point passes over to the curve for the mono complex as the thallium concentration increases. Finally at the highest thallium concentrations the experimental points shift over entirely to the curve corresponding to the mono complex. The reasonable coincidence of the points with the theoretical curves at the beginning and end of the range studied supports the values of the instability constants from
METHOD OF CONTINUOUS VARIATIONS

CIRCLES ARE EXPERIMENTAL POINTS
Δ-Δ ARE POINTS OBTAINED FROM THE STRAIGHT LINE IN GRAPH (33)

CURVE A: CALCULATED FROM VALUES OF $K_{TePh}^{+++} = 9.28 \times 10^{-9}$
CURVE B: CALCULATED FROM VALUES OF $K_{TePh_{2}}^{+++} = 3.41 \times 10^{-15}$
CURVE C: CALCULATED FROM VALUES OF $K_{TePh_{3}}^{+++} = 3.20 \times 10^{-22}$
which these figures are calculated. As an independent check three points from the linear graph (52) of optical density against thallium concentrations were selected for concentrations of $0.7\times10^{-4}$, $0.8\times10^{-4}$ and $0.9\times10^{-4}$M of thallium where the greatest experimental deviation occurred. A comparison of these values (indicated as $\Delta$ in graph (33)) with those obtained experimentally supports further the above argument.

The values of the dissociation constants obtained for the complex ions $\text{TlPhen}^{+++}$, $\text{TlPhen}_2^{+++}$ and $\text{TlPhen}_3^{+++}$ are shown in table (54) (Column 2) together with those obtained by Kul'ba and Mironov by a potentiometric method for the mono and bix complex ions (column 3).

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Instability Constants</th>
<th>Instability Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TlPhen}^3+$</td>
<td>$T = 25$ $\mu = 1$</td>
<td>$T = 25$ $\mu = 1$</td>
</tr>
<tr>
<td>$9.28 \times 10^{-9}$</td>
<td>$2.7 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>$3.41 \times 10^{-15}$</td>
<td>$0.5 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td>$3.20 \times 10^{-22}$</td>
<td>$--$</td>
<td></td>
</tr>
</tbody>
</table>

It is observed from the above table that the instability constants obtained in the present work are higher than those of Kul'ba and Mironov by a factor of $10^3$. It is however known that stability constant values obtained by different methods and under different conditions often lead to widely varying results. It is thus of interest to consider the differences between the two methods.
Kul'ba and Mironov in their potentiometric study maintained a constant ionic strength of 1M whilst in this work the ionic strength was 0.1M. A difference in ionic strength of the medium can cause some variation of the stability constant but it is unlikely that it would be as much as in the present case. A search of the literature was however made for information concerning this effect. The Chemical Society Publications on Stability Constants (28) indicates few cases where values are available at more than one ionic strength. In these few cases a difference of $\mu$ from 0.5M to 1M produces a variation of some $2 - 10\%$ which is considerably less than that between the present results and those of Kul'ba and Mironov (24).

A possibility that hydrolysis of the thallium (III) hydrate ion might influence the spectrophotometric method used in the present investigation was considered very unlikely since the hydrolysis products do not show an absorption at the wavelength used ($\lambda = 500nm$). The high stability constants of the complexes, ensuring that most of the thallium is in the form of complex ions, will tend to lower any hydrolytic effect. In any case the influence of hydrolysis was not considered in the work of Kul'ba and Mironov and so would not appear to be the cause of the difference between the two sets of results.

A detailed examination of the results was thus found
necessary. By employing Kul'ba and Mironov's instability constants for the complexes it is possible to check how their values fit the data in the present work. As a first check, the ratio of complexed thallium (in the case of the mono complex) to free thallium can be found from the relationship

\[ K_1 = \frac{[\text{Tl}^{+++}][\text{Phen}]}{[\text{TlPhen}^{+++}]} \]

\[ \frac{[\text{TlPhen}^{+++}]}{[\text{Tl}^{+++}]} = \frac{[\text{Phen}]}{K_1} \]

This is applicable to the first few experiments, where as shown by the use of Job's method, the mono complex is the dominant species. The assumption that the concentration of the tris complex is negligible here is true to a first approximation. The free phenanthroline concentration can be readily found from the ferrous:phenanthroline system as follows:

\[ \frac{[\text{FePhen}^{++}]}{[\text{FePhen}^{2+}]} = \frac{K_1 (\text{for FePhen}^{++})}{K_3 (\text{for FePhen}^{2+})} \]

The values for \( [\text{FePhen}^{2+}] \) and \( [\text{FePhen}^{2+}] \) for experiment (1) are derived independently of the thallium system. (Table (51))

Thus \( [\text{Phen}]^2 = \frac{K_2 (\text{for FePhen}^{2+}) [\text{FePhen}^{2+}]}{K_1 (\text{for FePhen}^{++}) [\text{FePhen}^{2+}]} \)

\( [\text{Phen}]^2 = \frac{5 \times 10^{-22} \times 2.65 \times 10^{-5}}{1.3 \times 10^{-6} \times 5.5 \times 10^{-6}} \)

\( [\text{Phen}]^2 = 4.2 \times 10^{-8} \)

This value is mainly dependent upon the optical density of
the tris-iron complex. A further check was made by obtaining the \( \text{FePhen}^{+7} \) concentration in a solution with no thallium but containing a slight excess of 1:10 Phenanthroline. Under these conditions most of the iron (II) is expected to be present as the tris complex. From the calculated values of \( \text{FePhen}^{+7} \) and \( \text{FePhen}^{+7} \) it was then possible to calculate a value for the free phenanthroline concentration. This was found to be \( 3.93 \times 10^{-7} \). This value is for a solution containing a slight excess of 1:10 phenanthroline and so confirms the order of magnitude of \( 10^{-8} \) for the phenanthroline concentration in the range of experiments carried out.

By employing this value for the free phenanthroline concentration and \( K_1 \) either from Kul'ba and Mironov's work or the present work, the following ratios are found respectively:

\[
\frac{\text{TlPhen}^{+++7}}{\text{Tl}^{+++7}} = 1.7 \times 10^{+4} \approx \frac{20,000}{1}
\]
\[
\frac{\text{TlPhen}^{+++7}}{\text{Tl}^{+++7}} = 4.2 \times 10^{-8} \approx \frac{0.928 \times 10^{-8}}{1}
\]

It is thus observed that this ratio is widely different in the two cases.

On the assumption that the ratio obtained by using Kul'ba and Mironov's constant is correct, i.e.
\[
\frac{[\text{TlPhen}^{+++}]}{[\text{Tl}^{+++}]} \approx \frac{20,000}{1}
\]
then all the thallium present would be virtually complexed. The value of \( y \) for experiment (1) then would be \( 1.5 \times 10^{-4} \) (i.e. the total thallium (III) concentration) instead of \( 1.15 \times 10^{-4} \). By employing the equation \( y = C_{\text{Phen}} \sqrt[3]{[\text{FePhen}^{+++}]} - [\text{FePhen}^{+++}] \) it is then possible to obtain by a reverse calculation a value for \( [\text{FePhen}^{+++}] \).

(To a first approximation, as will be seen from the following calculation, the value of \( \sqrt[3]{[\text{FePhen}^{+++}] \) can be neglected in the above equation for \( y \).) Thus for experiment (1) (Table (51)): \n
\[
y = 2 \times 10^{-4} - 3(2.65 \times 10^{-5}) - (0.55 \times 10^{-5}) = 1.15 \times 10^{-4}
\]
whilst neglecting \( \sqrt[3]{[\text{FePhen}^{+++}] \) \( y \) becomes \( 1.20 \times 10^{-4} \), which is sensibly the same order of magnitude.

Now \( 3(\text{FePhen}^{+++}) = C_{\text{Phen}} - y \)

\[
3(\text{FePhen}^{+++}) = 2 \times 10^{-4} - 1.5 \times 10^{-4} = 0.5 \times 10^{-4}
\]

\[
(\text{FePhen}^{+++}) = 0.167 \times 10^{-4} = 1.67 \times 10^{-5}
\]

The relationship between the optical density and \( [\text{FePhen}^{+++}] \) is given by \( \frac{\text{O.D.}}{1.07 \times 10^{-4}} \). The above value would therefore give an optical density of only 0.178 which is only some 60% of the value 0.284 actually obtained and beyond any possible experimental error. It would appear therefore that the Kul'ba instability constant is considerably too low. The potentiometric method which these authors employed was a differential one in which the change of potential of a \( \text{Tl}^{+++}/\text{Tl}^+ \) electrode on addition of
the ligand (1:10 phenanthroline or 2-2' bipyridine) was measured. Observation of their experimental figures (24) showed that they are very critically dependent upon the initial potential observed for the system. If this were too high the instability constants which they observed would be considerably raised. The present values further seem reasonable from their close resemblance to those of the very similar 1:10 phenanthroline iron complexes, i.e. $K_1$ for FePhen$^{++}$ ion is $1.3 \times 10^{-6}$, $K_2$ for FePhen$^{++}$ ion is $5 \times 10^{-22}$ whilst $K_1$ for TlPhen$^{+++}$ ion is $0.928 \times 10^{-8}$ and $K_3$ for TlPhen$^{+++}$ ion is $3.20 \times 10^{-22}$.

The figures obtained in the present investigation for the changes in optical density in the competitive reaction on addition of thallium (Table 5 column 3) are consistent with the comparable orders of magnitude of the stability constants as given above for the iron (II) and thallium (III) complex ion systems.
The absorption spectra of complexes of metal ions have been found to show three groups of absorption bands. The first two groups have been attributed to the electronic excitation of (a) the metal atom (or ions) and (b) to that of the co-ordinated molecule (or ions). The energy levels involved being perturbed by the formation of the complex. The last group has been attributed to electronic transitions involving those electrons, that participate in the metal ligand bond. Yamasaki and others in their study of the spectra of several metallic complexes of 2-2' bipyridine and 1:10 phenanthroline reported that the visible and ultra-violet absorption spectra of the aqueous solutions were generally composed of (A) weak absorption bands \((E = 1 - 10^{-2})\) in the visible and near ultra-violet regions characteristic of the central metallic cations; (B) of very strong absorption bands \((E = 10^{-4} - 10^{-5})\) in the ultra-violet region which were due to the organic ligand molecules and which were shifted in the complex somewhat towards longer wavelengths than the original position found for the free ligand molecule.

Since the thallium complexes are colourless they do not show bands in the visible region (type A) but it was thought of interest to study the influence of the thallium...
(III) ion on the bands of type B for the 2-2' bipyridine complexes. A continuous variations study was also carried out to attempt to establish the ratio of thallium (III) to ligand in the complexes with 2-2' bipyridine and 1:10 phenanthroline respectively.

Ultra-Violet Absorption Spectra of 2-2' Bipyridine Complexes

The ultra-violet absorption spectra of 2-2' bipyridine as shown in graph (34) consists of two bands: Band I, at 35, 710 cm$^{-1}$ (280 m$\mu$) and Band II, at 42, 735 cm$^{-1}$ (234 m$\mu$) at pH 7. The positions of the maxima and the extinction coefficients found for both the free ligand and for the complex with thallium are shown in table (55). Measurements of the spectra were made at pH 7 and 5 in the case of the free ligand and at pH 5 in the other cases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH</th>
<th>cm$^{-1}$ (m$\mu$)</th>
<th>$\varepsilon$ x10$^{-3}$</th>
<th>cm$^{-1}$ (m$\mu$)</th>
<th>$\varepsilon$ x10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2' Bipyridine</td>
<td>7</td>
<td>42,918 (233)</td>
<td>10.1</td>
<td>35,710 (280)</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>42,735 (234)</td>
<td>10.2</td>
<td>35,710 (281)</td>
<td>12.9</td>
</tr>
<tr>
<td>Thallium (III) perchlorate in 0.005M HCl</td>
<td>5</td>
<td>46,948 (213)</td>
<td>32.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thallium (III)-2-2' Bipyridine complex</td>
<td>5</td>
<td></td>
<td></td>
<td>32,894 (304)</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>31,850 (314)</td>
<td>16.2</td>
</tr>
</tbody>
</table>

The values obtained for the free base are in good agreement with those found by other workers (10,11) at the same pH. It had been observed by these authors (10,11) that the
GRAPH (34)

THE ULTRAVIOLET ABSORPTION SPECTRA OF 2-2' BIPYRIDINE
(a) pH 7.0  (b) pH 5.0  (1 cm cell)

[Graph showing the ultraviolet absorption spectra with two peaks labeled I and II, and a scale for optical density and wavelengths (μm) and cm⁻¹ x 10⁻³.]
280 nm maximum is both shifted to longer wavelengths and split on co-ordination. The position of the 235 nm maximum also changes. Only the effect of co-ordination with the thallium (III) ion on the long wavelength band of the free ligand was studied here. Thallium (III) perchlorate solutions were used throughout to minimise the formation of ion pairs. This was prepared by dissolving freshly precipitated thallic oxide in hot perchloric acid. Details of the standardisation and analysis of the solutions are given in the 'Stability Constants section'. The solutions of the complexes were prepared by mixing an aqueous solution of 2-2' bipyridine with variable amounts of the thallium (III) perchlorate. The concentration of the free base in the solutions was $4 \times 10^{-5}$ M for 2-2' bipyridine. Concentrations of the thallium (III) ion varied from $8 \times 10^{-3}$ to $1 \times 10^{-5}$ M.

The results in table (55) and graph (34) show that the spectrum of the free base is only very slightly sensitive to small pH changes. The measurements were however carried out at a constant pH of 5 maintained by a sodium acetate:acetic acid buffer (31). Graph (35) shows the effect of $1 \times 10^{-5}$ M thallium (III) perchlorate on the spectrum of the solution $4 \times 10^{-5}$ M in 2-2' bipyridine together with the spectrum of the free ligand at pH 5. As can be observed from the graph (35) with this dilute
GRAPH (38)

EFFECT OF THALLIUM (III) PERCHLORATE ON THE ABSORPTION SPECTRUM OF 2,2'-BIPYRIDINE

OPTICAL DENSITY

237.
concentration of thallium (III), band I is decreased in intensity and shifted towards longer wavelengths. Splitting indicates that formation of the complex occurs to a certain extent even with this low thallium concentration. Band II on the other hand is both increased in intensity and shifted towards shorter wavelengths. This is of course due to the absorption of thallium (III) perchlorate in this region. With increasing thallium (III) perchlorate concentration, as shown in graph (36), band I is shifted still further to longer wavelengths and split into two bands (I' and I''). Band I' on the lower wavelength side being more intense than band I''. Furthermore the absorption spectra show no further change except for a slight increase in intensity for concentrations of thallium perchlorate ranging from $8 \times 10^{-3}$ (h) to $5 \times 10^{-4}$ (f) as shown in graph (36).

A similar splitting of band I was found by Some and co-workers when studying various 2-2' bipyridine complexes of bivalent metals (m). A comparison of results show that their positions of the bands I' and II' for the lead and copper complexes are in close agreement with those obtained here for the corresponding thallium (III) bipyridine complex. They are shown in table (56) for comparative purposes.
GRAPH (36)

EFFECT OF THALLIUM (III) PERCHLORATE ON THE ABSORPTION SPECTRUM OF 2-2' BIPYRIDINE

OPTICAL DENSITY

\( \mu \)

\( \text{cm}^{-1} \times 10^3 \)
Some and co-workers further suggested that the splitting was due to the effect of the vibrational fine structures of the molecules.

A later report by Nakamoto (102) on the ultra-violet absorption spectra of 2-2' bipyridine in aqueous solutions at various pH's indicated that the bathochromic shifts of the 2-2' bipyridine bands, which occurs at high acidities, are due to the cis-configuration of the bipyridine mono cation. The spectrum of the latter was similar to that obtained for the metal complexes, except that no fine structure was observed in the spectrum of the mono cation. Nakamoto suggested that the blurring of the fine structure in the spectrum of this cation was due to non-planarity of the pyridine rings. In the case of the chelate compounds on the other hand a perfect planarity would be expected to be maintained by the stabilisation due to the resonance structures shown below and thus fine structure is observed.

**TABLE 56**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band I' cm⁻¹ (mm)</th>
<th>ε x 10⁻³</th>
<th>Band I'' cm⁻¹ (mm)</th>
<th>ε x 10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper complex</td>
<td>33,333 (300)</td>
<td>15.5</td>
<td>32,258 (310)</td>
<td>15.8</td>
</tr>
<tr>
<td>Lead complex</td>
<td>33,333 (300)</td>
<td>15.0</td>
<td>32,258 (310)</td>
<td>13.5</td>
</tr>
<tr>
<td>Thallium (III) complex</td>
<td>32,890 (304)</td>
<td>16.6</td>
<td>31,850 (314)</td>
<td>16.2</td>
</tr>
</tbody>
</table>
The bathochromic shifts have also been attributed to the existence of the above resonance structures, the degree of contribution of each, varying from metal to metal.

**Method of Continuous Variations (Job's Method)**

For the purpose of establishing the ratio of thallium (III) to 2-2' bipyridine in the complex the method of continuous variations, originally proposed by Job (109) was employed. Solutions of thallium (III) perchlorate and 2-2' bipyridine were mixed in various ratios so that the total concentration of thallium plus 2-2' bipyridine was kept constant. The range of concentrations used were of the order of $10^{-5} \text{M}$, the total molar concentration of ligand and thallium (III) being maintained at $4 \times 10^{-5} \text{M}$. The pH of the solutions was adjusted to 5 by means of a sodium acetate-acetic acid buffer. Dilution of the solutions was carried out by means of an accurate burette. As can be seen from graph (36) the thallium (III):2-2' bipyridine complex does not absorb radiation at wave numbers greater than 30,000 (333 μm). In order to ascertain the formula of the absorbing species, the ratio of thallium (III) to 2-2' bipyridine was varied from 1:9 to 9:1 using the above
$10^{-5}$M solutions. The optical densities of each solution were measured at various wave numbers between 30,030 (333 m$\mu$) and 38,020 (263 m$\mu$) and at a wavelength path of 1cm. Table (57) contains details of the data from which the ratio of thallium (III) to 2-2' bipyridine in the complex can be established.

![Table 57](image)

The difference between the observed extinction and that calculated on the assumption of no reaction between thallium (III) and 2-2' bipyridine was plotted against the ratio $M\text{Bipy}/M\text{Tl} + M\text{Bipy}$. The resulting curves show a maximum
at \( R = 0.640 \) for all the wavelengths employed. Graph (37) shows the curves obtained at \( 32,000 \text{ cm}^{-1} \) (313 m\( \mu \)) and \( 33,000 \text{ cm}^{-1} \) (303 m\( \mu \)). The theoretical ratio for the bis (TlBipy\(_2\))\(^{3+}\) and tris (TlBipy\(_3\))\(^{3+}\) complexes would be expected to be 0.667 and 0.750 respectively.

The above ratio for the observed maxima at 0.640 cannot be simply interpreted as evidence for a single complex with a one to two ratio of thallium to 2-2′ bipyridine in the solutions. The study of the instability constants for the 1:10 phenanthroline complexes indicates (page 206) that there are present complex species with one, two and three moles of ligand to metal ion. Thus the position of the maximum for this 2-2′ bipyridine system should also be interpreted as due to the combined effect of species with one, two and three molar proportions of ligand. Thus the maximum at 0.640 most probably represents a shift from the 0.750 position which would be characteristic of the (TlBipy\(_3\))\(^{3+}\) species, produced by the presence of smaller concentrations of the other two species. The only values available for the stability constants of the thallium (III):2-2′ bipyridine system are those reported by Kul’Ba and Mironov (24). It would appear that the absolute magnitude of these constants is somewhat uncertain from the present study of the corresponding instability constants of the 1:10 phenanthroline ligand with thallium (see
**GRAPH (37)**

**METHOD OF CONTINUOUS VARIATIONS**

(a) AT 32,000 cm⁻¹ (313 μm)

(b) AT 33,000 cm⁻¹ (303 μm)
Their values may however be used to give a rough estimate of the ratios of numbers of moles of the mono, bis and tris complexes of thallium (III) and 2-2' bipyridine. Assuming that for experiment 11 in table (57) the dominant complex is $\text{TlBipy}_3^{3+}$, an approximate value for the concentration of free 2-2' bipyridine may be calculated ($\sqrt{2\text{Bipy}} = 1.06 \times 10^{-6}$ see Method: page (254)). Since for the three species

$$
\frac{(\text{TlBipy})^{3+}}{(\text{TlBipy}_2)_2^{3+}} = \frac{K_3}{K_1(\text{Bipy})^2} \quad \text{and} \quad \frac{(\text{TlBipy})^{3+}}{(\text{TlBipy}_2)_2^{3+}} = \frac{K_2}{K_1(\text{Bipy})}
$$

it follows that taking $K_1/K_2/K_3:4 \times 10^{-10}/0.8 \times 10^{-16}/4.9 \times 10^{-22}$ as the stability constants for this system the ratio of the number of moles of mono/bis/tris complex is of the order 1/166/820 for this system. The instability constant for the tris complex ($K_3$) was not given by Kul'ba and Mironov and was therefore calculated from their experimental values.

The above ratios indicate that the bis complex is present in appreciable concentration i.e. $\frac{166}{980}$ and would thus shift the maximum for the tris complex from 0.75 to 0.62, in reasonable agreement with the observed figure. The maximum in graph (37) for the two different wavelengths studied, although almost constant, does appear to show a slight shift with wavelength (0.64 - 0.65) a characteristic of systems where more than one species is present. It can furthermore be noted that the maxima for the bipyridine-
thallium system is lower than that for the 1:10 phenanthroline system indicating a greater proportion of the lower complexes. The investigation of this bipyridine-thallium system was not considered further as the competitive reaction method used for the 1:10 phenanthroline complexes cannot be applied here as no certain data are available for the ferrous:bipyridine system.

Ultra-Violet Absorption Spectra of 1:10 Phenanthroline Complexes

By preliminary experiments it was found that the ultra-violet absorption spectrum of 1:10 phenanthroline in aqueous solutions was sensitive to small pH changes. The spectrum of the base was thus recorded at various pH's using an Unicam SP700 spectrophotometer fitted with a cell compartment which was thermostatted at 25°C. The positions, and molar extinction coefficients of the bands at pH of 6.5, 5.0 and 3.0 are shown in table (58). Graph (38) shows the spectrum over the range studied at the respective pH's. The pH of the solution was measured using a sensitive pH meter (Philips pH meter) and a glass electrode with a calomel electrode as the reference standard.
The ultra-violet absorption spectrum of the base 1:10 phenanthroline shows three clearly defined bands together with a shoulder or inflexion on the longest wavelength band. The long wavelength band, band I, lies near 37,000 cm\(^{-1}\) (270 m\(\mu\)); band II near 44,000 cm\(^{-1}\) (227 m\(\mu\)); band III near 50,000 cm\(^{-1}\) (200 m\(\mu\)). The positions and intensities of these bands depend on the pH of the solution. The shoulder or inflexion occurs at 34,700 cm\(^{-1}\) (288 m\(\mu\)).

A bathochromic shift of band I occurs with decrease in pH from 37,000 cm\(^{-1}\) (265 m\(\mu\)) at pH 6.5 to 36,700 cm\(^{-1}\) (272 m\(\mu\)) at pH 3.0. Band II is however shifted towards higher wave numbers from 43,800 cm\(^{-1}\) (228 m\(\mu\)) to 45,000 cm\(^{-1}\) (220 m\(\mu\)). Furthermore band I increases in intensity with decreasing pH whilst band II decreases in intensity. Band III appears only slightly shifted when the pH of the solution is changed; its intensity however does increase with pH. These observations are in agreement with those
GRAPH (38)
THE ULTRAVIOLET ABSORPTION SPECTRA OF 1:10 PHENANTHRONE

PH 6.5 (b) PH 5.0

OPTICAL DENSITY

200 210 220 230 240 250 260 270 280 290 300

248
of previous workers (\textsuperscript{111}). They have attributed both these shifts and the disappearance of the above inflexion to the formation of the mono 1:10 phenanthroline cation (i.e. Phen H\textsuperscript{+}). This will tend to occur increasingly on lowering the pH of the solution.

The effect of a $10^{-5}$M solution of thallium (III) perchlorate on the spectrum of 1:10 phenanthroline solution ($2 \times 10^{-5}$M) is shown in graph (39). This effect is observed to be much less here than in the case of 2-2' bipyridine. A bathochromic shift of the long wavelength band does occur however and the inflexion which in the free base appears at about $34,483 \text{ cm}^{-1}$ ($290 \text{ m} \mu \text{.}$) is observed as a small intensity band in the complex. The position of the latter is also shifted towards longer wavelengths. These facts are in agreement with the work of Sone and co-workers (\textsuperscript{111}) for various bivalent metal complexes of 1:10 phenanthroline. The positions of the maxima for the long wavelength bands for the thallium complex, as in the case of the corresponding 2-2' bipyridine complex (Page (240)), are in close agreement with those of the copper complex from Sone and co-worker's work. Their results are shown in table (59).

<table>
<thead>
<tr>
<th>Compound</th>
<th>cm\textsuperscript{-1} (m\mu)</th>
<th>(\varepsilon) x10\textsuperscript{-3}</th>
<th>cm\textsuperscript{-1} (m\mu)</th>
<th>(\varepsilon) x10\textsuperscript{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper complex</td>
<td>34,014 (294)</td>
<td>10.3</td>
<td>36,765 (272)</td>
<td>34.5</td>
</tr>
<tr>
<td>Thallium (III) complex</td>
<td>33,445 (299)</td>
<td>11.0</td>
<td>36,364 (275)</td>
<td>35.0</td>
</tr>
</tbody>
</table>
GRAPH (39)
ULTRA VIOLET ABSORPTION SPECTRA OF
(a) 1:10 PHENANTHROLINE
(b) THALLIUM (III) PERCHLORATE AND
(c) EFFECT OF THALLIUM (III) PERCHLORATE ON THE ULTRA VIOLET ABSORPTION SPECTRUM OF 1:10 PHENANTHROLINE.
Method of Continuous Variations (Job's Method)

In the continuous variations study, solutions of thallium (III) perchlorate and 1:10 phenanthroline were mixed in various ratios so that the total concentration of thallium (III) plus 1:10 phenanthroline was constant throughout the series. This total concentration was maintained at $2 \times 10^{-5} \text{M}$. The pH of the solutions was adjusted to 5 by means of a sodium acetate:acetic acid buffer. As can be seen from graphs (39) and ( ), the thallium (III): 1:10 phenanthroline complex does not absorb radiation at wavelengths greater than 30,000 cm$^{-1}$ (330 nm). In the ultra-violet spectral region between 50,000 cm$^{-1}$ (200 nm) and 33,333 cm$^{-1}$ (300 nm) the complex shows an absorption curve very similar to that of 1:10 phenanthroline. For this reason a blank containing an equal amount of 1:10 phenanthroline was used in all the measurements. In order to ascertain the ratio of 1:10 phenanthroline to thallium (III), the difference between the observed extinction and that calculated on the assumption of no reaction between thallium (III) and 1:10 phenanthroline was plotted against $C_{\text{Phen}}/C_{\text{Tl}} + C_{\text{Phen}}$.

Table (60) contains the data from which the ratio of thallium (III) to 1:10 phenanthroline in the complex was established.
The resulting curves in graphs (40) and (41) show a maximum at $R = 0.74 - 0.75$ for all the wavelengths employed.

The study of the stability constants of the three thallium (III):1:10 phenanthroline complexes (i.e. $\text{TlPhen}^3+$, $\text{TlPhen}_2^3+$, $\text{TlPhen}_3^3+$) indicates that all the three species may be present in appreciable concentration unless there is an excess of ligand. The more stable tris complex is then the predominant species. The instability constants obtained in section (IX) were $K_1 = 9.3 \times 10^{-9}$; $K_2 = 3.4 \times 10^{-15}$; $K_3 = 3.2 \times 10^{-22}$. On this basis the maximum of the curve at $R = 0.74 - 0.75$ cannot be interpreted as obviously pointing to the tris complex as the most abundant species present. Using the above values for the instability
METHOD OF CONTINUOUS VARIATIONS
(a) AT 33,333 cm⁻¹ (300 μm)
(b) AT 34,483 cm⁻¹ (290 μm)
(c) AT 36,000 cm⁻¹ (278 μm)
(d) AT 36,500 cm⁻¹ (274 μm)

\[ \Delta \text{O.D.} \]

\[ \frac{\epsilon_{\text{Phen}}}{C_{\text{Fe}^{3+}} + C_{\text{Phen}}} \]
constants it is however possible to calculate the ratio of the various species present and thus to calculate where the maximum of the plot of optical density versus the ratio of ligand to total concentration should occur.

Consider the various equilibria for the mono, bis and tris complexes:

\[ K_1 = \frac{(Tl)(Phen)}{(TlPhen^3^+)}; \quad K_2 = \frac{(Tl)(Phen)^2}{(TlPhen_2^3^+)}; \quad K_3 = \frac{(Tl)(Phen)^3}{(TlPhen_3^3^+)} \]

where \( K_1 \), \( K_2 \) and \( K_3 \) are the three instability constants.

Denote \( (Tl) = C_1 \); \( (Phen) = C_2 \)

Thus

\[ \frac{(TlPhen^3^+)}{K_1} = \frac{C_1C_2}{K_1}; \quad \frac{(TlPhen_2^3^+)}{K_2} = \frac{C_1C_2^2}{K_2}; \quad \frac{(TlPhen_3^3^+)}{K_3} = \frac{C_1C_2^3}{K_3} \]

The ratio of these species are then given by

\[ \frac{(TlPhen^3^+)}{(TlPhen_2^3^+)} = \frac{K_2}{K_1C_2} \]

(1); \[ \frac{(TlPhen^3^+)}{(TlPhen_3^3^+)} = \frac{K_3}{K_1C_2^2} \]

(2)

As can be observed from these two equations the value of \( C_2 \) is required so as to be able to obtain the ratios.

The value of \( C_2 \) can be calculated from the final experiment of the series on the assumption that with the ligand concentration 90% of the total, the thallium will be so far in the form of the tris complex that the proportions of the other complexes are negligible for this concentration.

To a first approximation the free phenanthroline concentration is given by:
\[ C_2 = C_{\text{Phen}} - 3(C_{\text{Tl}^{3+}}) \]

where \( C_{\text{Phen}} \) and \( C_{\text{Tl}^{3+}} \) are total concentrations.

From experiment 9 (Table 60), then:

\[
\frac{C_{\text{Phen}}}{C_{\text{Tl}^{3+}}} + \frac{C_{\text{Phen}}}{C_{\text{Tl}^{3+}}} = 0.9 \quad \frac{C_{\text{Phen}}}{C_{\text{Tl}^{3+}}} = 1.8 \times 10^{-5} \quad \text{and} \quad C_{\text{Tl}^{3+}} = 0.2 \times 10^{-5}.
\]

\[
C_2 = 1.8 \times 10^{-5} - 3(0.2 \times 10^{-5}) = 1.2 \times 10^{-5}
\]

Thus using equations (1) and (2):

\[
\frac{(\text{TlPhen}_{3+})}{(\text{TlPhen}_{2}^{3+})} = \frac{3.4 \times 10^{-15}}{3.05 \times 10^{-2}} = 1.13
\]

\[
\frac{(\text{TlPhen}_{3+})}{(\text{TlPhen}_{2}^{3+})} = \frac{3.2 \times 10^{-22}}{2.39 \times 10^{-4}} = 0.13
\]

\[
\text{TlPhen}^{3+} : \text{TlPhen}_{2}^{3+} : \text{TlPhen}_{3}^{3+} = 1 : 33 : 4184
\]

If the tris complex were the only species present the maximum of the curve would be expected to occur exactly at \( R = 0.75 \). However since the other species are also present the maximum would then be expected at \( R = \frac{4184}{4218} \times 0.75 = 0.74 \), which is in agreement with that obtained experimentally at \( R = 0.74 = 0.75 \). This agreement supports the previous set of stability constants in section (IX).
The various studies carried out on the thallium complexes considered in this work led to the following conclusions.

The polar character of solid compounds of the type $M_2\text{TLX}_6$ (X = Cl and Br) and $R_4\text{NTLX}_4$ (R = CH$_3$, C$_2$H$_5$ and X = Cl, Br and I) was established from the systematic diamagnetic study carried out on them. Molar magnetic susceptibility values for the $\text{TLX}_6^{2-}$ and $\text{TLX}_4^-$ anions in octahedral and tetrahedral coordination were obtained from experimental measurements on their salts, making use of the additivity relationships for polar salts. These showed similar systematic changes with increasing values of the effective atomic number $Z$ to those shown by other workers for simple alkali halides. Theoretical magnetic susceptibility values were calculated for these anions allowing for bond-shortening effects as indicated by crystal structure measurements. In all cases these were found in good agreement with the experimental values except in that of the $\text{TLCl}_6^{2-}$ anion. The experimental susceptibility for this anion was found to be slightly higher than the theoretical figure. The molar magnetic susceptibilities of these anions $\text{TLX}_4^-$ and $\text{TLX}_6^{2-}$ were then employed in interpreting the magnetic properties of complexes of the type $\text{TLTLX}_4$ and $\text{TL}_3\text{TLX}_6$. 

SECTION XI

CONCLUSION
(X = Cl and Br) and $[^\text{TlCrX_2_2}]^T\text{I}_4$ and $[^\text{TlCrX_2_2}^T\text{I}']^T\text{X}'$

(Crg = 2-2' bipyridine and 1:10 phenanthroline, X = Cl, Br and I and X' = I) and in correlating them with their structures. Magnetic properties of the TlTlX$_4^-$ and Tl$_3$TlX$_6$ complexes showed that these were Thallium (I)-Thallium (III) complexes from the systematic relationships with the TlX$_4^-$ and TlX$_6^{2-}$ complexes. The susceptibility value for the Tl$^+$ ion derived from them however although constant was somewhat lower than with pure thallium (I) compounds. It was thought possible that an interaction of the empty orbitals of thallium (I) with those of the complex anions TlX$_4^-$ and TlX$_6^{2-}$ could lead to a bond-shortening effect in these compounds. Attempts to prepare similar Ag$^+$ and Hg$^{II}$ halothallates to check this assumption were however not successful. The suggestion of such an interaction was supported by the crystal structure measurements of Hazell (7) on Tl-Br in the dibromide. An interesting effect was observed in the case of the more complex compounds of 2-2' bipyridine and 1:10 phenanthroline. The magnetic measurements provided evidence for their dimeric structures in the solid state, i.e. $[^\text{TlCrX_2_2}]^T\text{I}_4^+$. However subtraction of the respective anionic susceptibilities led to diamagnetic susceptibility values for $[^\text{TlCrX_2_2}^T\text{I}^+]$ ions, which were
almost the same for chloro, bromo and iodo complexes in each case. This fact indicated that the halogen contribution to the cationic diamagnetism was depressed by the large organic groups. Semitheoretical calculations for the cationic susceptibilities of these complexes led furthermore to the conclusion that the halogen ligand lowering effect present in the complexes followed the same sequence as the order of stabilities of the halothallate complexes. This is as follows:

Iodide > Bromide > Chloride

i.e. in the same order as the characteristic stability constant values for class (b) acceptors to which thallium (III) belongs.

An analytical study of the $R_4NTlX_4$ ($R = C_2H_5$, $C_6H_5(CH_3)_3$, $C_4H_9$ and $X = Cl, Br$ and $I$) was carried out in an attempt to employ the quaternary ammonium halides as analytical reagents for the gravimetric determination of thallium (III). Solubilities in water were found to follow in the expected order $Cl > Br > I$ and $CH_3 > C_2H_5 > C_6H_5(CH_3)_3 > C_4H_9$. The tetra-n-butyl and trimethylphenyl ammonium iodothallates were recommended as promising compounds for such determinations.

The compounds of the type $R_4NTlX_4$, $R_4NTlX'X''$, $\langle Tlorg_2X_2 \rangle TlX_4$ and $\langle Tlorg_2X'X'' \rangle$ were found by conductance measurements to behave as uni-univalent electrolytes in
organic solvents such as nitromethane, nitrobenzene and acetone.

'Infra-red studies on the 2-2' bipyridine and 1:10 phenanthroline halogeno complexes of thallium (III) were made in the 2000-500 cm$^{-1}$ range. In both series of compounds the free ligand bands were found in general to be shifted towards higher frequencies on coordination. This indicated that complexing had led to an increased localisation of the electrons in the aromatic ligand. As expected the infra-red spectra of these compounds were found to be similar. A conspicuous split of the band which in the free ligand has been assigned to the CH-out-of-plane-in phase bending modes was however found to occur in the case of the yellow $\left[\text{Tl}\text{bipy}_2\text{I}_2\right]\text{TlI}_4$. The presence of a cis configuration of the bipyridine rings in this complex was thus inferred. The spectra of the nitrato complexes of thallium with one, two and three molecules of 2-2' bipyridine and 1:10 phenanthroline were studied in the same infra-red region. In the case of the mono-diaquo complexes both covalent and ionic nitrate frequencies were observed, but no evidence for coordinated water was provided from the infra-red spectra. Structures of the type $\left[\text{Tl}\text{Org(NO}_3\right]_2\text{NO}_3\cdot2\text{H}_2\text{O}$ were thus put forward. For the bis and tris complexes only ionic nitrate frequencies were found indicating the structures:
TlOrg\(_2\)(NO\(_3\))\(_3\) and TlOrg\(_3\)(NO\(_3\))\(_3\)

These structures were found to be in good agreement with the conductivity results for uni-trivalent electrolytes. Metal ligand stretching frequencies could not be obtained because they occur below 500 cm\(^{-1}\), the instrument limit. A comparison with other M-N stretching frequencies suggests however that they probably occur in the 200-260 cm\(^{-1}\) range.

The ultra-violet absorption spectra of the tetra alkyl ammonium tetrahalothallates in ethanol and acetonitrile solutions showed characteristic bands of the complex anions TlCl\(_4\) and TlBr\(_4\) corresponding to \(e_n^b \rightarrow a_1^*\) transitions. The more complex iodothallate solutions gave rise to several bands arising from species formed on decomposition, (\(1^+\)Tl\(^{+}\)I\(^{+}\)). In the case of the intermediate compounds Tl\(_2\)TLX\(_4\) and Tl\(_3\)TLX\(_6\) (X = Cl and Br) characteristic thallium (I) transition bands were observed and overlapping with the TlX\(_4\) bands was furthermore indicated in the ultra-violet region. Solid reflectance spectra showed the Tl\(^{+}\)(I) - Tl\(^{+++}\)(III) charge transfer bands. The spectra of the 2-2' bipyridine and 1:10 phenanthroline halogeno complexes in ethanol showed the characteristic high intensity ligand bands. Overlapping of these with the less intense TlX\(_4\) bands was also suggested.

A study of the stability constants was furthermore undertaken for the 1:10 phenanthroline:thallium (III)
perchlorate system in aqueous solutions. The method of competitive reactions was employed and iron (II) was used as the auxiliary metal. Stability constants for the TlPhen$^{3+}$, TlPhen$_2^{3+}$ and TlPhen$_3^{3+}$ ions were calculated from the results of the above method. As a check a modified Job's method was employed in an attempt to determine the most abundant species in solution as indicated from the values of the stability constants obtained in the present work. A further study in the ultra-violet region for the 2-2' bipyridine and 1:10 phenanthroline thallium (III) perchlorate systems in aqueous solutions was carried out. Continuous variations studies were made for both systems and the ratios of concentrations for the various species present determined.
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ERRATA

Page 245: line 7: replace $1.06 \times 10^{-6}$ by $2.4 \times 10^{-5}$.
line 13: replace $1/166/820$ by $1/120/470$.
line 18: replace $\frac{166}{986}$ by $\frac{120}{590}$
line 19: replace 0.62 by 0.60

Page 131: line 19: replace 'covalent' by 'ionic'.
line 21: " " " "
line 25: " " " "

Page 132: Graph (19): " " " "

Page 133: line 4: replace covalent radii by ionic radii (mean literature values).