THE PREPARATION AND ~~CHARACTERISATION~~ PROPERTIES OF ~~SOME COMPLEXES OF~~ NICKEL IN THE OXIDATION STATE (III)

by

MAHESH CHANDRA

A THESIS

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

UNIVERSITY OF LONDON

Bedford College, London July, 1971

ABSTRACT

Several new series of nickel(III) compounds containing diamine ligands have been prepared and investigated by physical techniques.

The nickel(III) ion is six coordinate in the diamine complexes. Various salts have been prepared and their magnetic properties have been studied over a wide range of temperatures. The magnetic moments of the diamine complexes are in the range of 1.8 - 2.2 B.M. at room temperature and indicate the presence of one unpaired electron and low spin nickel(III). Some compounds show magnetic interactions and possibly have bridge or polymeric structures.

The reflectance spectra of the ethylenediamine, of the propylenediamine and of the alkyl and dialkyl substituted ethylenediamine complexes provide evidence for tetragonally distorted octahedral nickel(III) complexes. The charge transfer bands shift to longer wavelengths, as the bonding becomes more covalent. The bonding becomes more covalent as the number of alkyl groups in the ligand molecule increases.

E.s.r. spectra have also been measured for some compounds. The g-values splitting factors have been calculated, this gives information about the orbital degeneracy in the metal complexes.

Low and high spin behaviour, cross-over situations and Jahn-Teller distortion in octahedral species have also been discussed.

The infra-red spectra have been used to distinguish between coordinated and ionic species, and as a means for the differentiation of cis and trans isomers in the bis diamine complexes.

ACKNOWLEDGEMENTS

The author would like to thank his supervisor, Dr. M.E. Farago for her invaluable advice, guidance and helpful criticism. He is also indebted to Professor G.H. Williams for the provision of laboratory facilities.

The author would like to express his gratitude to Dr. V.C.G.Trew and Dr. R. Bolton of Bedford College and Dr. K.D. Sales of Queen Mary College for help and advice and to Mrs. D. Storey for help in the preparation and typing the thesis.

Thanks are also due to his whole family for their continued encouragement and support.

Finally, the award of a Research Assistantship and the purchase of the Newport magnetic balance from the SRC are gratefully acknowledged.

CONTENTS

CONTENTS (continued) PAGE

CHAPTER V MAGNETISM IN TRANSITION METAL COMPLEXES 135

CHAPTER I

INTRODUCTION

Historical Survey of Nickel in the Oxidation State III

The unipositive and tripositive oxidation states are unusual for nickel and hence comparatively little is known of the chemistry of the nickel(III).

The following problems are encountered in the establishment of the chemistry of nickel III:

(i) Difficulty in an oxidation to the tervalent state.
(ii) Indefinite period of stability.
(iii) Insolubility in most organic and inorganic solvents.
(iv) Dissociation in solid state.
(v) Rapid decomposition of solutions.

The metals of the first transition series from titanium to copper are noted for the variable valence which they display in their simple salts and complex compounds. This behaviour arises from the presence of an incomplete *3d* shell of electrons and the comparative ease of removal of electrons from the metal atom together with the availability of *d* orbitals for bond formation.

The bivalent state of nickel is stable and many diamine complexes are well known.

The stereochemistry and electronic configurations expected for the various oxidation states of nickel are set out in Table(1) using valence-bond treatment.

In nickel(III) we expect either three unpaired[1] electrons, if Hund's rules are obeyed, or one unpaired electron[1,14] if electron pairing takes place.

Electronic configuration of nickel complexes

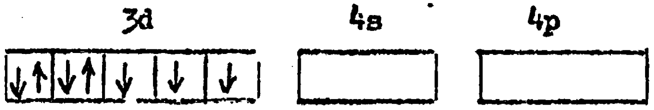
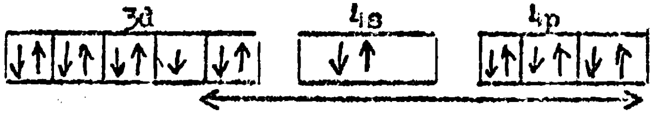
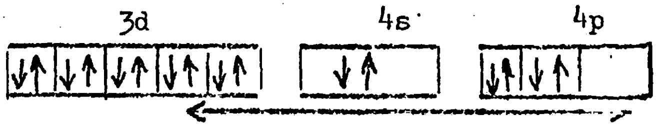
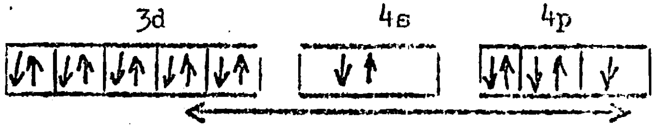
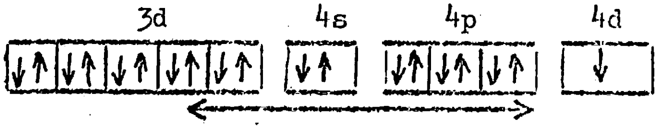
TABLE 1

(1)	(2)				(3)	(4)		(5)	(6)	(7)	(8)
Complex and valence state	Electronic Arrangements				Electrons unpaired	Magnetic moments (B.M)		Valence state	Bond orbitals	Shape	Coordination number
	3d	4s	4p			cal.	Exptl.				
Metallic nickel ground state	↓↑ ↓↑ ↓↑ ↓ ↓	↓↑	☐		-	Ferromagnetic		-	-	-	-
Ni^{0}	↓↑ ↓↑ ↓↑ ↓↑ ↓↑	↓↑	↓↑ ↓↑ ↓↑		0	Diamagnetic		0	$4s4p^3$	Tetrahedral	4
Ni^{II}(2)	↓↑ ↓↑ ↓↑ ↓ ↓	↓↑	↓↑ ↓↑ ↓↑ *		2	2.83	3.3	2	$4s4p^3$	Tetrahedral	4
Ni^{II}(2)	↓↑ ↓↑ ↓↑ ↓↑ ↓↑	↓↑	↓↑ ↓↑ ☐		0	0	0	2	$3d4s4p^2$	Square planar	4
Ni^{II}	3d ↓↑ ↓↑ ↓↑ ↓ ↓	4s ↓↑	4p ↓↑ ↓↑ ↓↑	4d ↓↑ ↓↑	2	2.83 -	3.1	2	$4s4p^34d^2$	Octahedral	6
Ni^{II}	3d ↓↑ ↓↑ ↓↑ ↓↑ ↓↑	4s ↓↑	4p ↓↑ ↓↑ ☐		0	0	0	2	$3d4s4p^3$	Square pyramid	5
Ni^{II}	3d ↓↑ ↓↑ ↓↑ ↓↑ ↓↑	4s ↓↑	4p ↓↑ ↓↑ ↓↑	5s ↓↑	0	0	0	2	$3d^24s4p^3$	Octahedral	6

* Bonding orbital shows ⟷

continued/.....

TABLE I (continued)

(1)	(2)	(3)	(4)		(5)	(6)	(7)	(8)
Complex and valence state	Electronic Arrangements	Electrons unpaired	Magnetic moments (B.M) cal.	Exptl	Valence state	Bond orbitals	Shape	Coordination number
Ni^{III} Ni^{+++} free ion		3	3.88		free ion	-	-	-
$Ni^{III}(3)$		1	1.73	1.9 -2.0	3	dsp^3 or $3d4s4p^3$	Covalent square pyramid	5
$Ni^{III}(3)$		1	1.73	1.9 -2.0	3	dsp^2	Covalent planar	5
$Ni^{III}(3)$		1	1.73	1.9-2.0	3	$3d^24s4p^2$	Square pyramid	
$Ni^{III}(3)$		1	1.73	1.9-2.0	3	$3d^24s4p^3$ or d^2sp^3	Octahedral "	6 6

Until recently the number of well established complexes of nickel(III) was relatively small. Nickel(III) complexes of oximes[2], phosphines[3,4], diphosphines[5], di and tri arsine[6], fluoride[8], nitrate[9] and various diacido-bis (diamino ethane) derivatives[10] have been reported.

The first clearly defined nickel(III) compound was described by Jensen[11] when the red planar compound $[NiBr_2[(C_2H_5)_3P]_2]^0$, bis (triethyl phosphine) dibromo nickel(II), was treated with bromine, a violet substance having the formula $NiBr_3[(C_2H_5)_3P]_2$ was obtained which was monomeric in freezing benzene. The results were explained by assuming that nickel atom is five covalent. Riebsomer[12] showed that the compound is paramagnetic, containing one unpaired electron.

Table 1 shows that the most probable bonding orbitals are $3\underline{d}$ $4\underline{s}$, $4\underline{p}^3$, if the unpaired electron remains in the $3\underline{d}$ shell. Such arrangement involves a $\underline{d}$ orbital having a principal quantum number one less than that of the $\underline{s}$ and $\underline{p}$ electrons. Such hybridization for square pyramidal condition was discussed by Daudel and Bucher[13]. The square pyramidal arrangement could also arise if the bonding orbitals were $3\underline{d}^2$ $4\underline{s}$ $4\underline{p}^2$, the unpaired electron being promoted .

Feigl[14] suggested that the red solution obtained by treating bis(dimethyl glyoxime)nickel(II) with oxidising agents in the presence of ammonia also contained nickel(III) or nickel(IV). However Polster[15] thought that the oxime and not the metal atom was oxidised.

Dubsky and Kuras[16] isolated six covalent nickel(III) complex by oxidation of an aqueous solution of the complex formed between the nickel salts and benzamide oxime. This process yielded a deep purple complex which was shown to be diamagnetic by L. Malatesta[17,18], and which was believed by Jensen[17] to be a mixture of nickel(II) and nickel (IV) in equal amounts.

Nyholm[19] prepared octahedral dichlorodiarsine nickel(III) chloride, a greenish brown compound by the oxidation of the red square planar nickel(II) complex of diarsine, $Ni(arsine)_2Cl_2$.

Oximes and diarsine which form rings with the central atom give stable nickel(III) complexes, while the phosphine compounds prepared by Jensen and Nygaard[3] without rings decompose rapidly. The geometry of the phosphine complexes is square pyramidal, however, the only experimental data available to prove the structures are the dipole moment and the magnetic moments.[3,19]

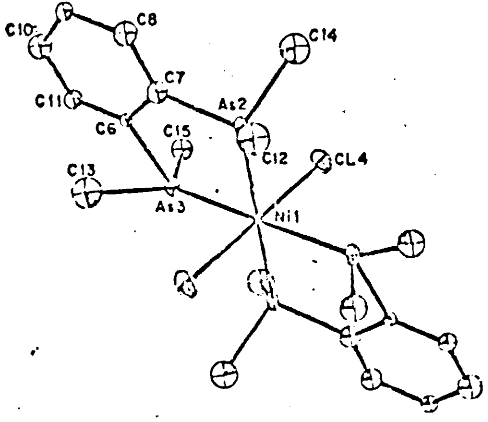
In the five coordinate square pyramidal complex,[20] one of the axial positions is free and the solvent can coordinate with the metal to convert the five coordinate complex to six coordinate,[20] with a consequent change in geometry and d orbital level scheme.

The electronic spectra of bis(triphenyl phosphine) nickel(III) bromide have been studied by Bhattacharyya et. al.[20]

Allen et. al.[21] studied the electronic spectra of hexafluoro nickelate(III) anion and have calculated that $Dq = 1620\ cm^{-1}$, $B = 703\ cm^{-1}$, $\beta = 0.63$ and $Ds/_{Dt} = 3.00$ for $[NiF_6]^{3-}$, and $Dt = 388\ cm^{-1}$ for the sodium compound . The spectra of hexafluoro nickelate (III) anion are analysed in terms of $^2Eg(t2g^6eg^1)$ (see page 102 Fig. 9), low spin ground state in which appreciable tetragonal Jahn-Teller distortion occurs. The d-d bands are interpreted by using the d^7 strong field matrices for D_4 symmetry (Fig.7,9 pages 97/102).

The molecular and electronic structure of dichlorobis(diarsino) nickel chloride is postulated by Kreisman et. al.[22] as distorted octahedral. The monocation $Ni(diars)_2Cl_2^+$ is monomeric and has the structure[22] shown in the figure given below.

Fig-(1)



The four arsenic atoms of two diars. ligands surround the nickel atom in approximately square-planar arrangement; the two chlorine atoms complete a slightly elongated octahedral structure.

$Ni(mnt)_2^-$ whose electronic structure has been the subject of vigorous discussion[23,24] has a rhombic g tensor with Δg = 0.16 found by Maki et. al.[24]

Square planar complexes of cyclic amines of nickel(III) have been prepared and isolated as perchlorate and tetrafluoroborate salts by polarographic method by Olson et. al.[25]

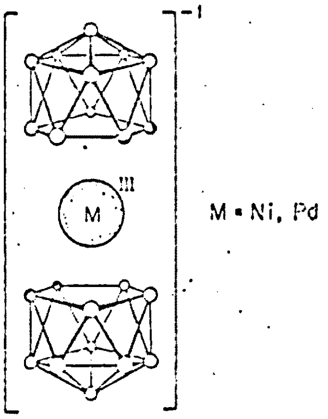
The nickel(III) dithiocarbonate complex have been prepared and e.p.r. of the solution have been studied by Kopitsya et. al.[29] which points low spin $S = \frac{1}{2}$ Ni(III) with a rectangular pyramidal structure.

Hawthorne[23] et. al. have studied X-ray diffraction, magnetic, spectral and electrochemical properties of bis[π-(3)-1,2-dicarbollyl] metalates of nickel and palladium. The nickel bis(dicarbollyl) systems contain various species with the metal atoms in the formal II(d^8, two unpaired electrons for nickel), III(d^7, one unpaired electron for nickel) and IV(d^6, diamagnetic) oxidation states.

Their physical investigations data show that the $\underline{d}^7(M^{III})$ anions possess a symmetrical "non-slipped" sandwich structure (Fig. 2), while the $\underline{d}^8(M^{II})$ metal complexes suffer a slip distortion from a symmetrical π sandwich, and the electrically neutral $\underline{d}^6(M^{IV})$ species maintain a 'cisoid' sandwich configuration in which the carbon atom pairs on opposing ligands reside on the same side of the molecule.

Complexes of nickel(III) with isomeric cyclic tetra-amines and nitrato or sulphato- ligands were made by Curtis[31,32] by the nitric acid oxidation under the mild condition of nickel(II) complexes. The dinitrato-tetra amine nickel(III) complexes being obtained as olive-green perchlorate salts with water of crystallisation or nitrate salts with nitric acid of crystallisation; trans dinitrato structures were suggested.

Fig.-(2)



Babaeva[10] et. al. have prepared some stable ethylenediamine complexes of nickel(III). The complexes are indefinitely stable in the solid state, but rapidly decompose in solution with the liberation of gases. The work of Babaeva[10] et. al. has been continued in the present work and a systematic study of the preparation and properties of nickel(III) complexes with the following mentioned ligands, and measurements of the magnetic, spectral and other physical properties have been made.

The following abbreviations are used in this thesis

		Abbreviations
(1)	Ethylenediamine	en
(2)	N-ethylethylene diamine	N-eten
(3)	N-Methylethylene diamine	N-Meen
(4)	N,N-Diethylethylene diamine	NN-2eten
(5)	N,N'-Diethylethylene diamine	NN'-2eten
(6)	N,N-Dimethylethylene diamine	NN-2meen
(7)	N,N'-Dimethylethylene diamine	NN'-2meen
(8)	The C-alkyl substituted diamines were used as Propylenediamine	Pn
	We also used the following ligands, but not mentioned in this work:	
(9)	1,10 Phenanthroline	Phen
(10)	Ethylenediamine tetraacetic acid	E.D.T.A.
(11)	2-Methyl 1,2-diamino propane	2mePn
(12)	γ-Picoline	Pic-γ

Aliphatic amines as ligands

The redox chemistry of the nickel-cyclic amine complexes has already received attention.[25-29] In the reduction process, a one electron reversible electrode reaction was observed by Olson et. al.[25] for nickel-cyclic amine complexes. A reversible electrode reaction is evidence of a simple electron transfer process with no chemical or structural changes in the depolariser[25,33], and therefore Olson[25] and co-workers believed that the product was a cyclic amine complex of nickel (I).

The same type of evidence established the oxidation products of nickel(II) cyclic amine complexes as complexes of nickel(III). From their overall electrochemical reactions, they observed two types of behaviour in the complexes.

(a) Compounds which undergo a two-electron reduction yielding the metal as a product; most nickel compounds fall into this class.

(b) This type is a characteristic of a class of the compounds having delocalised ground state, such as those formed by dithiolene[27] and *o*-phenylenediamine[34] ligands. In such cases the compounds may be considered complexes of nickel(II) with radical anion ligands. Two or more reversible single electron polarographic waves may be obtained. The electronic charge is localised mainly on the ligand so that the valence state of nickel remains essentially unchanged, i.e. it is primarily the ligand that is reduced or oxidised rather than the metal[25].

Although nickel cyclic aliphatic amine complexes undergo one electron reversible redox reaction, cyclic amines do not form complexes with delocalised orbitals, and these compounds should not be placed in category (b) for the following reasons. First, the polarographic data of Olson[25] shows that it is primarily the metal that is involved in the electron change rather than the ligand; and secondly, the cyclic amine (also ethylenediamine and substituted amines) ligands themselves are not readily oxidised or reduced, whereas the dithiolate and o-phenylenediamine ligands do undergo facile redox reactions. Hence, ethylenediamine and other alkyl and dialkyl substituted ethylene diamines were selected as ligands so that the complexes prepared would have a high probability of having the odd electron in the nickel atom.

CHAPTER II

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

Infra-red spectra: These were recorded on Unicam SP.200 and Grubb-Parsons GS.2A double-beam spectrophotometers. Spectra were taken of dispersions in nujol (B.P. grade) in the regions 2750 - 1500 cm^{-1} and 1250 - 450 cm^{-1}, and in hexachlorobutadiene (spectroscopic grade) over the regions 3600 - 2750 cm^{-1} and 1500 - 1250 cm^{-1}. Sodium chloride plates were used in the region 3600 - 2750 cm^{-1}, and potassium bromide plates from 2750 - 450 cm^{-1}. Both the instruments were calibrated using polystyrene film.

Visible absorption spectra: Solid state spectra were recorded on a Unicam SP.700 recording spectrophotometer fitted with a reflectance unit using freshly prepared magnesium carbonate as a standard. Ultra-violet and visible solution spectra were measured on a Unicam SP.800 recording spectrophotometer in stoppered 2 and 10 mm silica cells. The cell compartment was thermostatted at 20°C. Solvents were Analar or spectroscopic grades except dimethylformamide which was purified by the method described by Bolton et. al.[35] The instrument was calibrated with respect to optical density and wavelength with $K_2Cr_2O_7$.

Magnetic susceptibility measurements: Single temperature measurements were taken on a standard Gouy balance (fig.34 page 151). The balance constant was found by calibration with tris ethylenediamine nickel(II) thiosulphate[36] and $Hg[Co(SCN)_4]$.[37] Diamagnetic corrections were calculated from Pascal's constants.[37] The minimum length for a sample was found and shown in Fig.40 p.160. The optimum position for the base of the tube was found to be at the centre of the pole-piece. The suspension was made of nylon attached to a tight fitting aluminium collar around the susceptibility tube. Magnetic measurements over a range of temperatures were carried out on temperature dependent susceptibility Gouy type magnetic balance (fig.35 p.153).

Reagents.

Nickel chloride hexahydrate. Analar grade and Co-free nickel(II) chloride was used for the preparations of the complexes.

Ethylenediamine, propylenediamine and other alkyl and dialkyl substituted ethylenediamines:- Light and Co., and B.D.H. Sometimes these amines were dried by molecular sieves. Other chemicals and solvents used were normally of laboratory reagent grades and in the special cases Analar grade was used.

Analysis.

Microanalysis of C, H, N was carried out by Drs. Weiler and Strauss at Oxford, England and also by Dr. Bernhardt of Mulheim, Germany.

Metal and halogens were analysed by standard methods. In most of the cases nickel was estimated gravimetrically by the dimethylglyoxime method and some cases were confirmed by atomic absorbance spectrophotometry.

CHAPTER III

PREPARATION AND ANALYSIS

METHODS OF PREPARATION

Introduction

In the last few years the preparations of the nickel(III) complexes, e.g. diarsine[6], phosphines[3], oximes[2] and ethylenediamines[10] have been reported.

Most of the complexes contain ligands like diarsine, oximes and ethylenediamines, which form rings with the central atom, which may be able to stabilise the nickel(III) complexes. The complexes without rings e.g. phosphine complexes decompose rapidly.

Square planar transition metal complexes of some tetradentate macrocyclic amine ligands have been extensively studied by Curtis[31, 32]. These complexes are prepared by the condensation of aliphatic amines with ketones in presence of certain transition metal salts. They are remarkably inert to dissociation which suggested to Olson[25] et. al. that it could be possible to trap some of the more uncommon oxidation states of the transition metals by oxidation or reduction of the complexes, containing the metals in their normal oxidation states. Later their polarographic and the electrochemical investigations of these complexes confirmed their suggestion.

The halogenation process for the oxidation of platinum(II) halide complexes of tertiary arsines to the corresponding platinum(IV) complexes was used by Nyholm[19]. In this process the compound was treated in benzene solution at 0° - 5°, with theoretical quantity of chlorine.

Although white fumes of hydrogen chloride developed during the reaction because of the chlorination of benzene, the oxidation method was quite satisfactory. The halogenation of the benzene solvent was also demonstrated by Chatt[40] in the preparation of platinic tri-n-propylene phosphine chloride complexes.

This halogenation method with or without modification has been used for the oxidation of the bivalent nickel ethylenediamine compounds to the tervalent nickel ethylenediamine complexes in the present work.

The oxidation method used by Babaeva[10] et. al. to produce nickel(III) amine complexes was as follows.

The passage of chlorine through a saturated blue solution of ($Nien_2Cl_2$) in methanol, produced a brown-green finely dried precipitate, contaminated by colourless crystals of ethylenediammonium dichloride. The precipitate was filtered off, washed with methanol, purified by the treatment with aqueous hydrochloride acid (1:2 or 1:3) and dried in air.

However, in this work, the most satisfactory results were obtained when the bivalent nickel amine complex was just wetted with aqueous (2% H_2O) alcohol (methanol or ethanol) to form a paste. The paste was suspended in an aprotic solvent (carbon tetrachloride, acetonitrile, benzene), cooled and the controlled flow of chlorine was allowed to pass through the suspension, under constant stirring. The oxidised product was filtered and partially dried. The complex sometimes was contaminated with the diammonium dichloride of the amine and was then purified by the following treatment.

The crude product was ground using a pestle and mortar with a mixture of the appropriate concentrated acid, water and alcohol, in (6:2:2 or 8:2:2) proportions by volume. The product was filtered off. A sample of the product was dried and analysed for the presence of hydrogen halide in the complex, while the rest of the product was washed with alcohol and finally with ether, and dried in vacuum.

Compounds of the type $(Nien_2X_3)$ and $(Nien_2X_2Y)$

(See Table 2(a) and Table 2(b)pages

(1) $Ni(en_2)Cl_3$:

Dichloro bis(ethylenediamine)nickel(III)chloride$[NiCl_2(en_2)]Cl$.

Blue bis ethylenediamine nickel(II) chloride was made by the method of James[41] et. al. 5.0g of finely powdered $(Nien_2Cl_2)$ was taken in a two-necked 50 ml round bottom flask (Quick-fit). 5 ml of warm aqueous methanol was added drop by drop, under constant stirring using a magnetic stirrer. After 10 minutes 25 ml of carbon tetrachloride was added to the paste. Then one neck of the flask was connected to a water condenser and the other was connected to the chlorine cylinder. The flask was placed in ice-water bath, on the magnetic stirrer and stirred for 15 minutes. During this time chlorine was allowed to pass under controlled flow (2 bubble/second).

The bluish solid first changed to blue-green then to brown-yellow then green and finally to dark olive green. After 20 minutes the chlorine flow was stopped, but stirring was continued for a further 30 minutes, while the flask was left in the bath.

The dark green precipitate was filtered off, dried and then ground with 6:2:1 mixture of concentrated hydrochloric acid, water and methanol by volume. It was then filtered off. At this stage the product had the formula $Nien_2Cl_2Cl,HCl\ 2H_2O$. A sample of the product was taken and analysed. The chloride and nickel percentage agreed with the above formula.

nickel	chloride (percentage)	
16.40	39.41	calculated
16.48	39.30	found

In the tris series of complexes this type of hydro chloride was confirmed by complete analysis (see Table 4a page 55). In order to remove the hydrogen chloride the product was washed with methylated spirit and finally with ether and dried in vacuum.

Solubility

The complex was insoluble in ether, acetone, benzene, chloroform and carbon tetrachloride. It was sparingly soluble in ethanol, methanol, methylated spirit and methylene chloride. In aqueous alcohol or aqueous methylene chloride, in 2:1 or 1:1 alcohol:distilled water proportion gave yellow-green solutions which rapidly decomposed with the evolution of gases and finally the yellow-green solutions turned to blue solutions. The complex was soluble in water to give a yellow-green solution. This solution was unstable and turned blue with effervescence.

The Ni(III) green complex reacted with concentrated HNO_3, H_2SO_4, HCl and $HClO_4$ to give further Ni(III) complexes. (See pages 32, 33) The complex when heated above $\sim$ 30°C decomposed and its deep green colour changed to blue. The analytical data ~~is~~ are given in Table 2a page 35

(2) [Nien$_2$Br$_3$ 0.5H$_2$O]:

Dibromo bis(ethylenediamine)nickel(III)bromide,hemi-hydrate.

[NiBr$_2$(en$_2$)Br $\frac{1}{2}$H$_2$O]

8.0 g of finely powdered Nien$_2$Br$_2$ was added to 3 ml of aqueous methanol (see page 23) as wetting agent. The fine paste was transferred to a 50 ml round bottom flask (Quick-fit), surrounded by ice water. 25 ml of carbon tetrachloride was added slowly while the mixture was stirred as before. 5 ml Of cold liquid bromine was diluted with 5 ml of cold carbon tetrachloride in a 25 ml Quick-fit dropping funnel. The mixture was added drop by drop to the cold stirred suspension. The blue colour changed first to brown then red and finally to deep violet.

The complex was sometimes contaminated with ethylenediammonium dibromide as an impurity and hence the product was treated as before (see page 23). The violet precipitate was filtered off, partially dried and then ground, using a pestle and mortar, with aqueous acid alcohol mixture made by volume as follows:

8 ml	concentrated hydrobromic acid
2 ml	alcohol (ethanol)
2 ml	distilled water

It was then filtered off. A sample of the product was dried and analysed for nickel. Nickel analysis indicates that the complex, as in the case of chloride analogue, contained hydrogen bromide i.e has a formula $Nien_2Br_3,HBr\ 2H_2O$. The rest of the remaining product was washed with aqueous ethanol, and finally with absolute ethanol, to remove HBr. The filtrate was found to be yellow-brown. The complex was dried in vacuum.

The complex now contained 0.5 mole H_2O which was difficult to remove even when left for 3 days in a vacuum desiccator over P_2O_5. This complex had been reported as anhydrous by Babaeva et. al.[10] However, their analytical report confirms the water of hydration which is given below:

	(Percentage)			
Complex	C	H	N	
$Nien_2Br_3\ \frac{1}{2}H_2O$	11.22	4.08	13.10	Expected
	11.20	3.94	13.15	Found (ref. 10)
	11.33	4.08	13.10	Our result (Found)

The dry violet complex was orange-brown in transmitted light.

Solubility

The dry violet complex was insoluble in carbon tetrachloride; chloroform, acetone and ether decomposed the complex with the liberation of gases. The complex was sparingly soluble in methanol, ethanol and methylene chloride. In aqueous solvents, e.g. aqueous alcohol (ethanol or methanol) (2:1 or 1:1 alcohol:distilled H_2O) or aqueous methylene chloride, it gave brown solution which was unstable and changed to dirty blue with effervescence. The complex was soluble in water to give a yellow-brown solution. This solution was very unstable and turned blue with effervescence.

(3) $Nien_2I_3$

Di iodo bis(ethylenediamine)nickel(III) iodide

$[NiI_2(en_2)]I$

A molar alcoholic solution of iodine (cold) was added drop by drop to a cold benzene suspension of $Nien_2I_2$ with constant stirring. The crude deep violet complex was contaminated with ethylenediammonium di iodide, and hence the complex was treated with a mixture of the appropriate acid, water and alcohol in 8:2:2 (4:1:1) and filtered off. The crude deep violet product again contained hydrogen halide i.e. was $Nien_2I_3$,HI $2H_2O$. As was shown by the Nickel analysis: calcd: 8.12%, found 8.00%.

In the tris 'en' (ethylenediamine) series of complexes this type of hydrogen halide was verified by complete analysis (see page 55 Table 4(a)). In order to remove this hydrogen iodide the product was washed with absolute alcohol, and dried in vacuum.

Solubility

Although the deep violet-red compound was more soluble than the chloride and bromide complexes in methanol and ethanol it was, however, only sparingly soluble and unstable. It was insoluble in carbon tetrachloride, benzene and other organic solvents. It was decomposed immediately by acetone, by ether and by water with the evolution of gas and the production of nickel(II) complex.

Reactions of compounds of the type $Nien_2X_3$:

A. Reaction of $[Nien_2Cl_2]Cl$ with $\overset{Na}{N}Cl_2[PtCl_6]$: Preparation of $[Nien_2Cl_2]_2PtCl_6$:

A solution of sodium hexachloroplatinate(IV) acidified with hydrochloric acid was added to $[Nien_2Cl_2]Cl$. This produced a sparingly soluble complex which was almost black but with a green tint, it was filtered off and dried in vacuum.

The metal analyses agreed well for the above formula:

Ni	Pt	
(Percentage)		
12.95	21.48	calculated
12.89	21.32	found
12.90	21.40	found

The reaction showed that nickel(III) remained six coordinate and it was further found that one anion could easily be replaced by ClO_4^-, HSO_4^-. NO_3^- and halides. This result was also confirmed by potentiometric titration,

B. Reaction of $[Nien_2Cl_2]Cl$ with HBr:

Preparation of the complex of the formula $Nien_2Cl_2Br$:

When a solution of hydrobromic acid was allowed to react with a deep-green complex of $Nien_2ClCl_2$, a brick-red product was formed. It was filtered off, washed with alcohol (absolute ethanol) and dried. The complex was analysed for metal.

Calculated for $Nien_2Cl_2Br$	Ni (Percentage)
calculated	17.78
found	17.80, 17.82

C. Reaction of $[Nien_2Cl_2]Cl$ with bromine:

Preparation of the compound of the formula $Nien_2Br_2Cl,\frac{1}{2}H_2O$:

(i) 5 ml Liquid bromine diluted with 5 ml of benzene was allowed to react with $[Nien_2Cl_2]Cl$, and a deep brick-red product was formed. This was filtered off, washed carefully with alcohol (absolute ethanol) and dried in vacuum. This deep red product was analysed completely (Table 7(a) page 35).

(ii) Alternatively, 2N HCl was allowed to react with a violet complex of $[Nien_2Br_2]Br,\frac{1}{2}H_2O$. This resulted in a deep brick-red product, which was filtered off, washed with absolute ethanol and dried. The product was analysed only for metal and of the formula $Nien_2Br_2Cl,\frac{1}{2}H_2O$.

Calculated for $[Nien_2Br_2]Cl,\frac{1}{2}H_2O$		Ni (Percentage)
	calculated	15.28
	found	15.16

(iii) The third method for preparing such salt was as follows. A cold bromine/alcohol solution (in molar proportions) was added dropwise to a paste of $Ni(II)en_2Cl_2$ in carbon tetrachloride, with constant stirring. The deep brick-red product was obtained, but which was contaminated with ethylene diammonium dibromide. The product was treated with a 4:2:2 mixture of HBr, water and alcohol. It was filtered off and washed with absolute alcohol, and vacuum dried. The product was analysed for metal, which confirmed the formula $Nien_2Br_2Cl,\frac{1}{2}H_2O$

	Ni (Percentage)
calculated	15.28
found	15.20

D. Reaction of [Nien$_2$Cl$_2$]Cl with potassium iodide:

Preparation of the compound of the formula Nien$_2$Cl$_2$I:

10% KI solution was added to a green complex of [Nien$_2$Cl$_2$]Cl, a red product gradually developed, which was filtered off, washed with absolute alcohol and dried in vacuum. The complex was analysed for metal only.

Calculated for Nien$_2$Cl$_2$I	Ni (Percentage)
calculated	15.59
found	15.46

E. Reaction of [Nien$_2$Cl$_2$]Cl with iodine:

Preparation of the compound of the formula Nien$_2$I$_2$Cl:

(i) 10 ml of Iodine solution in benzene when allowed to react with [Nien$_2$Cl$_2$]Cl, produced a deep red substance which was filtered off, washed with absolute ethanol and dried. The complex was analysed for metal only.

Calculated for Nien$_2$I$_2$Cl	Ni (Percentage)
calculated	12.88
found	12.78

(ii) Alternatively, 2N HCl solution was allowed to react with violet-red [Nien$_2$I$_2$]I and the deep red product developed. This was filtered off, washed with absolute alcohol and dried. The product was analysed for metal only.

	Ni (Percentage)
calculated	12.88
found	12.80

(iii) A third method for the preparation of the salt was as follows. A cold concentrated alcoholic solution of iodine was added dropwise to a cold benzene suspension, containing a paste of Ni(II)en_2Cl_2 with constant stirring; the deep red product was filtered off and treated as before. The product was [$Nien_2I_2Cl$] and was analysed for nickel, found 12.82%.

F. Reaction of [$Nien_2I_2$]I with HBr:

Preparation of the compound of the formula $Nien_2Br$:

When hydrobromic acid solution was allowed to react with the deep violet complex [$Nien_2I_2$]I, a deep red product was formed. It was filtered off, dried and analysed for metal only.

Calculated for $Nien_2I_2Br$	Ni (Percentage)
calculated	11.50
found	11.46

G. Reaction of [$Nien_2I_2$]I with bromine:

Preparation of the compound of the formula $Nien_2Br_2I$

5 ml of Liquid bromine diluted with 5 ml of benzene was treated with [$Nien_2I_2$]I and a red complex was formed. It was filtered off, washed with absolute ethanol and dried by vacuum. This red-violet complex $Nien_2Br_2I$ was completely analysed as shown in Table 2a page 35

Reactions with acid

(1) Halogen acids. - The complex of the formula $Nien_2X_3$ was ground with the appropriate mixture of acid HX : alcohol : water in 6:2:1 or 8:2:2 proportion by volume, using a pestle and mortar. The product was filtered off, washed with aqueous acid (containing a few drops of ethylenediamine) and dried in vacuum. The product was identical to $Nien_2X_2,HX,2H_2O$ found in the original preparation; e.g. $Nien_2Cl_2I$ was ground using a pestle and mortar with 4:1:1 proportion of a mixture of concentrated hydrochloric acid : alcohol : water. The colour changed from red to olive green. The product was filtered off, washed with aqueous acid (3:1) proportion (having 0.5% en) and dried in vacuum.

This green product was identical to $Nien_2Cl_2Cl,HCl,2H_2O$ found in the original preparation.

1. Reaction of $[Nien_2Cl_2]Cl$ with 20% $HClO_4$:

Preparation of the compound of the formula $Nien_2Cl_2(ClO_4)$:

A cold 20% $HClO_4$ solution was added to $Nien_2Cl_2Cl$. The green precipitate formed was filtered off, washed with absolute ethanol and finally with ether, filtered off and dried in vacuum. The complex was not explosive and its analytical results are shown in Table 2(b) page 36 Infra-red spectroscopy indicates that the compound contains ionic perchlorate (see page 76).

2. Reaction of $[Nien_2Cl_2]Cl$ with 60% $HClO_4$:

Preparation of the complex of the type $Nien_2(ClO_4)_2Cl$:

$[Nien_2Cl_2]Cl$ was added to 60% $HClO_4$ solution to make a paste. The paste was transferred to a 25 ml flask (Quick-fit), containing 15 ml of 60% perchloric acid + 0.5% ethylenediamine. The reaction mixture was refluxed under nitrogen for 48 hours with caution. The deep green-black product was formed. The solvents were removed by Soxhlet extraction. The deep green-black product was filtered off, washed with absolute ethanol and finally with ether, filtered off and dried in vacuum (see Table 2(b) page 36 for analytical data). The compound was not explosive.

3. Reaction of $[Nien_2Cl_2]Cl$ with 20% HNO_3:

Preparation of the compound of the formula $Nien_2Cl_2(NO_3)$:

20% HNO_3 was added to a green-black $[Nien_2Cl_2]Cl$. The colour changed from green to brown. The product was filtered off, after evaporating off most of the solvent. The brown complex was washed with absolute ethanol, and dried in vacuum. The analytical results are recorded in Table 2(b) page 36

4. Reaction of $Nien_2Cl_2Cl$ on 50% nitric acid:

Preparation of the compound of the formula $Nien_2(NO_3)_2Cl$:

50% HNO_3 was added to $[Nien_2Cl_2]Cl$ to make a paste which was transferred to a 50 ml (Quickfit) flask containing 20 ml of 50% HNO_3 + 0.5 ml ethylenediamine. The reaction mixture was refluxed for 48 hours under nitrogen then the mixture was allowed to cool and was filtered. The clear filtrate was once again placed in the flask and most of the solvent was removed. The product was filtered off, washed with absolute ethanol, filtered off and dried under vacuum. The complex was analysed for metal and chloride (see Table 2(b) page 36) and agreed with the formula given above.

5. Reaction of $[Nien_2Cl_2]Cl$ with 20 H_2SO_4:

Preparation of the compound of the formula $Nien_2Cl_2(HSO_4)$:

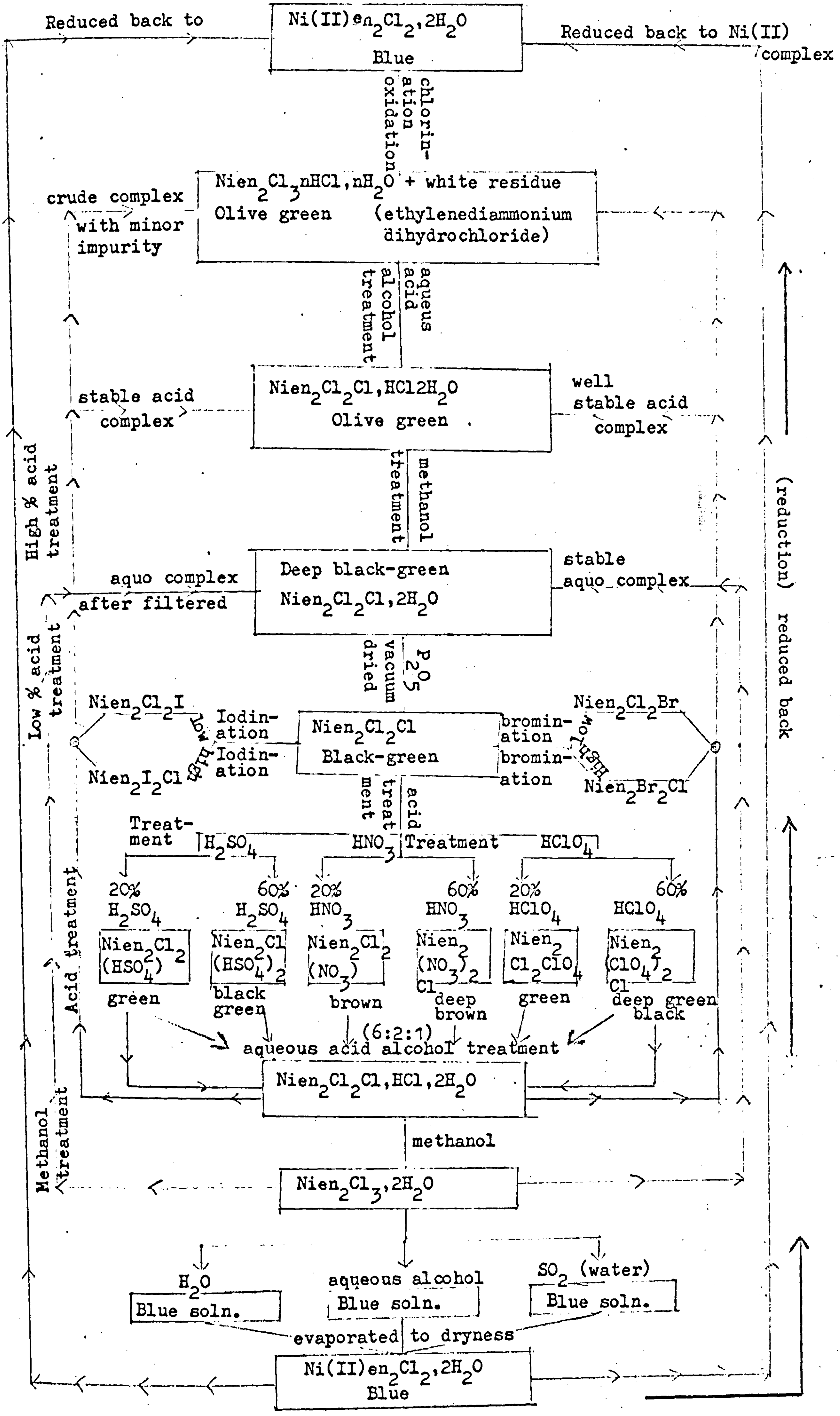
20% sulphuric acid was allowed to react with $[Nien_2Cl_2]Cl$ and a deep green product was formed. It was filtered off, washed with absolute ethanol and finally with ether, filtered off and dried in vacuum. The analytical results are shown in Table 2(b) page 36 . These analyses were agreed well with the formula $Nien_2Cl_2(HSO_4)$.

6. Reaction of $[Nien_2Cl_2]Cl$ with 60% H_2SO_4:

Preparation of the compound of the formula $Nien_2(HSO_4)_2Cl$:

$[Nien_2Cl_2]Cl$ was added to cold 60% H_2SO_4 and made into a paste. The paste was transferred to a 50 ml flask containing 20 ml of 60% H_2SO_4 containing 0.5% ethylenediamine. The mixture was refluxed under nitrogen for 48 hours, cooled and filtered. The clear filtrate was replaced in the flask and the solvent was partially removed. The dark green nearly black product was filtered off, washed with absolute ethanol and finally with ether and dried in vacuum. The analytical results are shown in Table 2 b and have a formula of $Nien_2(HSO_4)_2Cl$.

FLOW DIAGRAM



Compounds of the type ($Nien_2X_3$)

TABLE 2 (a)

Microanalyses

	Compound	Colour	Elemental Analysis (Microanalysis) (Percentage)					
				C	H	N	Ni	halides
(1)	$Nien_2Cl_3$	deep-green	Calcd:	16.82	5.65	19.64	20.58	37.28
			Found	17.39	6.31	20.09	21.01	36.99
(2)	$Nien_2Br_3\frac{1}{2}H_2O$	violet	Calcd:	11.22	4.08	13.10	13.73	53.73
			Found	11.33	4.06	13.10	13.75	53.01
(3)	$Nien_2I_3$	violet-red	Calcd:	8.58	2.89	10.01	10.51	68.03
			Found	8.72	2.86	10.4	10.86	67.49
(4)	$Nien_2Br_2Cl\frac{1}{2}H_2O$	brick-red	Calcd:	12.49	4.46	14.58	15.28	39.26
			Found	12.29	5.28	14.30	15.06	38.39
(5)	$Nien_2Br_2I$	violet-red	Calcd:	10.31	3.46	12.31	12.60	61.59
			Found	11.28	3.56	12.85	12.80	62.01
(6)	$Nien_2I_3$ (repeated)	violet-red	Calcd:	8.58	2.89	10.01	10.51	68.03
			Found	8.98	2.61	10.36	10.48	67.66

Compounds of the type ($Nien_2X_3$)

TABLE 2 (b)

Other Analyses

	Compound	Colour		(Percentage)			
				metal	chloride	ClO_4 / SO_4	
(7)	$Nien_2Cl_2(NO_3)$	brown	Calcd:	18.76	22.67		
			Found	18.71	22.54		
(8)	$Nien_2Cl(NO_3)_2$	deep brown	Calcd:	17.24	10.41		
			Found	17.09	10.12		
(9)	$Nien_2Cl_2(HSO_4)$	deep green	Calcd:	16.92	20.44	27.70	(SO_4)
			Found	16.87	20.03	27.16	(SO_4)
(10)	$Nien_2Cl(HSO_4)_2$	green-black	Calcd:	14.35	8.68	47.02	(SO_4)
			Found	14.29	8.55	46.87	(SO_4)
(11)	$Nien_2Cl_2(ClO_4)$	deep-green	Calcd:	16.86	20.35 (No ClO_4)	28.56	(ClO_4)
			Found	16.89	20.00	27.81	(ClO_4)
(12)	$Nien_2Cl(ClO_4)_2$	green-black	Calcd:	14.20	8.58 (WITHOUT ClO_4)	48.12	(ClO_4)
			Found	14.26	8.16	47.67	(ClO_4)

Compounds of the type $NiPn_2X_3$ and $NiPn_2X_2Y$

(See Table 3(a) and Table 3(b), pages 45, 46)

1. Dichloro bis(1:2-propylenediamine)nickel(III) chloride dihydrate, $[NiCl_2Pn_2]Cl,2H_2O$

8.0 g of blue $Ni(II)Pn_2Cl_2,2H_2O$ was finely powdered and wetted with aqueous ethanol (see page 23). The paste was transferred to a two-necked 50 ml round bottom flask (quickfit) and placed in an ice-bath. 20 ml of carbon tetrachloride was added and the mixture was stirred as before for 15 minutes. One neck of the flask was connected to a water condenser and the other to the chlorine cylinder. Chlorine was passed at two bubbles per second.

The bluish solid first changed to green-blue, then to light green-black and finally to black-green. The reaction was more vigorous and exothermic compared with the ethylenediamine complexes and consequently there was a great possibility of the formation of propylenediammonium dichloride. This impurity was not easily seen but it was found when the product was examined under a microscope. The complex was filtered off, partially dried and then ground with 6:2:2 mixture of concentrated hydrochloric acid, water and ethanol by volume. It was then filtered off. At this stage the product had the formula of $NiPn_2Cl_2Cl,HCl,2H_2O$. To confirm the formula sample was analysed.

Calculated for $NiPn_2Cl_3HCl,2H_2O$	Ni	Cl (Percentage)
calculated	15.72	35.09
found	15.82	34.96

In the bromide complex this type of hydro halide was confirmed by complete analysis (see Table 3(a), page 45). In order to remove the hydrogen chloride the product was washed with methylated spirit, absolute ethanol and finally with ether and dried in air. This product was hygroscopic and difficult to filter. Some light bronze particles floated on the surface during the washing of the complex. The bronze particles were found not to be metallic, their electronic spectra were identical with $[NiPn_2Cl_2]Cl$.

Dichloro bis(1:2-propylenediamine)nickel(III) chloride

$[NiPn_2Cl_2]Cl$

3.49130 g of $NiPn_2Cl_2Cl,2H_2O$ was left in a vacuum desiccator containing P_2O_5 and paraffin for 48 hours. The product was weighed again and was found to be 3.13130 g, indicating the loss of two water molecules. When the anhydrous product was left in air, once again it re-absorbed the two water molecules.

Solubility:

Both the hydrated and anhydrous compounds were sparingly soluble in methanol, ethanol, acetonitrile and chloroform. The complexes were insoluble in acetone, ether, carbon tetrachloride and benzene. In aqueous alcohol, in aqueous methylene chloride and in 3:1 or 2:1 alcohol : water mixtures the complexes gave yellow-green solutions which rapidly decomposed with the liberation of gases and finally turned to blue. The complexes were soluble in water and gave yellow-green solutions which turned almost immediately to blue. The reactions of the complex $NiPn_2X_3$ with HNO_3, H_2SO_4, $HClO_4$, HCl and other halides to give further Ni(III) complexes (discussed later in pp. 43 and 44). When heated above 30°C the complexes decomposed and changed to blue, indicating the presence of Ni(II). The complete analytical data for both the complexes are given in Table 3(a), page 45.

2. Dibromo bis(1:2-propylenediamine)Nickel(III) bromide

$[NiPn_2Br_2]Br$

10 ml of Cold liquid bromine solution diluted with 5 ml of cold benzene was added to a benzene suspension containing a fine paste of $NiPn_2Br_2,2H_2O$ (6 g) with aqueous alcohol. The blue compound gradually

changed to black-green. The product was filtered off and partially dried. At this stage the product was impire and contained propylenediamminium dihydrobromide. To remove this impurity the product was ground using a pestle and mortar with a mixture made by volume as follows:

hydrogen bromide	6 ml
ethanol	2 ml
water	2 ml

The product was filtered off and washed with aqueous acid alcohol mixture., filtered off and dried in vacuum. The product was completely analysed and shown in Table 3(a) page 45 . This product was found to have the formula $NiPn_2Br_2Br,HBr,2H_2O$. This complete analysis suggested that in propylene diamine systems the hydrogen halide molecule or acid of crystallisation also remained present as in the case of the ethylenediamine series. In order to remove this hydrogen bromide the product was washed with absolute alcohol, and dried under vacuum. The green-black product was analysed for metal and halide only.

$[NiPn_2Br_2]Br,2H_2O$	Ni	Br	(Percentage)
Expected	12.16	49.67	
Founf	12.20	49.88	

A known weight of $[NiPn_2Br_2]Br,2H_2O$ was left in a vacuum dessicator, containing P_2O_5 and paraffin for 48 hours and the product was weighed again. The reduced weight was due to loss of two water molecules. This green-black compound was completely analysed as shown in Table 3(a) page 45 having the formula $[NiPn_2Br_2]Br$.

Solubility:

The complexes were insoluble in carbon tetrachloride and chloroform. Acetone, ether and water decomposed the complexes with the evolution of gases. The complexes were sparingly soluble in methanol, absolute alcohol, methylene chloride, the yellow-brown solutions were unstable, and changed to blue with effervescence. The bromide complexes were less stable compared with the chloride complexes, and the bromide complexes were found to be more soluble than the chloride complex. Both anhydrous chloride and bromide complexes when left opened in the air absorbed moisture and finally decomposed. The anhydrous complexes were also decomposed by prolonged hard grinding. The green-black complex when heated to ~ 30°C turned blue.

Reactions of compounds of the type $NiPn_2X_3$.

(A) Preparation of $[NiPn_2Cl_2]_2PtCl_6$.

An acidified solution of sodium hexachloroplatinate(IV) was added to $[NiPn_2Cl_2]Cl$. This sparingly soluble green-black product was filtered off and dried in vacuum. The nickel metal analysis agreed with the above formula.

Compound $[NiPn_2Cl_2]_2PtCl_6$	Ni	Pt (Percentage)
expected	12.18	20.25
found	12.22	20.19

It was also found that one acid residue could easily be replaced by ClO_4^-, HNO_3^-, HSO_4^- and other halides. This result was also confirmed by potentiometric titration,

(B) Reaction of $[NiPn_2Cl_2]Cl$ with hydrobromic acid

Preparation of the compound of the formula $NiPn_2Cl_2Br$.

(i) Black $[NiPn_2Cl_2]Cl$ complex was added, a small portion at a time to a cold solution of hydrobromic acid, while the mixture was stirred. The black-green product was filtered off, washed twice with absolute ethanol containing 0.5% propylenediamine, and finally with absolute ethanol and dried in vacuum.

(ii) An alternative method of preparation of $NiPn_2Cl_2Br$ was as follows. A cold paste of $Ni(II)Pn_2Cl$ was suspended in carbon tetrachloride and a cold bromine/ethanol (molar) solution was added dropwise with constant stirring. The blue colour changed to black-green. The product was filtered off and treated with aqueous alcohol acid mixture (3:1:1 : HCl : ethanol : water) to remove the propylenediammonium dihalide impurity. The complex was filtered off and washed with methylated spirit, and finally with absolute ethanol, filtered off and dried in vacuum. It was identical to that formed in method (i) and was analysed for metal.

Calculated for $[NiPn_2Cl_2Br]$	Ni (Percentage)
calculated	16.40
found	16.28

The complex prepared by the first method was completely analysed and shown in Table 3(a) page 45.

(C) Reaction of $[NiPn_2Cl_2]Cl$ with iodine solution.

Preparation of the compound of the formula $NiPn_2I_2Cl$.

(i) A saturated solution of iodine in benzene was mixed with $[NiPn_2Cl_2]Cl$ and a deep red product was obtained. It was filtered off and washed with absolute ethanol and dried in vacuum. The metal analysis agreed the above formula.

	Ni (Percentage)
calculated	11.86
found	11.80

(ii) Another method of preparing the salt was as follows. A cold concentrated (ethanolic) solution of iodine was added dropwise to a cold benzene suspension containing a paste of $Ni(II)Pn_2Cl_2$ with constant stirring. A violet red product developed which was filtered off. It was then treated with aqueous acid, alcohol mixture (3:1:1 : HCl; alcohol: H_2O) and finally the product was washed with absolute alcohol and dried in vacuum. The nickel analysis confirmed the formula $NiPn_2I_2Cl$

Compound $NiPn_2ClI_2$	Ni (Percentage)
calculated	11.86
found	11.92

(D) Reaction of $[NiPn_2Cl_2]Cl$ with potassium iodide.

Preparation of the compound of the formula $NiPn_2Cl_2I\ 2H_2O$

(i) When 10% KI solution was added to a black-green complex of $NiPn_2Cl_2Cl$, a brown-red complex was formed. It was filtered off, washed with absolute alcohol and dried in vacuum. The complex was analysed completely and shown in Table 3 (a) page 45.

When this hydrated complex was left in a vacuum desiccator it lost two water molecules as confirmed by metal analysis.

	Ni (Percentage)
calculated	14.51
found	14.62

(ii) An alternative method for preparing the hydrated salt $NiPn_2Cl_2I\ 2H_2O$ was as follows. A cold paste of Ni(II) Pn_2I_2 was suspended in carbon tetrachloride and chlorine solution was added dropwise under constant stirring. The brown-red product was filtered off, partially dried and treated with a mixture of aqueous acid alcohol in 3:1:1 proportion (HCl : H_2O : C_2H_5OH). The product was filtered off, washed with absolute ethanol and dried in vacuum. The product was analysed only for metal.

Calculated for $NiPn_2Cl_2I\ 2H_2O$	Ni (Percentage)
calculated	13.32
found	13.26

(E) Reaction of $[NiPn_2Br_2]Br$ with HI.

Preparation of the compound of the formula $NiPn_2Br_2I$.

When hydroiodic acid solution was allowed to react with a black-green $[NiPn_2Br_2]Br$ complex the brown-red product was formed. It was filtered off, washed with absolute ethanol and dried in vacuum. The brown-red complex was left in a desiccator containing P_2O_5 and paraffin for 24 hours to give the anhydrous complex $NiPn_2Br_2I$ which was completely analysed (see Table 3(a) page 45).

(F) Reaction of complexes of the type $NiPn_2X_3$

(i) The complex of the formula $Ni(III)Pn_2X_2Y$ was ground with appropriate mixture of acid : alcohol : water in 3:1:1 proportion by volume using pestle and mortar. The product was filtered off, washed with aqueous acid and dried in vacuum. The product was identical to $NiPn_2X_2HX,2H_2O$ found in the original preparation, e.g. $NiPn_2Br_2I$.

This brown-red complex was ground in pestle and mortar containing the appropriate mixture of hydrogen bromide, ethanol and water (3:1:1). The product was filtered off, washed with aqueous acid (HBr) containing (0.5% Pn) in 3:1 proportion by volume and dried. The brown-red colour turned to black. The black product was analysed for metal and halides only and had a formula of $NiPn_2Br_2BrHBr,2H_2O$ which was identical to $NiPn_2Br_2BrHBr,2H_2O$ found in the original preparation (see page 39).

Complex $NiPn_2Br_2BrHBr,2H_2O$	Ni	Br	(Percentage)
calculated	10.41	56.76	
found	10.23	57.00	

(G) Reaction of $[NiPn_2Cl_2]Cl$ with $HClO_4$

(a) Action of 20% perchloric acid. Preparation of $NiPn_2Cl_2(ClO_4)$.

A cold solution of perchloric acid (20%) was added to the black-green complex, $[NiPn_2Cl_2]Cl$. The deep green complex which was formed was filtered off, washed with ethanol and dried in vacuum. The analytical results are shown in Table 3(b) page 46 . This analysis for the metal was satisfactory for $NiPn_2Cl_2(ClO_4)$.

(b) Action of 60% $HClO_4$. Preparation of $NiPn_2Cl(ClO_4)_2$

A cold solution of 60% $HClO_4$ was added to $[NiPn_2Cl_2]Cl$ to make a paste. The paste was transferred to a 50 ml (Quickfit) flask, containing 15 ml of 60% perchloric acid and 0.5% propylenediamine. The reaction mixture was refluxed under nitrogen for 48 hours cautiously. The mixture was cooled and filtered. The deep green-black filtrate was replaced in the flask. The solvent was partially removed and the deep green product which formed was filtered off, washed with absolute ethanol and finally with ether and dried in vacuum. The metal and anions analyses are shown in Table 3(b) page 46.

This method was also used for other complexes, using the appropriate acids.

(H) Action of 20% HNO_3 and action of 20% H_2SO_4

These solutions were added to $[NiPn_2Cl_2]Cl$ and gave respectively:

(i) a brown product for HNO_3, and (ii) a green-black product for H_2SO_4. These products were filtered off, washed with alcohol (ethanol) and dried in vacuum. Both the products were analysed (see Table 3(b) page 46) and having the following formulae:

Dichloro bis(propylenediamine) nickel(III) nitrate

$$[NiPn_2Cl_2]NO_3$$

Dichloro bis(propylenediamine) nickel(III) hydrogen sulphate

$$[NiPn_2Cl_2]HSO_4$$

(I) Action of 60% HNO_3. Preparation of $NiPn_2Cl(NO_3)_2$

60% HNO_3 acid was added to $[NiPn_2Cl_2)Cl$ to make a paste which was added to 15 ml of 60% HNO_3 and 0.5% propylenediamine. The mixture was refluxed for 48 hours under nitrogen cautiously. The product was

Compounds of the type ($NiPn_2X_3$)

TABLE 3(a)

Microanalyses

	Compound	Colour	Elemental Analysis (Microanalysis) (Percentage)					
				C	H	N	Ni	halides
(1)	$NiPn_2Cl_3\ 2H_2O$	black-green	Calcd:	20.62	6.90	16.05	17.0	30.49
			Found	20.75	6.74	16.09	16.89	30.67
(2)	$NiPn_2Cl_3$	black-green	Calcd:	22.96	6.30	17.8	18.40	33.96
			Found	22.80	6.49	16.74	18.28	34.18
(3)	$NiPn_2Br_3HBr\ 2H_2O$	black-green	Calcd:	12.70	4.0	9.56	10.41	56.76
			Found	-	3.91	9.95	10.05	55.99
(4)	$NiPn_2Br_3$	black-green	Calcd:	16.13	4.48	12.54	13.14	53.67
			Found	15.66	4.24	12.13	13.12	53.04
(5)	$NiPn_2Br_2I$	brown-red	Calcd:	14.60	4.08	11.35	11.91	58.92
			Found	14.60	3.68	11.49	11.69	59.09
(6)	$NiPn_2Cl_2I\ 2H_2O$	brown-red	Calcd:	16.30	5.60	12.71	13.32	45.33
			Found	15.89	-	12.35	13.09	44.98
(7)	$NiPn_2Cl_2Br$	black-green	Calcd:	21.03	5.62	16.29	16.40	42.14
			Found	21.22	-	16.50	16.38	42.06

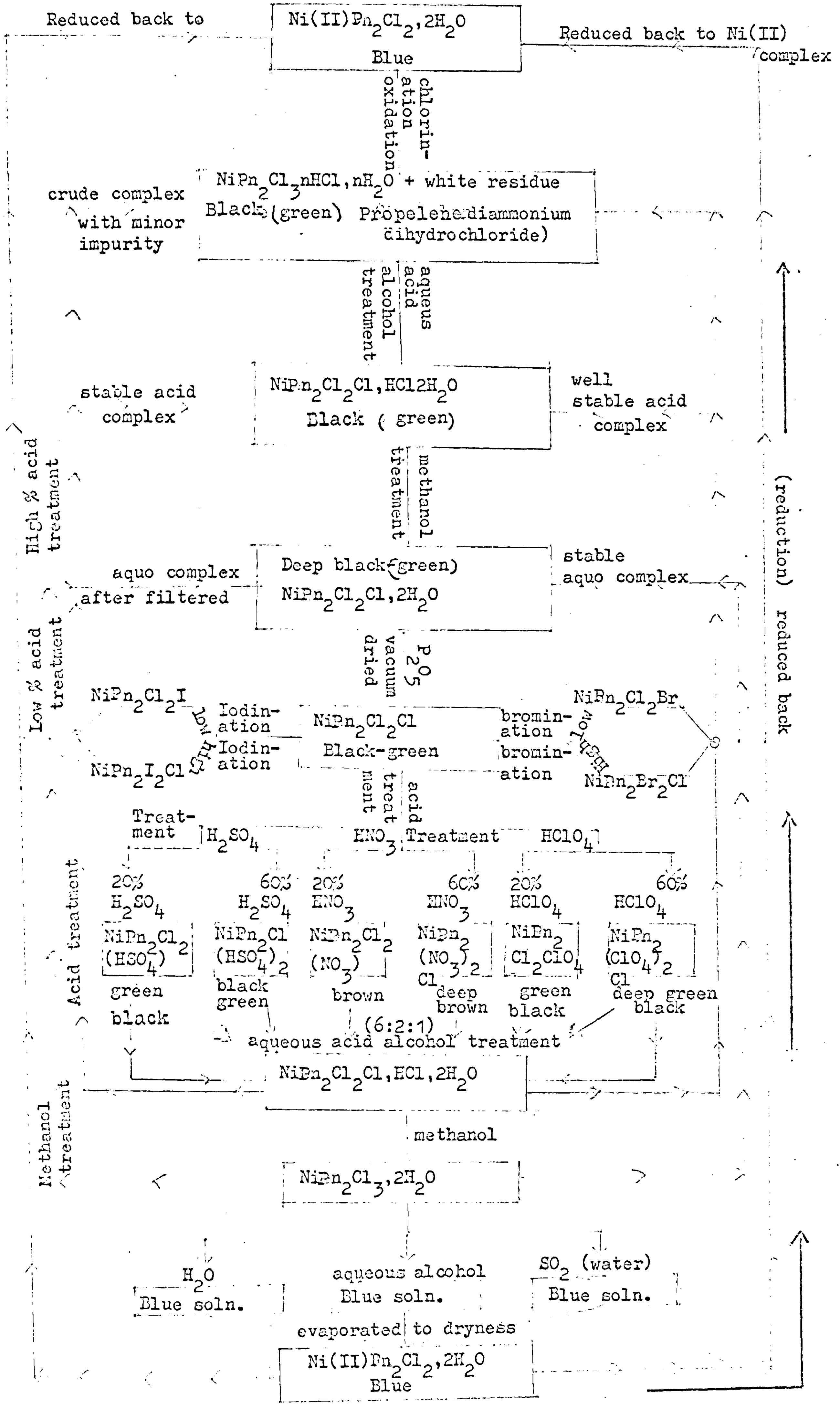
Compounds of the type ($NiPn_2X_3$)

TABLE 3(b)

Other Analyses

	Compound	Colour		Metal %	Chloride%	SO_4^{2-} or ClO_4^-
(8)	$NiPn_2Cl_2(NO_3)$	brown	Calcd:	17.23	20.81	
			Found	17.20	20.05	
(9)	$NiPn_2Cl(NO_3)_2$	deep brown	Calcd:	16.69	9.62	
			Found	16.62	9.68	
(10)	$NiPn_2Cl_2(HSO_4)$	deep green	Calcd:	15.66	18.92	25.64 (SO_4)
			Found	15.61	18.88	25.60
(11)	$NiPn_2Cl(HSO_4)_2$	black-green	Calcd:	12.44	7.503	40.70 (SO_4)
			Found	12.48	17.000	40.63
(12)	$NiPn_2Cl_2(ClO_4)$	deep green	Calcd:	15.57	18.80	25.78
			Found	15.29	18.66 (without ClO_4)	25.09
(13)	$NiPn_2Cl(ClO_4)_2$	black-green	Calcd:	13.30	8.04	45.09
			Found	13.00	7.99	44.06

FLOW DIAGRAM



a deep brown-red. The analytical results are shown in Table 3(b) page 46.

(J) Action of 60% H_2SO_4. Preparation of $NiPn_2Cl(HSO_4)_2$.

$[NiPn_2Cl_2]Cl$ was made into a paste with cold 60% sulphuric acid. This was transferred to a flask containing 15 ml of H_2SO_4 (60%) and 0.5% propylenediamine. The mixture was refluxed for 48 hours and treated as before. The deep green-black complex was analysed for metal and sulphate as shown in Table 3(b)

Compounds of the type ($Nien_3X_3$) and ($NiPn_3X_3$).

(A) (i) Tris(ethylenediamine)nickel(III) chloride, hydrogen chloride, dihydrate. $Nien_3Cl_3,HCl,2H_2O$.

(ii) Tris(ethylenediamine)nickel(III) chloride, trihydrate. $Nien_3Cl_3,3H_2O$.

(iii) Tris(ethylenediamine)nickel(III) chloride. $Nien_3Cl_3$.

Finely powdered pink $Nien_3Cl_2,2H_2O$ was wetted with aqueous ethanol (see page 23), and the chlorination process was carried out in the same way as before (see page 24). The crude green product was ground with an aqueous acid alcohol mixture (6:2:1 : concentrated HCl, water and ethanol by volume) and filtered off. It was washed with absolute ethanol and dried in vacuum. A sample of the black-green nickel(III) complex was dissolved in water, the resulting yellow-green solution turned blue. Analysis of the complex for metal and halide indicated that the oxidation of the tris ethylenediamine complex produced bis(en)nickel(III) complex. Some modifications of the process were therefore made, and the proportion of the mixture of aqueous acid alcohol used in the grinding treatment was changed.

Two different proportions of aqueous acid/alcohol were used to treat the crude nickel(III) black complex. First, the following mixture was tried:

6 ml of conc. HCl
2 ml of ethanol (containing 1.0% en)
1 ml of distilled water (containing 1.0% en)

The product was filtered off. The colour was deep green-black but with some white particles. It was again ground with the second mixture:

3 ml of conc. HCl
2 ml of alcohol)
2 ml of distilled water) (containing 1.0%en)

The product was filtered off, dried in vacuum and analysed as $Nien_3Cl_3,HCl,2H_2O$. The complete analytical report is given in Table 4(a) page 55.

In order to remove this hydrogen chloride the product was washed with methylated spirit containing 0.5% ethylenediamine, and finally with ether containing 0.5% en and dried in vacuum. The deep green complex was analysed for $Nien_3Cl_3,3H_2O$ and the complete analytical results are recorded in Table 4(a) page 55.

This trihydrated tris(ethylenediamine)nickel(III) chloride complex was left in a desiccator containing P_2O_5 and paraffin for 48 hours, and the loss in weight was determined. The analysis of metal and halogen are given below for the anhydrous complex $Nien_3Cl_3$.

Complex $Nien_3Cl_3$	Ni	Cl (Percentage)
calculated	17.07	30.44
found	17.10	30.52

This complex ($Nien_3Cl_3$) absorbed 3 mol of H_2O when left open in the air and decomposed on standing.

Solubility

All the three complexes were sparingly soluble in methanol, ethanol, methylene chloride, chloroform. They were insoluble in acetone, ether, carbon tetrachloride and benzene. Aqueous alcohol or aqueous methylene chloride in 2:1 or 2:2 proportion (alcohol : distilled H_2O) gave yellow-green solutions which rapidly decomposed with the evolution of gases, and finally these yellow-green solutions turned to blue. But when the aqueous alcohol contained 1.0% ethylenediamine the solutions turned pink. The complexes were soluble in water to give yellow-green solutions, which were unstable, and which turned pink if water contained 1% ethylenedimaine. When $Nien_3Cl_3,3H_2O$ or $Nien_3Cl_3$ was ground with hydrochloric acid the product was $Nien_3Cl_3HCl,2H_2O$ which was identical to $Nien_3Cl_3,HCl,2H_2O$ found in the original preparation.

(B)

(i) Tris(ethylenediamine)nickel(III) bromide, hydrogen bromide dihydrate.

$Nien_3Br_3,HBr,2H_2O$

(ii) Tris(ethylenediamine)nickel(III) bromide, dihydrate.

$Nien_3Br_3,2H_2O$

(iii) Tris(ethylenediamine)nickel(III) bromide.

$Nien_3Br_3$

8.0 g of finely powdered (pink) $Nien_3Br_2,2H_2O$ was added to 4 ml of aqueous methanol, to make a paste. The fine paste was transferred to a 50 ml round bottom flask (Quickfit), containing benzene and 1.0% ethylenediamine, surrounded by ice-water. 4 ml of liquid bromine was diluted with 8 ml of benzene in a 25 ml Quickfit dropping funnel. This diluted bromine solution was added drop-wise to the cold stirred suspension. The pink solid changed to brown-red, which was filtered off and partially dried. The brown-red product was ground with aqueous halogen/benzene mixture using a pestle and mortar. The proportion of the mixture was:

Liquid bromine	4 ml	
Benzene	4 ml	containing 1% ethylenediamine
Water	1 ml	

The deep violet-red product was filtered off, partially dried, transferred to a pestle and mortar and again ground with aqueous acid benzene mixture in the following proportion, by volume;

Conc. hydrobromic acid	4 ml
Benzene	2 ml
Water	3 ml

The product was filtered off and dried. At this stage the product was analysed completely as shown in Table 4(a) page 55 and was found to be $Nien_3Br_3,HBr,2H_2O$. The brown-red complex was washed with absolute ethanol containing 1.0% ethylenediamine and dried in vacuum, and analysed for $Nien_3Br_3,2H_2O$. The complete analytical results are shown in Table 4 (a)

This dihydrate complex when left in a desiccator containing P_2O_5 for 48 hours lost its two water molecules of crystallisation. This anhydrous complex was analysed for metal and halide only given below which agreed with the formula $Nien_3Br_3$.

Solubility

All varieties of the complexes were insoluble in carbon tetrachloride, benzene and chloroform. In acetone and ether the complexes were immediately decomposed and turned to pink. They were sparingly soluble in methanol, ethanol, methylene chloride and the solutions were unstable. In aqueous alcohol, the complexes gave yellow-brown solutions which rapidly decomposed with the evolution of gases and finally the yellow-brown solutions turned to blue. If, however, the solvents contained 1% ethylenediamine the final colour was pink. Complexes decomposed when heated above 30°C and also on hard grinding.

$Nien_3Br_3,2H_2O$ and $Nien_3Br_3$ were ground with hydrobromic acid in a pestle and mortar, filtered off and dried in vacuum. The product in both cases was $Nien_3Br_3,HBr,2H_2O$, which was identical to $Nien_3Br_3,HBr,2H_2O$, found in the original preparation.

(C)

(i) Tris(ethylenediamine)nickel(III) iodide, hydrogen iodide dihydrate.

$Nien_3I_3,HI,2H_2O$

(ii) Tris(ethylenediamine)nickel(III) iodide, dihydrate.

$Nien_3I_3,2H_2O$

(iii) Tris(ethylenediamine)nickel(III) iodide.

$Nien_3I_3$

6.0 g of finely powdered pink $Nien_3I_2,2H_2O$ was added to 3 ml of aqueous ethanol to make a paste, which was transferred to a cooled round bottom flask and stirred to slurry with benzene containing 1% ethylenediamine. A molar solution of iodine in benzene was added dropwise to this cold benzene suspension. The complex gradually changed to brown then to buff and finally to violet. The product was filtered off, and partially dried. At this stage the product was contaminated with enthylenediammonium di-iodide. For the removal of this impurity the product was treated in the same way as before, with the following mixtures:

First grinding: 4:1:1 : saturated iodine solution in ethanol : alcohol ethanol : distilled water

Second grinding: 4:2:2 : hydroiodic acid : alcohol : distilled water

1% ethylenediamine was added to each mixture.

The product was filtered off, dried and analysed for metal and iodide as shown in Table 4(a) page 55. This analysis confirmed that the complex had hydrogen iodide with two water molecules. The violet product was washed with methylated spirit and finally with absolute ethanol, and dried in vacuum. This violet complex was analysed and was found to be $Nien_3,I_3,2H_2O$.

	Ni	I	(Percentage)
calculated	8.96	58.13	
found	9.00	57.69	

$Nien_3I_3,2H_2O$ was left in a desiccator containing P_2O_5 for 48 hours and lost two water molecules to give anhydrous $Nien_3I_3$. The complete analysis of this last compound is shown in Table 4 (b) page 56.

Solubility

Although the complexes were more soluble than the dichloride and bromide in methanol, ethanol, methylene chloride, methylated spirit they were, however, sparingly soluble and unstable. These were decomposed immediately by acetone, ether and water with effervescence to give blue solutions and pink solutions if the solvents contained 1% ethylenediamine. The complexes decomposed when heated above 30°C or on hard grinding of the dry complexes.

(D)

(i) Tris(propylenediamine)nickel(III) chloride, hydrogen chloride, dihydrate.

$NiPn_3Cl_3HCl,2H_2O$

(ii) Tris(propylenediamine)nickel(III) chloride, dihydrate.

$NiPn_3Cl_3,2H_2O$

(iii) Tris(propylenediamine)nickel(III) chloride.

$NiPn_3Cl_3$

The paste of $NiPn_3Cl_2,2H_2O$ was transferred to a cooled round bottom flask containing a solution of 1% propylenediamine in carbon tetrachloride. Chlorine was passed through the mixture with constant stirring. The colour of the solid gradually changed from violet to brown, to buff, to green and to black-green. It was filtered off, treated in the same way as the tris ethylenediamine complexes (see pages 48, 49) and analysed for nickel. The nickel analysis confirms the formula.

$NiPn_3Cl_3,HCl,2H_2O$	Ni (Percentage)
calculated	15.14
found	15.00

To remove hydrogen chloride, the complex was washed with ethanol containing 1% propylenediamine and finally with ether also containing 1% propylenediamine and dried. The green-black $NiPn_3Cl_3,2H_2O$ was analysed for metal and halogen as shown in Table 4(b)page 56.

$NiPn_3Cl_3,2H_2O$ was left in a desiccator over P_2O_5 and lost two water molecules. Metal and halide analyses shown below confirmed the formula $NiPn_3Cl_3$.

$NiPn_3Cl_3$	Ni	Cl (Percentage)
calculated	19.98	35.15
found	19.86	35.60

(E) The following propylenediamine complexes have been prepared by methods analogous to those used in the ethylenediamine series.

(i) Tris(propylenediamine)nickel(III) bromide, dihydrate

$NiPn_3Br_3,2H_2O$

(ii) Tris(propylenediamine)nickel(III) bromide

$NiPn_3Br_3$

The complete analyses were carried out for both complexes in Table

(iii) Tris(propylenediamine)nickel(III) iodide

$NiPn_3I_3$

This complex was analysed for metal and halide (see Table 4(b)page 56).

Solubility:

These complexes showed similar solubility behaviour to their ethylenediamine analogues.

Compounds of the type [$Ni(en)_3X_3$] and [$Ni(Pn)_3X_3$]

TABLE 4(a)

	Compound	Colour	Elemental Analysis (Microanalysis) (Percentage)					
				C	H	N	Ni	halides
(1)	$Nien_3Cl_3$ $3H_2O$	deep green-black	Calcd:	18.03	6.07	21.04	14.70	26.63
			Found	18.05	6.22	20.85	14.68	26.02
(2)	$Nien_3Cl_3HCl$ $2H_2O$	deep green-black	Calcd:	17.23	6.9	20.10	13.47	32.31
			Found	17.85	6.27	20.50	13.38	32.89
(3)	$Nien_3Br_3$ $2H_2O$	brown-red violet	Calcd:	13.99	5.48	16.00	11.41	46.38
			Found	14.00	5.22	15.43	11.09	46.00
(4)	$Nien_3Br_3HBr$ $2H_2O$	brown-red violet	Calcd:	12.10	4.70	14.10	9.91	53.95
			Found	12.17	3.78	13.94	10.00	52.96
(5)	*$Nien_3I_3HI$ $2H_2O$	violet	Calcd:	-	-	-	7.49	64.71
			Found	-	-	-	7.46	(64.00) (63.03)

*Compounds analysed for metal and halides only.

Compounds of the type [Ni(en)$_3$X$_3$] and Ni(Pn)$_3$X$_3$]

TABLE 4(b)

	Compound	Colour	Elemental Analysis (Microanalysis) (Percentage)					
				C	H	N	Ni	halides
(6)	Nien$_3$I$_3$	violet-red	Calcd:	11.63	3.90	13.56	9.47	61.43
			Found	11.82	3.81	13.45	9.21	60.87
(7)	*NiPn$_3$Cl$_3$ 2H$_2$O	green-black	Calcd:	-	-	-	13.71	31.33
			Found	-	-	-	13.69	30.44
(8)	NiPn$_3$Br$_3$ 2H$_2$O	green-black	Calcd:	19.33	6.10	15.10	10.54	43.06
			Found	18.92	6.7	14.95	10.38	42.92
(9)	NiPn$_3$Br$_3$	green-black	Calcd:	20.74	5.8	16.15	11.27	46.03
			Found	21.13	5.60	16.41	11.08	45.93
(10)	*NiPn$_3$I$_3$	violet	Calcd:	-	-	-	8.88	57.55
			Found	-	-	-	8.93	(56.92) (56.34)

*Compounds analysed for metal and halides only.

Compounds of the type $Ni(AA)_2X_3$ where AA = N-meen, N,N-2meen,

N,N'-2meen (see Tables 6(a) and 6(b) pages 63,64)

N-eten, N,N-2eten, N,N'-2eten
(see Tables 5(a), 5(b), pages 61,62)

Introduction

Alkyl substitution on the nitrogen atoms of ethylenediamine would be expected to increase the basicity of the nitrogen. It has been shown that the greater the complexity of N-alkyl groups the less the interaction of the ligand with the central metal ion. The reason for this apparent anomaly is that steric interactions are of greater magnitude than the increased inductive effect exerted on the donor nitrogen atoms by the alkyl groups. Since chemical reactivity is closely related to the steric requirements of a system, it can be seen that there exists a definite, although undefined, relationship between the electronic structure of a complex, the steric requirements of its ligands and its chemical reactivity. Because the increasing steric hindrance effected the stability of the tervalent nickel complexes, the preparations were carried out under nitrogen.

A. Bis(N-ethylethylenediamine)nickel(III) bromide. $Ni(N\text{-}eten)_2Br_3$

5.0 g of finely powdered Bis N-ethylethylenediamine nickel(II) bromide, dihydrate $Ni(N\text{-}eten)_2,Br_2,2H_2O$ made by the method of James[41] et.al was wetted with hot aqueous alcohol (3 ml) to make a paste. The paste was transferred to a 25 ml round bottom flask (two necked) and surrounded by a water bath. 3 ml Of liquid bromine, diluted with 3ml of benzene was added dropwise to the stirred benzene suspension, via one neck of the flask. Nitrogen was passed through the other. After the addition, the solvents were evaporated off and the brown mass was treated with the following mixture:

3 ml liquid bromine
2 ml benzene
1 ml distilled water

The violet-brown product was filtered off and dried. At this stage the nickel analysis confirmed the presence of hydrogen bromide with two water molecules. The product was analysed as $Ni(N\text{-}eten)_2Br_3,HBr,2H_2O$. (To confirm the presence of hydrogen halides in alkyl and dialkyl substituted ethylenediamine series, bis and mono complexes, two samples (i) $Ni(N,N\text{-}2eten)_2I_3,HI,2H_2O$ and (ii) dibromo mono (N,N'-2eten) nickel bromide, hydrogen dihydrate:- $Ni(N,N'\text{-}2eten)Br_3,HBr,2H_2O$ were sent for complete analysis (see Table 5(a))). To remove hydrogen bromide, the complex was washed with absolute ethanol and dried in vacuum for 48 hours over P_2O_5. The resulting anhydrous $Ni(N\text{-}eten)_2Br_3$ was completely analysed as shown in Table 5(a) page 61 .

B. By using analogous methods the following compounds were prepared.

(i) Dichloro bis(N-eten)nickel chloride

$Ni(N\text{-}eten)_2,Cl_3$

(ii) Di-iodo bis(N-eten) nickel iodide

$Ni(N\text{-}eten)_2I_3$

Both these complexes contained hydrogen halides with two water molecules. Hydrogen halides could be removed by treatment with alcohol. The former compound (chloride) was analysed for metal and halides as shown in Table 5(b). The complex (ii) was completely analysed (see Table 5(a) page 61).

C.

(i) Di-iodo bis(N,N-2eten) nickel iodide, hydrogen iodide, dihydrate

$Ni(N,N\text{-}2eten)_2I_3,HI,2H_2O$

(ii) Di-iodo bis(N,N-eten) nickel iodide

$Ni(N,N\text{-}2eten)_2I_3$

6.0 g of blue $Ni(N,N\text{-}2eten)_2I_2,2H_2O$[41] was added to 3 ml of hot aqueous alcohol to make a paste, which was transferred to a 50 ml Quickfit flask containing 20 ml of a 1% diamine solution in methylated spirit. 8 ml Of iodine solution(saturated) was diluted with 4 ml of methylated spirit, containing 2 ml of distilled water. This diluted mixture was added dropwise to the stirred methylated spirit suspension under nitrogen as before. The reaction mixture was refluxed under nitrogen for 48 hours. The violet product was formed. The solvents were partially removed from the violet product using a Soxhlet unit. The deep violet product was filtered off, partially dried and ground with the following mixture:

4 ml iodine solution (saturated in ethanol)
2 ml benzene
1 ml water
1 drop diamine

The product was filtered off, dried in vacuum and was analysed completely as shown in Table 5 (a) page 61 . The analysis confirmed the formula $Ni(N,N\text{-}2eten)_2I_3,HI,2H_2O$. To remove this hydrogen iodide from the complex, the product was washed with absolute ethanol containing 1% N,N'-2eten and dried in a vacuum. The complex was left in a desiccator for 48 hours containing P_2O_5. The complete analytical results for the anhydrous $Ni(N,N\text{-}2eten)_2I_3$ are shown in Table 5 (a)

D. The following complexes were prepared by analogous methods.

(i) Dichloro bis(N,N-2eten)nickel(III) chloride dihydrate

$Ni(N,N\text{-}2eten)_2Cl_3,2H_2O$

(ii) Dichloro bis(N,N'-2eten)nickel(III) chloride dihydrate

$Ni(N,N'\text{-}2eten)_2Cl_3,2H_2O$

(iii) Dibromo bis(N,N-2eten)nickel(III) bromide dihydrate

$Ni(N,N\text{-}2eten)_2Br_3,2H_2O$

(iv) Dibromo bis(N,N'-2eten)nickel(III) bromide dihydrate

$Ni(N,N'\text{-}2eten)_2Br_3,2H_2O$

(v) Di-iodo bis(N,N'-2eten)nickel(III) iodide dihydrate

$Ni(N,N'\text{-}2eten)_2I_3,2H_2O$ (5(a) p.61)

The analytical results are shown in Table 5(b) and p.62.

E.

(i) Dibromo mono(N,N'-2eten)nickel(III) bromide, hydrogen bromide hydrate

$Ni(N,N'\text{-}2eten)Br_3,HBr,2H_2O$

(ii) Dibromo mono(N,N-2eten)nickel(III) bromide hemiethyl alcohol

$Ni(N,N\text{-}2eten)Br_3\tfrac{1}{2}C_2H_5OH$

These last two compounds resulted when the complexes were treated in the same identical conditions and proportions for the bromination of nickel(III) complexes, shown as above but without the presence of diamine in the washing liquids.

The two complexes were completely analysed and satisfactory for the formulae given above. (See page 61).

The complexes of the type $Ni(AA)_2X_3$, where AA = N-meen, N,N-2meen and N,N'-2meen were prepared by the analogous methods. The analytical results are shown in Tables 6(a) and 6(b), pages 63 and 64.

Compounds of the type $[Ni(AA)_2X_3]$ where AA = N-eten, N,N-2eten and NN'-2eten and
X = Cl, Br or I (for abbreviations see p. 15).

TABLE 5(a) Microanalyses

	Compound	Colour	Elemental Analysis (Microanalysis) (Percentage)					
				N	H	N	Ni	halides
(1)	$Ni(N\text{-}eten)_2Br_3$	violet-brown	Calcd:	20.32	5.09	11.87	12.42	50.71
			Found	-	4.99	11.19	12.67	50.91
(2)	$Ni(N\text{-}eten)_2I_3$	violet-red	Calcd:	15.66	3.94	9.53	9.50	61.83
			Found	15.68	4.16	9.63	9.48	61.00
(3)	$Ni(NN\text{-}2eten)_2I_3$	violet-red	Calcd:	21.45	4.80	8.48	8.74	56.67
			Found	21.54	5.26	8.22	8.63	57.11
(4)	$Ni(NN\text{-}2eten)_2I_3HI\ 2H_2O$	violet-red	Calcd:	18.85	5.00	7.90	7.02	60.70
			Found	18.75	5.12	7.52	7.00	59.38
(5)	$Ni(NN'\text{-}2eten)_2I_3\ 2H_2O$	violet-red	Calcd:	20.35	5.10	8.06	8.28	53.79
			Found	20.51	5.6	8.24	8.34	52.30
(6)	$Ni(NN'\text{-}2eten)Br_3HBr\ 2H_2O$	violet	Calcd:	13.66	4.09	5.26	11.03	60.15
			Found	13.33	4.29	5.42	11.01	58.99
(7)	$Ni(NN\text{-}2eten)Br\frac{1}{2}C_2H_5OH$	violet	Calcd:	17.43	-	-	13.39	54.76
			Found	17.56	-	-	13.01	53.33

Compounds of the type [Ni$(AA)_2X_3$] where AA = N-eten, N,N-2eten and NN'-2eten and
X = Cl, Br or I (for abbreviations see p. 15)

TABLE 5(b) Other Analyses

	Compound	Colour		Elemental Analysis (Percentage) metal	halides
(8)	Ni(N-eten)$_2$Cl$_3$	green-deep (black)	Calcd:	17.16	31.10
			Found	16.99	30.32
(9)	Ni(NN-2eten)$_2$Cl$_3$ 2H$_2$O	green-black	Calcd:	13.52	24.49
			Found	13.50	24.03
(10)	Ni(NN'-2eten)$_2$Cl$_3$ 2H$_2$O	green-black	Calcd:	13.52	24.49
			Found	13.90	24.60
(11)	Ni(NN-2eten)$_2$Br$_3$ 2H$_2$O	violet	Calcd:	10.34	18.73
			Found	10.33	18.70
(12)	Ni(NN'-2eten)$_2$Br$_3$ 2H$_2$O	violet	Calcd:	10.34	18.73
			Found	10.38	18.27

Compounds of the type [$Ni(AA)_2X_3$] where AA = N-meen, and NN-2meen and NN'-2meen and X = Cl, Br and I

(for abbreviations see p.15)

TABLE 6(a)

	Compound	Colour		Elemental Analysis (Microanalysis) (Percentage)				
				C	H	N	Ni	halides
(1)	$Ni(N\text{-}meen)_2Cl_3\ 2H_2O$	green-black	Calcd:	20.62	6.90	16.0	17.0	30.49
			Found	21.01	6.85	⊕	17.08	30.55
(2)	$Ni(N\text{-}Neen)_2Br_3$	black-green	Calcd:	16.13	4.49	12.55	13.14	53.67
			Found	16.68	4.46	12.69	13.12	52.94
(3)	$Ni(N\text{-}Neen)_2I_3$	violet	Calcd:	12.26	3.44	9.53	9.99	64.76
			Found	⊕	4.13	9.63	10.12	63.89
(4)	$Ni(NN\text{-}2meen)_2Cl_3HCl\ 2H_2O$	green deep black	Calcd:	22.0	7.63	8.13	14.19	34.26
			Found	21.61	7.20	7.82	14.23	34.01
(5)	$Ni(NN\text{-}2meen)_2Cl_3\ 2H_2O$	deep green	Calcd:	25.40	7.5	12.5	15.56	28.13
			Found	24.57	7.00	⊕	15.46	27.96

*Analysis carried out only for metal and halides

⊕Not done

Compounds of the type [$Ni(AA)_2X_3$] where AA = N-meen, and NN-2meen and NN'-2meen and X = Cl, Br and I

(for abbreviations see p.15)

TABLE 6(b)

	Compound	Colour	Elemental Analysis (Microanalysis) (Percentage)	C	H	N	Ni	halides
(6)	$Ni(NN\text{-}2meen)_2Cl_3$	green-black	Calcd:	35.53	7.1	7.8	17.22	31.13
			Found	35.39	⊕	⊕	17.38	31.09
(7)	$Ni(NN\text{-}2meen)_2Br_3\ 2H_2O$	violet	Calcd:	18.72	5.1	10.96	11.49	46.92
			Found	⊕	⊕	10.92	11.50	47.08
(8)	$Ni(NN\text{-}2meen)_2I_3\ 2H_2O$	violet-red	Calcd:	15.60	3.90	9.10	9.01	58.42
			Found	15.56	3.29	8.83	8.94	57.09
(9)	$Ni(NN'\text{-}2meen)_2Cl_3\ 2H_2O$	green-black	Calcd:	25.46	7.55	12.5	15.56	28.13
			Found	25.77	7.75	⊕	16.00	28.09
(10)	*$Ni(NN'\text{-}2meen)_2Br_3\ 2H_2O$	violet	Calcd:	18.72	5.1	10.96	11.49	46.92
			Found	⊕	⊕	⊕	11.35	46.06
(11)	$Ni(NN'\text{-}2meen)_2I_3\ 3H_2O$	Violet-red	Calcd:	14.08	3.88	7.08	8.77	55.56
			Found	13.5	3.51	⊕	8.62	54.99

CHAPTER IV

SPECTROSCOPY

Infra-red Absorption Spectra

Diamine Complexes

Tentative assignments of the infra-red bands in Nickel(III) ethylenediamine complexes were made using earlier assignments of Baldwin[68,69] Powell[70-72] and others. The assignments of the NH_2 modes given by Powell[70] also agree with those for Co(III) ethylenediamine complexes studied by Baldwin[68] with those in the present work. In the solid state the vibrational modes of the metal chelate rings are affected by

(1) the orientation of the chelate molecules around the metal atom;

(2) the spatial configurations of the individual chelate molecules and the non-bonded interactions between them; and

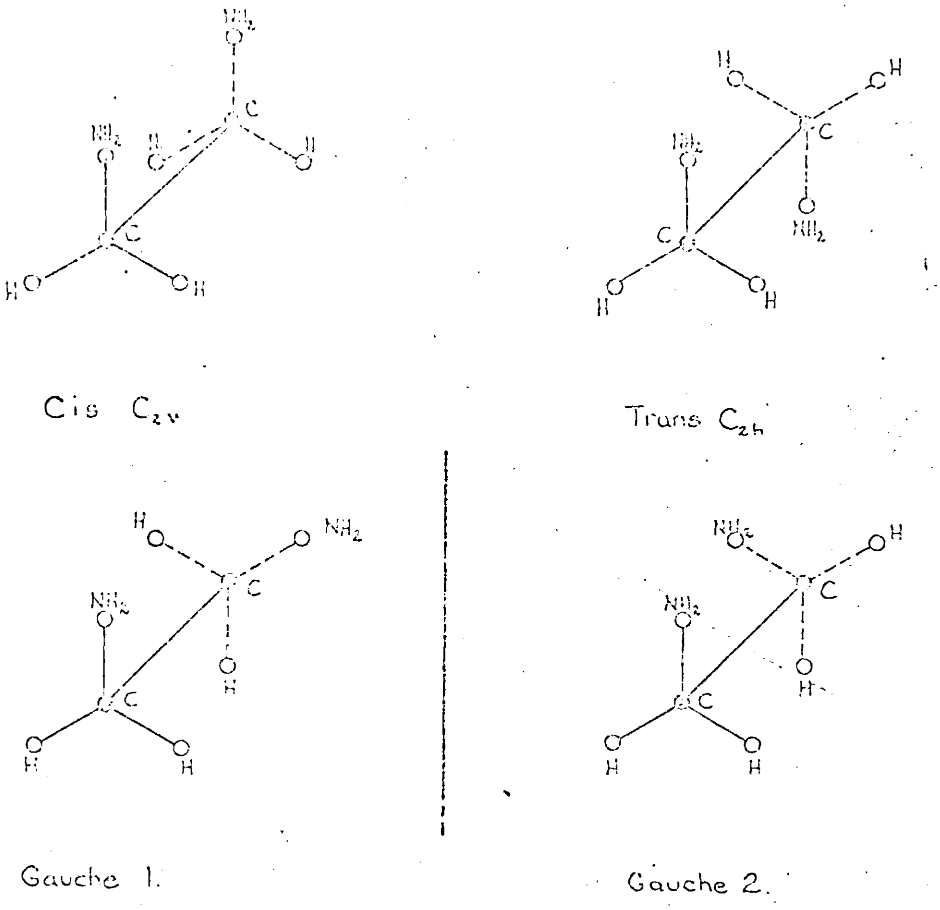
(3) ionic interaction or hydrogen bonding between the anion and cation in a salt.

Ethylenediamine can exist in *cis*, *trans* or *gauche* form depending on the angle of internal rotation. It has been pointed out by Bailar and Corey[86] that an isolated metal ethylenediamine ring in the *gauche* form can adopt either two configurations (k and k') which are energetically and geometrically equivalent.

Quagliano and Mizuschima[75] have indicated that cobalt ethylenediamine ring is in the *gauche* conformation, which also supports later from X-ray crystallographic data on the compounds $[Coen_2Cl_2]Cl,HCl, 2H_2O$ and $[Coen_3]Cl_3$.[76,77] The trans form is not suitable for coordination because the two nitrogen atoms are far apart (see Fig.3 p.67). The i.r. spectra of nickel(III) ethylenediamine complexes show the same general band type as cobalt(III) ethylenediamine complexes. It seems reasonable to assume that this general band structure is typical of the *gauche* conformation of all the metal ethylenediamine rings.

The principal modes of vibration of the NH_2 groups are: symmetrical stretching, asymmetrical stretching, bending, wagging, twisting and rocking; in the regions $\sim 3350\ cm^{-1}$, $\sim 1560 - 1610\ cm^{-1}$, FIGURE:-- 3

Conformations of the ethylenediamine molecule



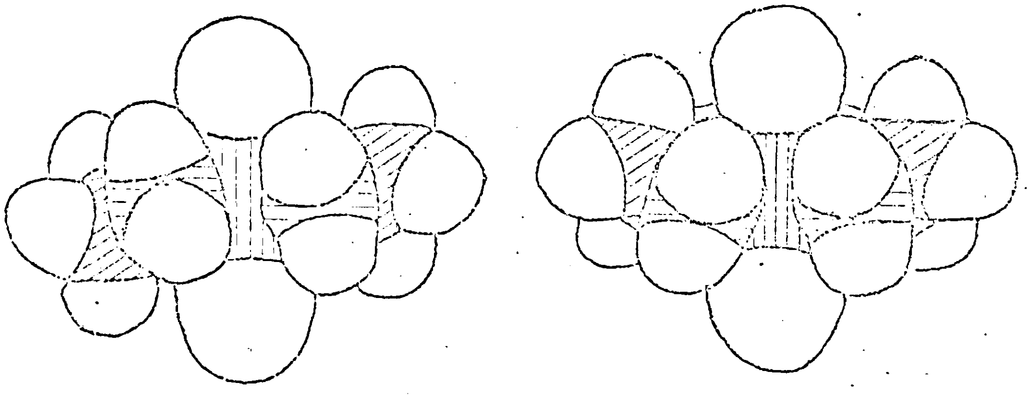
Cis C_{2v}

Trans C_{2h}

Gauche 1.

Gauche 2.

C_2.



kk form

kk' form

Relation of two coordinated bidentate ethylenediamine molecules in the gauche form

1170 - 1165 cm^{-1}, ~ 980 cm^{-1}, and ~ 750 cm^{-1} respectively. The NH_2 stretching region occurs between 3300 and 3073 cm^{-1}. The band finds at about ~1600 cm^{-1} may be assigned to NH_2 banding vibration. The N-H stretching vibration occurs in the range 3390 - 3160 cm^{-1}. In tris diamine (and substituted diamine) complexes show three main bands in this region. The other spectra show a complicated band structure. The variation of N-H stretch bands varies considerably in decreasing resolution Cl > Br > I may be due to hydrogen bonding of the type M-H....X were shown by Fujita[73], Baldwin[68,69] and also by Powell and Sheppard.[70]

N- substituted diamines show somewhat different characteristics. Basolo et. al.[87] have shown that alkyl substitution on a nitrogen atom of the 'en' increases the basic strength of the amines, all the metal formation constants of a metal complex is lower than those of the unsubstituted amines. This is because it is due to steric effects of the N-substituents, and Dq value decreases in the octahedral or distorted octahedral complexes from en > N Meen > N eten > NPn > NN 2Meen > NN' 2eten. As alkyl substitution groups increase, showing that steric interactions are greater than inductive effects in these ligands. The bands which appear in the regions ~1460 cm^{-1}, ~1380 cm^{-1}, ~ 1286 cm^{-1}, and ~890 cm^{-1} may be assigned to the vibrations of CH_2 groups, CH_2 band, CH_2 wag and CH_2 rock, respectively. The band near 1080 cm^{-1} which is sharp and strong could be a result of the stretching vibration of either the C-N or C-C bond of the diamine skeleton.

Chamberlain and Bailar[81] suggested that the region 1120 - 1150 cm^{-1} can be used to distinguish <u>cis</u> and <u>trans</u> bis ethylenediamine isomers. This region may not be well clear when the complex contains coordinated or ionic oxy-anions. In the halide ion complexes the trans compounds show two sharp peaks in the ranges 1120-1110 cm^{-1}. Baldwin[68,85] reported that in a trans bis (ethylenediamine) cobalt(III) complex a sharp single band occurs in the range of 1605 - 1575 cm^{-1}, whereas in the cis and trans complex there is splitting and the bands occur over the wide range 1634 - 1527 cm^{-1}. These bands have been assigned to N-H bending vibration by Merrit and Wiberly[78] in agreement with the previous assignment of Richard and Thompson.[79] Morris and Bush[80] also found a splitting of this band in the trans complexes. Thus it was suggested by Baldwin[85] that CH$_2$ rocking region between 870 - 900 cm^{-1} provides a means for the differentiation of cis and trans isomers of bis(ethylenediamine) type, cis complexes show two bands while complexes with trans configuration show one band. Hughes and McWhinnie[82] investigated the i.r. spectra of thirteen cis and eight trans bis ethylenediamine cobalt(III) complexes in the regions 1630 - 1520 cm^{-1}, 1150 - 1120 cm^{-1}, and 900 - 870 cm^{-1} and who found the best correlation between the stereochemistry and bands splitting lies in the 900 - 870 cm^{-1}region. However, the bands in this region are weak and hence it is difficult to assign the stereochemistry on the basis of these results.

Balwin's[68, 85] empirical rules are generally applicable to the Ni(III) diamine complexes, but not to the nickel(II) complexes made by James.[41]

Anions

(a) Perchlorate

In the absence of dissymmetric interactions with neighbouring atoms the perchlorate ion belongs to Td symmetry, and has four different vibrational frequencies $(A_1 + E + 2T_2)$. Of the four fundamentals only ν_3 (T_2) antisymmetrical stretch (ca. 1100 cm^{-1}) and ν_4 (T_2) antisymmetric band (ca. 625 cm^{-1}) are infrared active. The non-degenerate symmetrical stretch ν_1 (A_1) which is Raman active is usually observed as a weak band at about 930 cm^{-1}. Harris and McKenzie[88] showed that on coordination Td symmetry is lowered to C_3, or C_2v, depending on whether the perchlorate group is acting as uni- or bidentate. If the coordination is through a single oxygen the ν_3 bands at 1100 cm^{-1} in the free ion splits into two bands. If the coordination is through two oxygens the ν_3 band is split into three.

(b) Nitrate

The free nitrate has D_{3h} symmetry which is lowering to C_2v on coordination through one or two oxygens. On coordination the ν_3 and ν_4 modes of the free ion are split. Cotton et. al.[84] showed that it is not always possible to determine the coordination of the nitrate group from the infrared spectra alone. Some other physical measurements like conductivity measurements are also required for coordination. But as other oxyanions it could be reasonable to suggest that the nitrate group is probably unidentate coordinated.

(c) Sulphate

The free sulphate ion has Td symmetry according to Kohlaransch,[89] the four vibrational freqeuncies of the sulphate ion are:

ν_1 (A)	981 cm^{-1}	stretching vibrations
ν_2 (E)	451 cm^{-1}	bending vibrations
ν_3 (T_2)	1104 cm^{-1}	stretching vibrations
ν_4 (T_2)	613 cm^{-1}	bending vibrations

In the solid state i.r. spectra of sulphates (or HSO_4) ν_1 is invariably present while the triply degenerate frequencies ν_3 and ν_4 sometimes split into two or three bands corresponding to lowering of the symmetry of the ion to C_3v and C_2v respectively. There are mainly three reasons of lowering of the symmetry in the solid.

(i) Distortion of the SO_4^{2-} in the crystal lattice.

(ii) Covalent bonding of the sulphate to the metal through one or more oxygen.[90]

(iii) A non uniform field due to water molecules around the cation.

The results of such a decrease in a symmetry on the i.r. spectrum are summarised below.

Species	Symmetry	ν_1	ν_2	ν_3	ν_4
Free SO_4	Td	-	-	T_2	T_2
Monodentate	C_{3v}	A_1	E	A_1+E	A_1+E
Bidentate	C_{2v}	A_1	A_1	$A_1+B_1+B_2$	$A_1+B_1+B_2$

The frequencies corresponding to ν_1 (A_1) for the SO_4^{2-} tetrahedron is usually found in the region of 980 - 990 cm^{-1} in the spectra of crystalline sulphates. It was suggested by Finholt et. al.[115] that coordinated water groups denote absorbed peaks in 900 to 1500 cm^{-1} region. Hence any observed peaks in this region of the spectra of the complex (containing HSO_4^{-2} or SO_4^{-2}) group can be attributed to sulphate group vibrations. In the region 900 - 1300 cm^{-1} three infrared active bands should be observed for a monodentate sulphate and four for a bidentate sulphate.

Stretching	Regions in cm^{-1}
ν_1 (A_1)	977
ν_3 (T_2)	1050 - 1170
ν_4 (T_2)	580 - 670

It is also difficult to distinguish between bridging sulphate and bidentate sulphate groups as both have symmetry $C_2\nu$.

Results and Discussion

The complexes of all types are shown in Tables 7 - 11, pages 73 - 90. The i.r. spectra of diamine complexes were very similar to those for diamine complexes of cobalt(III) reported by Baldwin[68]. Complexes like $[Ni(en_2Br_2)Br]$ or $Nien_2IBr_2$ which may be $[Ni(en_2IBr)Br]$ or $[Ni(en_2Br_2)I]$ ~~has~~ have the cis structure. I.r. spectra of the oxyanion complexes in the region 1500 - 1000 cm^{-1} were very similar to those for perchlorato[91], nitrato[92] and sulphato[83] complexes. The band positions for these groups are shown in Tables 7(c), 7(d), 8(c) and 8(d).

In the perchlorate complexes, perchlorate was also coordinated through only one oxygen. In the complexes containing HSO_4 ion the absence of strong i.r. bands due to sulphate close to 1220 cm^{-1} suggested that this anion was present as a bridging rather than a chelating group.

The complexes show a broad band/strong band between 1070 - 1120 cm^{-1} indicating the presence of ionic groups NO_3^-, HSO_4^- or ClO_4^-.

Abbreviations in the following tables are as follows:

m = moderate
s = strong
vs = very strong
sh = shoulder
w = wide

TABLE 7(a)

I.R. Spectra in the region 4000 - 600$^{cm^{-1}}$

Compounds of the type (1) - $Nien_2X_3$

Compound: ⟶	$Nien_2Cl_3$	$Nien_2Br_3.5H_2O$	$Nien_2I_3$	$Nien_2BrCl,2.5H_2O$	$Nien_2Br_2I.5H_2O$
HOH and NH_2 stretching	3330 m 3208 s 3104 s	3318 m 3123 s 3098 s	3330 m 3220 s 3130 s	3320 m 3275 s 3200 s	3318 m 3196 s 3136 s
CH_2 stretching	2928 m 2887 m	2953 m 2889 m	2953 m 2889 m	2950 m 2889 m	2950 m 2945 m
NH_2 scissors	1600 s 1587 m	1598 s 1578 m	1583 s 1562 m	1597 s 1570 m	1590 s 1578
CH_2 scissors	1468 m	1465 m	1475 w 1468 m	1468 m	1468 m
CH_2 wag	1386 s 1376 m	1380 s 1370 m	1385 s 1375	1380 s 1373 m	1384 w 1373 m
NH_2 wag	1328 m 1310 m	1328 m 1308 m	1330 m 1318 m	1325 m 1308 m	1326 m 1313 w
CH_2 twist	1296 m 1278 w	1289 m 1272 w	1278 m 1268 w	1290 m 1278 w	1286 m 1270 w
NH_2 twist	1148 m	1165 m	1133 w	1150 m	1140 w
Ring skeletal	1116 vs 1110 vs 1070 vs	1110 vs 1088 vs 1068 vs	1108 vs 1088 vs 1068 vs	1110 vs 1080 vs 1060 vs	1109 vs 1088 vs 1066 vs

TABLE 7(b)

I.R. Spectra in the region 4000- 600cm^{-1}

Compounds of the type (1) - $Nien_2X_3$ (continued)

Compound: ⟶	$Nien_2Cl_3$	$Nien_2Br_3.5H_2O$	$Nien_2I_3$	$Nien_2BrCl,2.5H_2O$	$Nien_2Br_2I.5H_2O$
unassigned N = broad band	1105 m N	1098 m N	N N	1096 m N	1096 m N
NH_2 twist	980 m 960 m	980 m	980 m	980 m	980 m
CH_2 ROCK or ring skeletal	890 m 880 m 875 s	890 m 878 m 865 s	869 m 860 m	892 m 880 m 865 s	891 m 880 m 863 s
NH_2 ROCK	720 m 710 sh 699 s	718 m 710 sh 690 sh	715 m 708 sh 695 s	718 s 708 sh 695 s	718 m 707 sh 690 s

TABLE 7(c)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Type (1) [Oxyanions (ClO_4, NO_3 and HSO_4)]

Compounds of the type $Nien_2X_3$

Compound: ⟶	$Nien_2Cl_2(NO_3)$	$Nien_2Cl(NO_3)_2$	$Nien_2Cl_2(HSO_4)$	$Nien_2Cl(HSO_4)_2$	$Nien_2Cl_2(ClO_4)$
HOH and NH_2 stretching	3300 m 3283 s 3173 s	3286 m 3175 s	3320 sh 3290 sh 3257 m 3134 s	3320 sh 3290 sh 3253 m 3210 s 3184 s	3316 m 3226 s 3190 m 3118 m
CH_2 stretching	2969 m 2900 m	2978 m 2900 m	2965 m 2902 m	2969 m 2902 m	2979 m 2899 m
NH_2 scissors	1600 s	1602 s 1592 m	1608 s 1596 m	1606 s 1592 m	1602 vs
CH_2 scissors	1468 w	1467 w	1468 w	1466 w	1468 w
CH_2 wag	1386 m	1390 w 1378 m	1397 w 1376 m	1395 m 1380 m	1398 w -
NH_2 wag	1328 w 1308 m	1327 m 1306 w	- -	1330 w	1330 w -
CH_2 twist	1298 m 1276	1296 m 1280 w	1298 m 1278	1298 m 1280 w	-
NH_2 twist	1152 m	1150 m	1152 m	1150 m	1138 m

TABLE 7(d)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Type (1) [Oxyanions (ClO_4, NO_3 and HSO_4)]

Compounds of the type $Nien_2X_3$ (Continued)

Compound: ⟶	$Nien_2Cl_2(NO_3)$	$Nien_2Cl(NO_3)_2$	$Nien_2Cl_2(HSO_4)$	$Nien_2Cl(HSO_4)_2$	$Nien_2Cl_2(ClO_4)$
Ring skeletal	1120 vs 1108 s	1118 vs 1110 vs	1120 vs 1102 vs	1100 vs 1098 s	1120 ms
NH_2 twist	1033 vs	1033 vs	1033 vs	1033 vs	-
unassigned N = Very broad band	N	N	N	N	N
NH_2 twist	985 m 968 m	982 m 970 m	983 m 970 m	981 m 970 m	980 -
CH_2 rock or ring skeletal	885 m 838 s 824 m	886 m 835 s 819 m	886 m 838s -	881 m 836 s -	896 m 840 s
NH_2 rock	700 m 790 s	768 m 700 m 689 s	762 m 723 s 699 s 689 s	768 m 726 m 700 m 690 s	689 s 671 sh
<u>Oxyanions</u>	1396 w 1300 w 830 m	1510 vs 1320 vs 1028 s 828 m	1390 w 1328 w	3030 s 1136 vs 1090 vs 1040 m 770 m	1110 m 1060 vs 940 w

TABLE 8(a)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type (2) $NiPn_2X_3$

Compound: ⟶	$NiPn_2Cl_3$	$NiPn_2Cl_3,2H_2O$	$NiPn_2Br_3$	$NiPn_2Br_3,2H_2O$	$NiPn_2I_3,2H_2O$
HOH and NH_2 stretching	3368 w 3248 m 3180 m	3452 m 3373 w 3250 m 3180 m	3366 w 3246 m 3184 m	3454 m 3270 w 3184	3390 m 3426 m 3180m
CH_2 stretching	2950 s 2782 s	2950 s 2786 s	2948 s 2780 s	2950 s 2784 s	2952 s 2783 s
NH_2 scissors and HOH banding	1600 vs 1568 m 1518 m	1600 vs 1568 m 1520 m	1600 vs 1566 m 1520 m	1600 vs 1566 m 1520 m	1600 vs 1566 m 1518 m
CH_2 scissors	1470 s	1468 s	1468 s	1466 s	1470 s
CH_2 wag	1378 m	1382 m	1376 m	1380 m	1376 m
NH_2 wag	1338 m	1340 m	1338 m	1339 m	1336 m
CH_2 twist	1298 m	1300 m	1302 m	1300 m	1303 m
NH_2 twist	1160 s 1148 m	1162 s 1150 m	1166 s 1146 m	1165 s 1146 m	1167 s 1146 m
Ring skeletal	1092 vs	1090 vs	1093 vs	1098 vs	1090 vs

TABLE 8(b)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type (2) $NiPn_2X_3$ (Continued)

Compound: ⟶	$NiPn_2Cl_3$	$NiPn_2Cl_3,2H_2O$	$NiPn_2Br_3$	$NiPn_2Br_3,2H_2O$	$NiPn_2I_3,2H_2O$
NH_2 twist	1033 vs 1018 vs	1040 vs 1020 vs	1041 vs 1020 vs	1038 vs 1019 vs	1040 vs 1020 vs
unassigned N = broad band	1106 s N	1106 s N	1105 s N	1103 s	1106
NH_2 twist	978 m	989 m	970 m	975 m	968 m
CH_2 rock or ring skeletal	862 s 828 w	862 s 826 w	865 s	866 s	880 s 820 s
NH_2 rock	780 m 670 sm	780 m 670 sh	780 m 676 sh	780 m 676 sh	780 m 680 sh

TABLE 8(c)

I.R. Spectra in the region 4000 - 600cm^{-1}

Compounds of the type (2) $NiPn_2X_3$

Compound: ⟶	$NiPn_2BrCl_2$	$NiPn_2I_2Cl$	$Pn_2Cl_2(ClO_4)$	$Pn_2Cl_2(NO_3)$	$Pn_2Cl(HSO_4)_2$
H-O-H and NH_2 stretching	3390 m 3248 w 3182 m	3246 w 3180 m	3240 m	3246 m	3320 sh 3254 m 3244 w
CH_2 stretching	2953 s 2783 s	2950 s 2780 s	2886 s 2760 m	2889 s 2760 m	2886 s 2760 m
NH_2 stretching	1600 vs 1567 m 1518 m	1600 vs 1562 m 1520 m	1560 m 1516 m	1566 m 1518 m	1560 m 1516 m
CH_2 scissors	1470 s	1468 s	1466 s	1468 s	1468 s
CH_2 wag	1378 m	1374 m	1370 m	1370 m	1370 m
NH_2 wag	1338 m	1338 m	1330 m 1308 m	1328 m	1330 m
CH_2 twist	1300 m	1303 m	1290 m 1286 w	1296 m 1280 w	1298 m 1280 w
NH_2 twist	1162 m 1150 s	1166 m 1150 s	1150 m	1150 m	1150 m
Ring skeletal	1090 vs	1090 vs	1088 s	1086 vs	1092 m

TABLE 8(d)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compound of the type (2) $NiPn_2X_3$ (Continued)

Compound: ⟶	$NiPn_2BrCl_2$	$NiPn_2I_2Cl$	$Pn_2Cl_2(ClO_4)$	$Pn_2Cl_2(NO_3)$	$Pn_2Cl(HSO_4)_2$
NH_2 twist	1040 s 1020 vs	1040 s 1020 vs	1035 vs	1035 vs	1035 vs
unassigned N = Broad band	1106 s N	1106 s N	1106 s N	1106 s N	1106 s N
NH_2 twist	976 m	976 m	-	986 m 968 m	980 m 965 m
CH_2 rock or ring skeletal	880 s 820 m	886 s 820 m	896 s 876 w 838 m	883 s 875 w 840 m	881 s 872 w 840 m
NH_2 rock	780 m 680 m	780 m 680 sh	688 m 668 sh	700 m 690 sh	728 m 690 sh
Oxyanions			1110 m 1045 s 937 w	1390 w 1300 w 828 m	3028 s 1130 vs 1087 vs

TABLE 9(a)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Nien_3X_3$ and $NiPn_3X_3$

Compounds: ⟶	$Nien_3Cl_3,HCl,2H_2O$	$Nien_3Cl_3,3H_2O$	$Nien_3Br_3,HBr,2H_2O$	$Nien_3Br_3,2H_2O$	$Nien_3I_3HI,2H_2O$
HOH and NH_2 stretching	3450 w 3340 m 3248 sh 3151 m	3462 w 3320 m 3250 sh 3151 m	3472 w 3380 w 3250 sh 3100 m	3487 w 3320 m 3250 sh 3150 m	3480 w 3200 sh 3100 m
CH_2 stretching	2950 m 2870 s 2800 m	2956 m 2874 s 2788 m	2950 sh 2870 s 2800 m	2950 sh 2868 s 2802 m	2960 m 2910 m 2868 m
NH_2 scissors	1600 vs 1565 s 1508 m	1608 vs 1570 s 1510 m	1580 vs 1570 s 1520 m	1625 s 1586 s 1565 m	1590 s 1566 m
CH_2 scissors	1462 m	1465 m	1462 m	1465 m	1458 m
CH_2 wag	1380 vs 1348 s	1408 sh 1380 vs	1380 vs 1350 s	1380 vs 1350 s	1378 vs 1350 s
NH_2 wag	1335 m 1320 m	1336 m 1320 s	1320 m	1329 m	1320 vs
CH_2 twist	1295 s 1270 s	1298 s 1272 s	1300 s 1274 s	1300 sh 1275 s	1300 -
NH_2 twist	1155 m 1138 m	1148 m 1138 m	1155 m 1140 m	1153 m 1145 m	1153 m
Ringskeletal	1090 m	1091 m	1090 m	1090 m	1090 m
NH_2 twist	1020 s	1020 s	1020 s	1018 s	1020 s

TABLE 9(b)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Nien_3X_3$ and $NiPn_3X_3$ (continued)

Compounds: ⟶	$Nien_3Cl_3,HCl,2H_2O$	$Nien_3Cl_3,3H_2O$	$Nien_3Br_3,HBr,2H_2O$	$Nien_3Br_3,2H_2O$	$Nien_3I_3HI,2H_2O$
unassigned	1098 m 1062 m	1098 m 1062 m	1123 sh 1040 m	1115 m 1090 m	1108 m 1068
NH_2 twist	980 s 965 w	985 s	980 m	980 m	980 m
CH_2 rock	886 m	885 m	895 s	895 s	878 s
Ring skeletal	873 s 860 s	870 s	880 s	883 s	860 s
NH_2 rock	662 m	665 m	668 m	670 m	680 m

TABLE 9(c)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Nien_3X_3$ and $NiPn_3X_3$

Compounds: ⟶	$Nien_3I_3$	$NiPn_3Cl_3$	$NiPn_3Br_3$	$NiPn_3I_3$
HOH and NH_2 stretching	3200 sh	3450 w	3458 w	
	3100 m	3375 w	3387 w	3390 w
		3251 m	3221 m	
		3181 m	3181 m	3186 m
CH_2 stretching	2960 m	2951 m	2952 m	2956 m
	2910 m	2789 m	2786 m	2786 m
	2870 m			
NH_2 scissors	1586 s	1605 vs	1600 vs	1600 vs
	1576 m	1568 s	1570 s	1572 s
			1520 m	1528 m
CH_2 scissors	1460 m	1466 s	1468 s	1470 s
CH_2 wag	1380 vs	1385 vs	1383 vs	1383 vs
	1365 s			
NH_2 wag	1322 m	1340 m	1340 m	1340 m
CH_2 twist	1305 s		1308 s	1306 s
	1268 s	1294 s	1265 m	
NH_2 twist	1152 m	1160 m	1157 m	1165 m
		1152 m	1150 m	
Ring skeletal	1090 m	1098 m	1099 m	1093 m
NH_2 twist	1020s	1035 s	1035 s	1039 s
		1020 s	1010 s	1018 s

TABLE 9(d)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Nien_3X_3$ and $NiPn_3X_3$ (continued)

Compounds: ⟶	$Nien_3I_3$	$NiPn_3Cl_3$	$NiPn_3Br_3$	$NiPn_3I_3$
unassigned	1109 m 1065 m	1098 m 1065 m	1120 m 1076 m	1118 m 1078 m
NH_2 twist	975 m	978 m	967 m	970 m
CH_2 rock	878 s		895 s	878 s
ring skeletal	860 s	868 s	870 s	870 s
NH_2 rock	675 m	670 m	670 m	702 m 669 m

TABLE 10(a)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Ni(AA)_2X_3$ where AA = N-eten, N,N-2eten and N,N'-2eten

Compounds: ⟶	$Ni(N,N\text{-}2eten)Cl_3,2H_2O$	$Ni(N,N\text{-}2eten)Br_3,2H_2O$	$Ni(N,N'\text{-}2eten)_2Br_3$	$Ni(N,N\text{-}2eten)_2I_3,2H_2O$
HOH and NH_2 stretching	3468 w	3464 w	3465 w	
	3368 w	3308 s		
	3280 w		3290 s	3280 s
	3150 s			3170 s
CH_2 stretching	2950 m	2955 m	2940 m	2938 m
	2910 m			
	2860 m	2898 m	2898 m	2896 m
NH_2 scissors	1700 s	1680 m		
	1600 s	1562 s	1598 s	1590 vs
	1640 m	1642 m	1640 m	1637 m
CH_2 scissors	1470 s	1465 vs	1460 vs	1468 vs
		1420 vs	1417 vs	1419 vs
CH_2 wag	1390 s	1385 s	1383 s	1390 vs
NH_2 wag	1340 m	1350 m	1340 m	1336 m
	1320 m			
CH_2 twist	1270 m	1280 m	1280 m	1278 m
			1264 m	
NH_2 twist	1170 m	1170 m	1165 m	1170 m
	1134 s	1137 s		1137 s

TABLE 10(b)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Ni(AA)_2X_3$ where AA = N-eten, N,N-2eten and N,N'-2eten (continued)

Compounds: ⟶	$Ni(N,N\text{-}2eten)Cl_3,2H_2O$	$Ni(N,N\text{-}2eten)Br_3,2H_2O$	$Ni(N,N'\text{-}2eten)_2Br_3$	$Ni(N,N\text{-}2eten)_2I_3,2H_2O$
Ring skeletal	1090 s	1090 vs 1065 s	1088 vs 1066 s	1088 vs
NH_2 twist	1037 s 1020 s	1010 s 1002 sh	1015 s 1002 sh	1016 s
	b	b	b	b
NH_2 twist	990 m 970 m	968 m 937 m	966 m 940 m	970 m
CH_2 rock or ring skeletal	890 s 815 s	880 s 837 s	880 s 818 s	887 s 821 s
NH_2 rock	770 m 720 m	768 m 740 m	770 m 720 m	769 m 718 m

Note: b = unassigned broad absorption in this region.

TABLE 10(c)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Ni(AA)_2X_3$ where AA = N-eten, N,N-2eten and N,N'-2eten

Compounds: ⟶	$Ni(N,N'-2eten)_2I_3,2H_2O$	$Ni(N-eten)_2Cl_3$	$Ni(N-eten)_2Br_3,2H_2O$	$Ni(N-eten)_2I_3$
HOH and NH_2 stretching	3460 w 3365 w 3176 s	3468 w 3368 w 3280 w 3150 s	3474 w 3370 m 3148 s	3464 w 3370 m 3130 s
CH_2 stretching	2930 m 2890 m	2969 m 2780 m	2970 m 2883 sh 2780 m	2940 m 2780 m
NH_2 scissors and HOH	1590 vs 1637 m	1583 vs	1572 s 1637 m	1570 s
CH_2 scissors	1470 vs	1473 vs	1470 vs	1468 vs
CH_2 wag	1385 s	1383 s	1380 s	1380 s
NH_2 wag	1334	1348 m	1348 m	1350 m
CH_2 twist	1270 m	1289 m 1258 m	1288 m 1260 m	1286 m 1256 m
NH_2 twist	1134 m	1137 m	1140 m	1141 m
Ring skeletal	1086 vs	1083 vs	1080 vs	1090 vs

TABLE 10(d)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type $Ni(AA)_2X_3$ where AA = N-eten, N,N-2eten and N,N'-2eten (continued)

Compounds: ⟶	$Ni(N,N'\text{-}2eten)_2I_3,2H_2O$	$Ni(N\text{-}eten)_2Cl_3$	$Ni(N\text{-}eten)_2Br_3,2H_2O$	$Ni(N\text{-}eten)_2I_3$
NH_2 twist	1010 s	1030 s	1028 s	1026 s
unassigned (n = broad band	n	n	n	n
NH_2 twist	966 m	968 m	950 m	947 m
CH_2 rock or ring skeletal	880 s 816 s	837 s	846 s	860 s
NH_2 rock	720 m	689 m	720 m	720 m

TABLE 11(a)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type Ni(AA)$_2$X$_3$ where AA = N-meen, N,N-2meen and N,N'-2meen

Compounds: ⟶	Ni(N-meen)$_2$ Cl$_3$, 2H$_2$O	Ni(N-meen)$_2$ Br$_3$	Ni(N-meen)$_2$ I$_3$	Ni(N,N-2meen)$_2$ I$_3$,2H$_2$O	Ni(N,N'-2meen)$_2$ I$_3$,3H$_2$O	Ni(N,N-2meen)$_2$ Br$_3$,2H$_2$O	Ni(N,N'-2meen)$_2$ Br$_3$,2H$_2$O	Ni(N,N'-2meen)$_2$ Cl$_3$,2H$_2$O
HOH and NH$_2$ stretching	3379 m 3208 w 3158 sh	3208 w 3160 m	3230 m 3148 m	3460 m 3390 w 3192 m	3458 m 3372 w 3181 m	3390 m 3372 w 3092 m	3559 sh 3380 m 3178 w	3620 m 3180 m 3092 w
CH$_2$ stretching	2958 m 2708 s	2928 m 2820 s	2950 m	2933 w 2733 w	2926 w 2745 w	2924 w 2700 w	2960 w 2765 w	2960 w 2765 w
NH$_2$ scissors and HOH band	1570 m 1630 s	1568 m	1580 m	1599 vs 1633 m	1600 vs 1635 m	1616 vs 1593 vs 1636 m	1602 s 1598 vs 1638 m	1608 s 1604 vs 1638 m
CH$_2$ scissors	1465 m 1418 m	1462 m	1470m	1469 m 1419 m	1467 m 1416 m	1470 s	1470 s	1471 s 1422 m
CH$_2$ wag	1410 s	1402 s	1400 s	1405 s 1393 sh	1409 m 1382 s	1380 m	1384 m 1374 m	1390 m
NH$_2$ wag	1341 m	1340 m	1365 m 1320 sh	1324 vs	1324 vs	1322 m	1320 m	1330 vs
CH$_2$ twist	1287 s 1232 s	1290 vs 1230 s	1287 vs 1228 vs 1218 s	1288 s 1250 s	1286 vs 1247 vs	1290 vs 1278 vs	1291 vs 1280 vs	1288 vs 1250 vs
NH$_2$ twist	1138 m	1168 m 1138 m	1166 m 1136 m	1185 m 1140 m	1182 m 1138 m	1182 m	1185 m 1108 m	1187 m 1140 m

TABLE 11(b)

I.R. Spectra in the region 4000 - 600 cm^{-1}

Compounds of the type Ni(AA)$_2$X$_3$ where AA = N-meen, N,N-2meen and N,N'-2meen (Continued)

Compounds: ⟶	Ni(N-meen)$_2$ Cl$_3$,2H$_2$O	Ni(N-meen)$_2$ Br$_3$	Ni(N-meen)$_2$ I$_3$	Ni(N,N-2meen)$_2$ I$_3$,2H$_2$O	Ni(N,N'-2meen)$_2$ I$_3$,3H$_2$O	Ni(N,N-2meen)$_2$ Br$_3$,2H$_2$O	Ni(N,N'-2meen)$_2$ Br$_3$,2H$_2$O	Ni(N,N'-2meen)$_2$ Cl$_3$,2H$_2$O
Ring skeletal	1068 vs	1066 vs	1090 vs 1065 vs	1065 vs	1068 vs	1066 vs	1068 vs	1066 vs
NH$_2$ twist	1037 s	1037 s	1040 vs 1018 s	1037 m 1018 s	1037 s 1020 s 1016 s	1016 vs 1009 vs	1016 vs 1010 vs	1020 vs 1000 vs
	b	b	b	b	b	b	b	b
NH$_2$ twist	996 m	996 m 976 s 955 m	926 m	940 m	940 m	940 m	968 m	990 m
CH$_2$ rock	890 s 830 m	880 s 820 m	835 m	890 m	892 m	890 m 820 s	890 m 822 s	820 s
NH$_2$ rock	760 s 718 m	733 s 720 m	726 m	748 s 720 m	780 s 719 m	726 s 679 m	730 s 680 m	748 s 688 m

Note: b = unassigned broad absorption in this region.

Visible And Ultra Violet Spectra Of The Transition Metal Complexes

There are mainly three current theories which may be used to describe the bonding in transition metal complexes. Chronologically but not according to increasing complexity, they are:

(a) The valance bond theory

(b) The crystal field theory

(c) The molecular orbital theory.

A brief account of the crystal field theory is given here.

Crystal field theory and ligand field theory

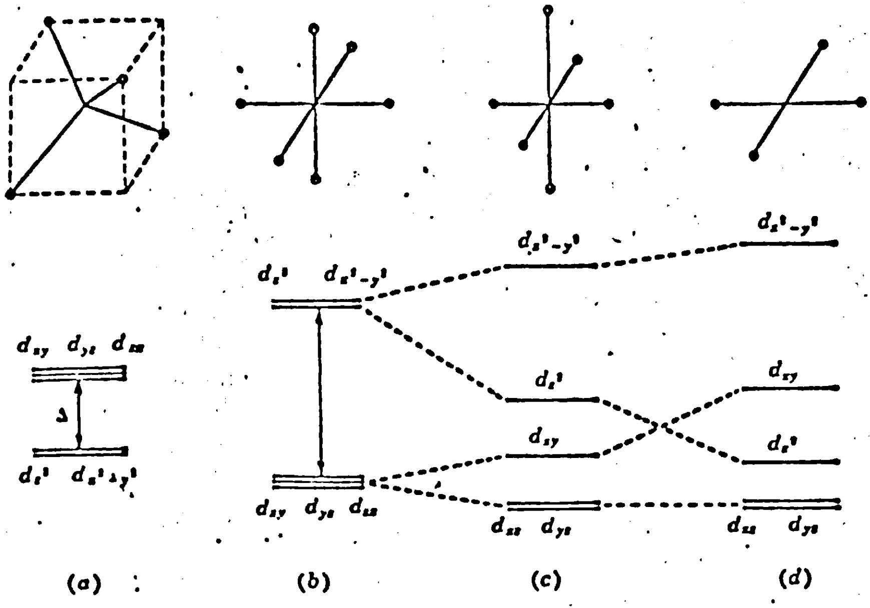
The bonding in transition metal complexes is considered to be electrostatic (ion-ion or ion-dipole). Since ligands carry charges or behave as electric dipoles with the negative poles directed towards the metal ion, they produce an electrostatic field. This field acts on the central metal ion and its strength depends mainly on the nature of the ligands. The precise effects of this field on the orbital degeneracy of the metal ion will depend on the symmetry and strength of the electrostatic field. This purely electrostatic approach is called the crystal field theory which holds surprisingly well for a large number of complexes. It is frequently used in the interpretation of opitcal and megnetic properties of transition metals. A more advanced approach has been developed by van Vleck,[42,43] Mulliken,[44] Orgel,[52] Liher[51] and Figgis, which is known as ligand field theory which the basic electrostatic theory takes into account metal ligand bonding.

The crystal field approximation views the complex as a central metal ion surrounded by a suitable number of ligands. The influence of the ligands on the electronic energy of a system is then imagined to be a simply coloumbic perturbation of the central ion atomic energy level, Fig.4 p.92 shows:

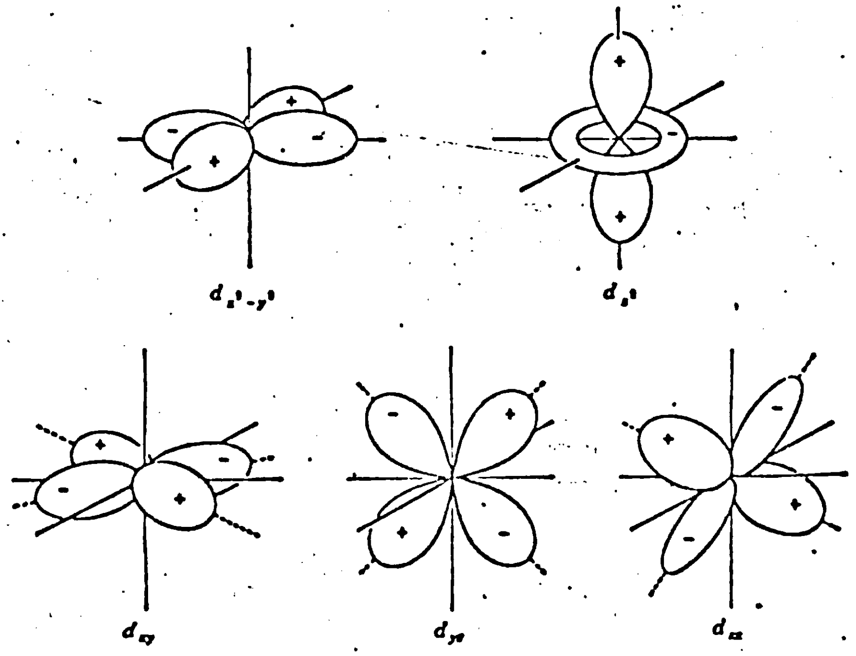
(a) Orbitals dz^2 and $dx^2 - y^2$ with their lobes directed along the z and the x and y axes respectively, the e_g orbitals.

FIG. 4

Ligand field splitting of the d orbitals.(a) Tetrahedral, (b)Octrahedral. (c)Octahedron with tetragonal distortion.(d)Square Planar



Real forms of d orbitals



REPRODUCED FROM 'INTRODUCTION TO MAGNETIC RESONANCE'

ALAN CARRINGTON & ANDREW D. McLACHLAN

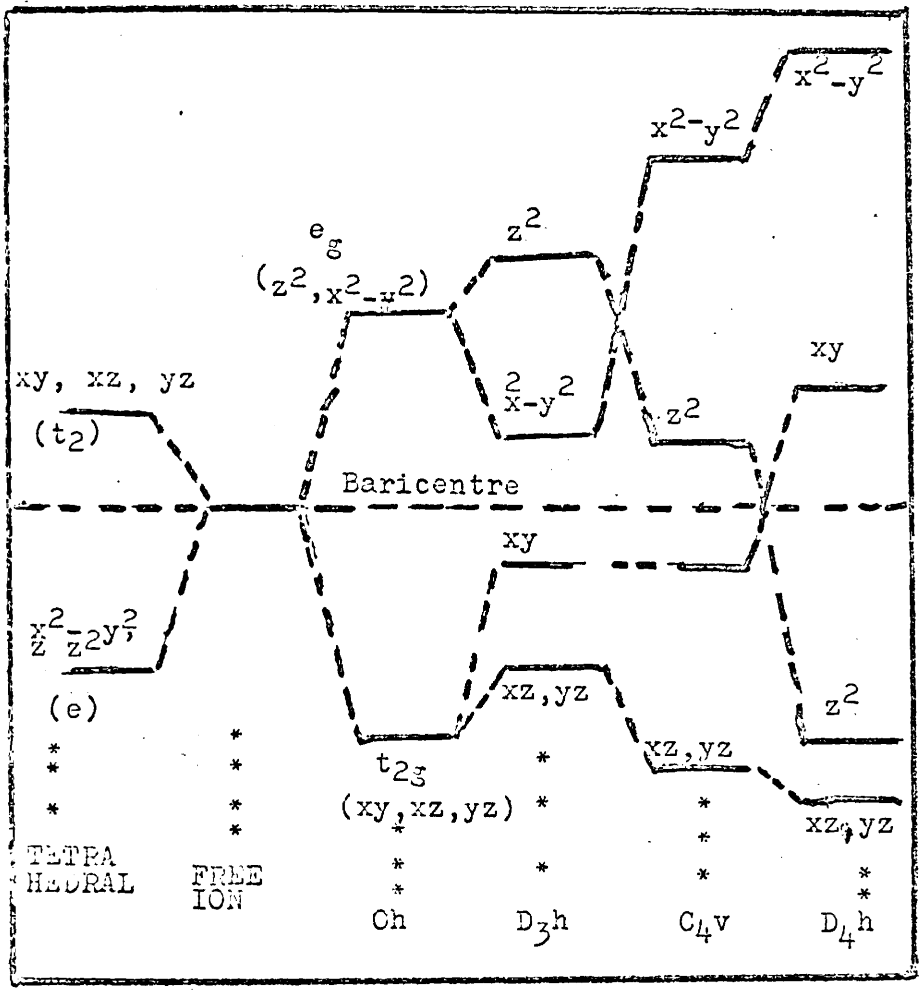
(b) Orbitals dxy, dxz and dyz with their lobes directed between the axes, the t_{2g} orbitals.

It can easily be seen that the two d orbitals, namely eg, which lie with the maxima in their lobes along these coordinates, and thus point directly at the charges must assume a different and higher energy than the three d orbitals "$t_{2}g$' whose lobes point between the coordinates. An electron occupying an 'eg orbital' will suffer greater repulsion than an electron occupying $t_{2}g$ or de orbital, as the former points towards the negative charges and the latter points between the charges. In terms of energy levels, the original degeneracy of the d orbitals in the field-free ion or atom in vacuo is removed. A field of Oh symmetry, causes the d orbitals to split into the two sub-levels shown in Fig.4 p.92 However, environments of other symmetries are often found in complexes such as Td (Tetrahedral); D_{4h} (tetragonal); ~~D2d~~ D_{2d} (dodecahedral); ~~D3h~~ D_{3h} (trigonal bipyramidal); C_{4v} (square pyramidal) see Fig.5 p.94.

The gain in energy achieved by the preferential filling of the lower lying d levels is called the crystal field stabilisation energy, CFSE, and the relation of CFSE with Δ will be discussed.

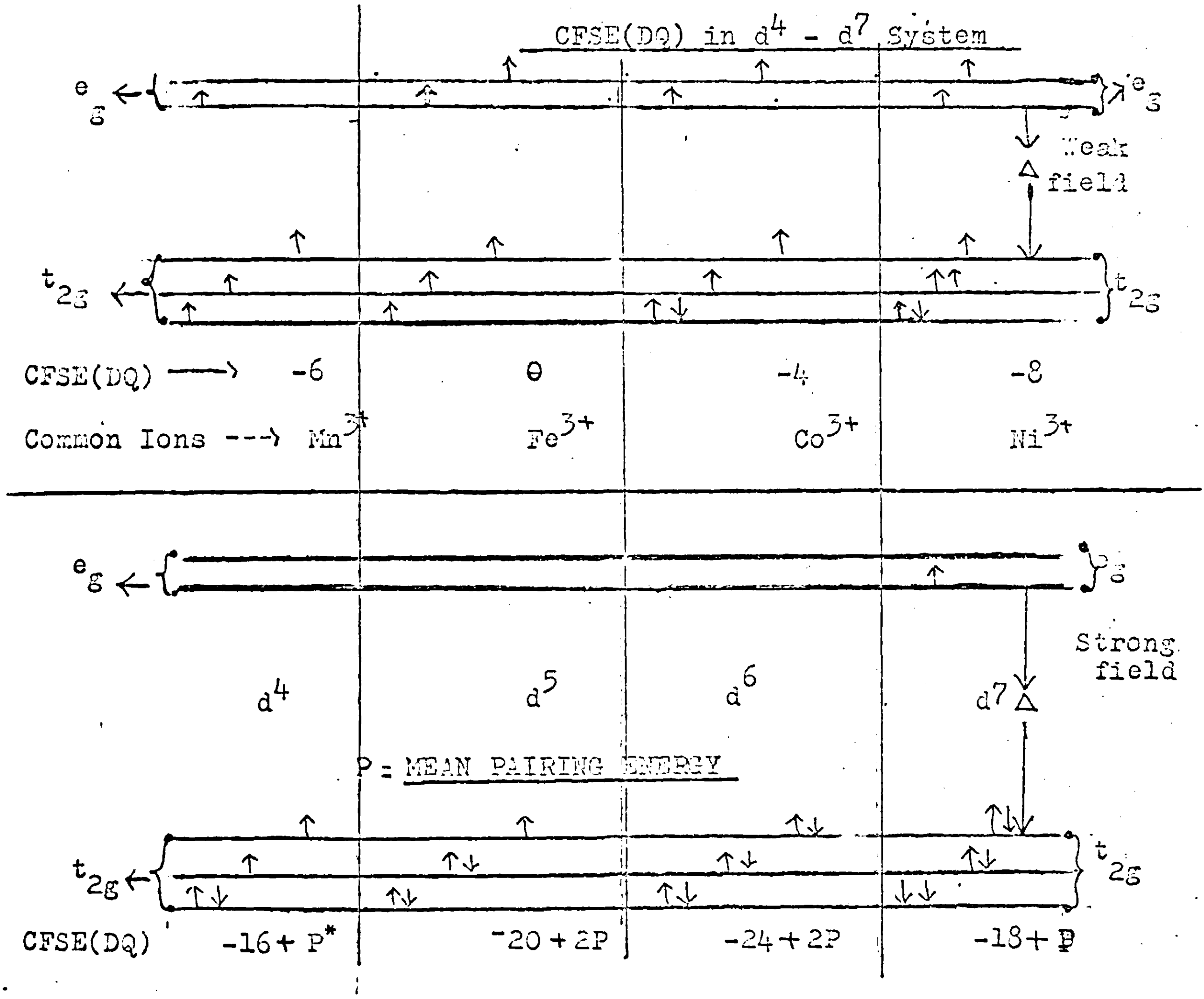
Two important and opposite factors determine the population distribution of d electrons under the influence of purely an electroststaic crystal field. One is the tendency for electrons to occupy as far as possible, the lower energy orbitals. The other is the tendency for electrons to enter different orbitals with their spin parallel in accordance with Hund's first rule. For 1, 2, 3, 8, 9, or 10 d electrons there are no uncertainties as to where the electrons will go, regardless of the magnitude of Δ_o or the total interelectronic repulsion

FIG. 5



RELATIVE ONE ELECTRON d- ORBITAL SPLITTING FOR CRYSTAL FIELDS OF SEVERAL SYMMETRIES energy. But for d^{4-7} system we have two extreme possibilities for each system depending upon the relative magnitudes of the splitting energy Δ_o, and the mean pairing energy of the electrons P. The energy required to pair two electrons is of the order of 20 kk (20,000 cm^{-1}), the higher the fields can cause a breakdown of Hund's rules so that the lower t_{2g} orbitals are first completely filled before electrons enter in the upper e_g orbitals.

FIG. 6



In order for spin-pairing to occur that is low-spin state to prevail the value of (Δ_o - P) should be greater than zero. Values of P may be calculated from the interelectron repulsion parameters determined for gaseous ions. In each case P > Δ_o spin-free or high spin complexes are found and where Δ_o > P spin-paired or low spin complexes are found.

On the basis of experimental data Δ_o is about 40% to 80% larger for complexes of tervalent than for bivalent cations. The common ligands may be arranged in a regular order known as the spectro chemical series such as that Δ_o for their complexes with most metal ions, in their common lower oxidation states, increases along the sequence, e.g. $I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < -NCS^- <$ py $NH_3 <$ en $<$ dipy $<$ OPhen $<$ OPhen $< -NO_2^- < -CN^-$.

Jahn-Teller effect in octahedral complexes

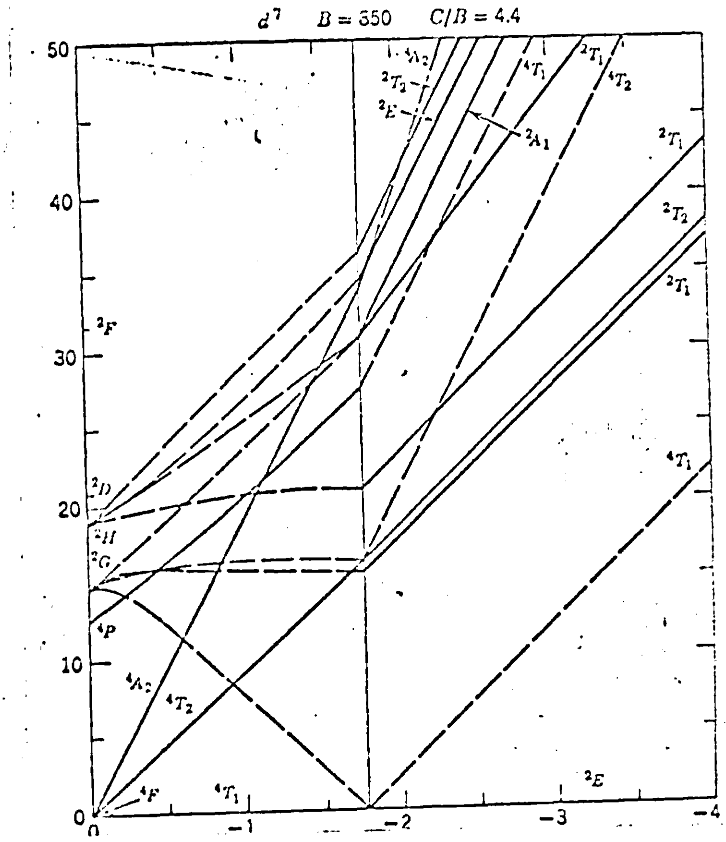
In 1937 Jahn and Teller[63] suggested that any non linear molecular system in a degenerate electronic state will be unstable and will undergo some kind of distortion which will lower the symmetry and split the degenerate state. In practice distortions have been observed in certain octahedral complexes of ions and whenever there is an odd number of electrons in the eg orbitals we should expect large Jahn-Teller distortions for the following common system.

$d^4 - t_{2g}^3e_g^1$	high spin	Cr(II), Mn(III)
$d^7 - t_{2g}^6e_g^1$	low spin	Co(II), Ni(III)
$d^9 - t_{2g}^6e_g^3$	Cu^{2+}, Ag^{2+}	Cu(II), Ag(II)

The distortion may result in a compressed or elongated octahedron. Structural evidence shows that almost invariably there are four short and two long bonds.

FIGURE:- 7

ENERGY LEVELS OF THE d^7 CONFIGURATION AS A FUNCTION OF Dq FOR OCTAHEDRAL FIELDS.



THE CROSSOVER POINT FOR THE HIGH SPIN, $^4T_{1g}(F)$ ($t_{2g}^5e_g^2$), AND LOW SPIN , $^2E_g(H)$ ($t_{2g}^6e_g$), GROUNDS STATES OCCURS AT APPROXIMATELY 10 Dq + 4B + 4C = 0. FOR HIGH SPIN THE SPIN- ALLOWED TRANSITIONS TO $^4T_{2g}(F)$, $^4T_{1g}$ (P), AND $^4A_{2g}(F)$ WILL BE OBSERVED. THREE HIGH ENERGY SPIN ALLOWED TRANSITIONS FROM ^2E_g TO $^2T_{1g}$, $^2T_{2g}$ AND $^2T_{1g}$ WILLBE OBSERVED FOR LOW SPIN. ONE SPIN FORBIDDEN TRANSITION $^4T_{1g}$ MAY BE OBSERVED.

THIS DIAGRAM IS REPRODUCED FROM REFERENCE 123

In the octahedral complex the ground state of a d^7 ion can be either $^4T_1$ $(t2g)^5(eg)^2$ or ^2Eg $(t2g)^6(eg)^1$, depending upon the strength of the crystal field. The gaseous Ni^{+++} ion has the ground state ^4F with the excited state ^4P . Under the influence of a cubic field these levels will split up into $^4T_1g(F)$, $^4T_2g(F)$, $^4A_2g(F)$ and $^4T_1g(P)$. $^4T_2g(F)$, $^4A_2g(F)$ and $^4T_1g(P)$ arranged in order of increasing energy. This level scheme was first given by Abraham and Pryce.[49] Located just a bit higher than ^4P is a ^2G state which eventually at the limit of a strong field becomes the ground state. As seen from the level diagram given by Tanabe and Sugano,[50] the 2_{Eg} crosses all the quartet levels on its way down (see Fig. 7). The features conntected with the crossing are however more complicated because of the effects of spin-orbit coupling and many authors[51] have neglected this effect in their calculations. The crystal field theory predicts distortions from octahedral symmetry for the d^7 low spin configuration (see page 95). Hence this ground state could not be degenerate and leads to future splitting of t_{2g} and eg levels. Regular octahedral configuration is not expected, but rather one in which the octahedron is elongated or compressed along one of its four fold axis to give tetragonally distortion systems.[63] In aqueous d^4 complexes, Holah[55,56] attributed the broad highly asymmetric band, in the visible region to a tetragonal distortion of the octahedron because of the Jahn-Teller[63] effect. This has been also confirmed by crystallographic studies[58] in chromium(II) compounds.

The energy level diagram predicted by Holah[55,56] and Larkworthy[57] for this system shows three visible and near infrared absorption bands are expected corresponding transitions.

$$B_1g \longrightarrow B_2g$$

$$B_1g \longrightarrow Eg$$

$$B_1g \longrightarrow A_1g$$

The analysis of the spectrum of the hexafluoro nickelate(III) ion[21] NiF_6^{3-} indicates the presence of at least four ligand transitions of comparable intensities and thus rules out the possibility of a high spin ground state for which two spin allowed ligand field bands are permitted. The Ni(III) ion has d^7 configuration and the magnetic data carried by Brandt et. al.[61,62] suggest $t_2g^6eg^1$ low spin ground state, although the very large temperature dependence of the magnetic moment is surprising for a non-magnetic Eg level. But their measurements based on four parameters indicate ^2E_g ground state, in agreement with observations on the behaviour of Ni^{3+} Al_2O_3 hosts.[62] For an Eg ground state though there is no orbital contribution to the magnetic moment and the moment should therefore normally be essentially temperature independent in contrast to the observed behaviour. Even at 90°K the magnetic moment is significantly above the spin only value, and thermal equilibrium between low and high spin configurations has therefore been considered, so that the value of $Dq/_B$ lies only slightly beyond $^4T_1$ - ^{2}Eg cross over point. Allen[21] et. al. fixed the $^C/B$ ratio for Ni^{3+} at 4.9, which yields a value of 2.26 for $Dq/_B$ at the cross over point. Their results indicate that it is not possible to obtain a satisfactory fit of the ligand field bands using Tanabe Sugano[50] matrices for d^7 O_h systems. The bands assigned for the fluoride complexes (~6~7 kk, ~12~13 kk, ~15~16 kk and -19~20 kk) are all of moderate intensity and at 6 7 kk the band is not possible to assign to the spin forbidden ^2E - ^4T_1g excitation. The inclusion of spin-orbit coupling also fails to improve the situation.

The complete strong field matrices for d^3 (and hence d^7) system in O_h symmetry have been evaluated by Liehr[51] and others.[52] The results of Barraclough[65] show that the thermal high spin - low spin equilibrium it is not strictly necessary for the temperature dependent magnetic moment which should only be observed when $Dq/_B$ lies very close to the cross over point on the low spin side. For ^{2}Eg ground state there is a single electron in the doubly degenerate level which would give substantial Jahn-Teller distortion.[63] The inclusion of spin orbit coupling does not affect this conclusion as ^{2}Eg ground state is not a Kramer's doublet and hence can therefore be split by Jahn-Teller distortion.

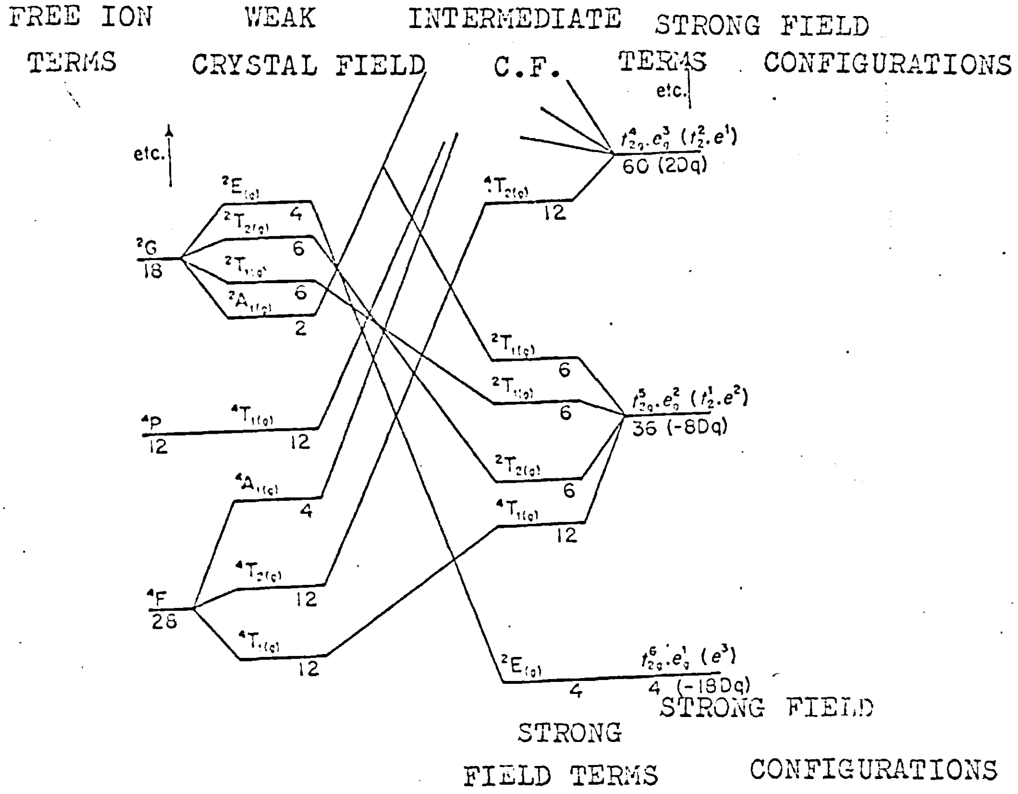
The spectra of all the nickel(III) complexes have been interpreted by assuming tetragonal distortion. This has been found to increase as we increase the bulk of the alkyl groups, e.g. NN'dieten > NN dimethyl ethylenediamine > N ethyl ethylenediamine etc. The fitting of the observed bands are made by using strong field repulsion matrices neglecting spin orbit effects for d^7 systems in $D4_h$ symmetry without calculated interelectron repulsion parameters. The spectra require both the assumption of a low spin ground state with $^{Dq}/B$ slightly above the ^{2}Eg - $^{4}T_1$g cross over and also some measures of tetragonal distortion to account for the well marked low energy band at 8 - 12 kk.

The matrices of electrostatic repulson for d^3 and hence d^7 were obtained by Otsuka,[65] the one electron contributions to the diagonal matrix elements are incorrectly given in his papers. The correct method for counting the Ds and the Dt splittings is reported by Ballhansen, who encountered +ve values of Dt represent elongation along four fold axis and negative values correspond to compression.

Matrices for several d^4 system in D4 symmetry have also been given by Berzulenu and Ivanov,[65,66] but this is also not satisfactory. A most valid approach has been given by Perumareddi[53,54], in which the tetragonal distortion in the d^3 systems is treated as an axial perturbation to the strong field cubic scheme. The resulting splitting diagram (Fig. 9) shows that the tetragonal distortion as represented by $Dt_{/B}$ has by far the greatest influence on the ground state (see Fig. 9 page 102).

FIG. 8

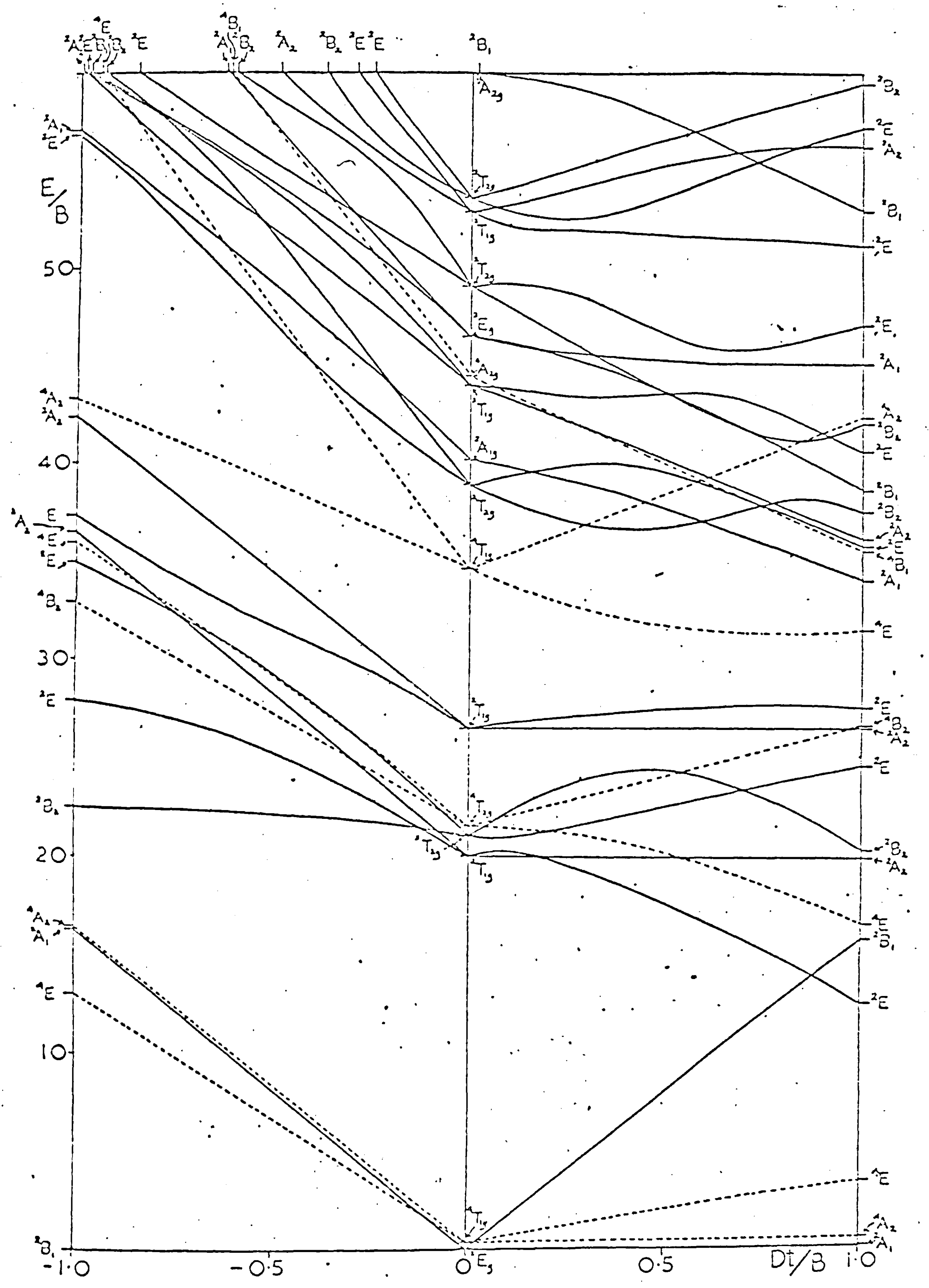
CORRELATION DIAGRAM FOR FREE- ION TERMS---- STRONG-FIELD CONFIGURATIONS FOR d^3 IN Td, AND d^7 IN Oh



THIS DIAGRAM IS NOT TO SCALE EXCEPT ON THE FAR RIGHT HAND SIDE. THE g SUBSCRIPT IS DELETED FOR Td SYMMETRY. THE NUMBERS UNDER A TERM ARE THE TOTAL DEGENERACY.

THIS DIAGRAM IS REPRODUCED FROM REFERENCE 67

FIGURE: 9



ENERGY LEVEL DIAGRAM FOR d^7 CONFIGURATION IN TETRAGONAL(D4) FIELD

ξ = 0, C /B = 4.90, Dq/B = 2.30, AND Ds/Dt = 3.0

THIS DIAGRAM IS REPRODUCED FROM REFERENCE 21

The energy level diagram for d^7 ions in the strong field case is given in Figs. 7 and 9.

The correlation diagram of Figgis[67] for d^3 in Td and d^7 in O_h is also shown in Fig. 8. Here there is a change in the ground term as the crystal field strength increases $^4T_1(g) \longrightarrow {}^2E(g)$. Thus a sufficiently strong cubic crystal field reduces the three unpaired electrons of tetrahedral d^3 or octahedral d^7 to one.

Because of strong field and Jahn-Teller effect a regular octahedral would be changed into tetragonally distorted octahedral.

TABLE 12

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type Nien$_2$X$_3$

Nien$_2$Cl$_3$	Nien$_2$Br$_3$, $\frac{1}{2}$ H$_2$O	Nien$_2$I$_3$	Nien$_2$Br$_2$ Cl $\frac{1}{2}$ H$_2$O	Nien$_2$Cl$_2$I	Nien$_2$Cl$_2$ (NO$_3$)	Nien$_2$Cl$_2$ (ClO$_4$)	Nien$_2$Cl$_2$ (HSO$_4$)	Nien$_2$Cl (NO$_3$)$_2$	Nien$_2$Cl (HSO$_4$)$_2$	Nien$_2$Cl (ClO$_4$)$_2$
		8,300					8,400	8,000	7,800	8,000
	11,000	11,500	10,900		11,000	10,990	11,000		12,000	12,000
13,600	13,500	13,900	13,800	13,500	14,000	14,000	14,000	13,900	13,900	
17,000		16,800	17,000	16,000		16,000	16,000	16,000		15,500
	18,600	18,600	18,800	19,500			19,500			20,000
26,200	26,000	26,200	26,000	26,300	26,000	26,000	26,400	26,000	26,000	26,000) 26,700)
37,000	31,600	31,500			33,000	33,200	33,000	33,200	33,500	31,800
46,800	38,000	38,200	37,000	38,000	38,000	38,000	38,000	38,200	38,000	38,200
	45,000	45,800	43,500	44,000	46,000	45,000	44,000	44,500	45,000	44,500

TABLE 13(a)

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type $NiPn_2X_3$

$NiPn_2Cl_3$ $2H_2O$	$NiPn_2Cl_3$	$NiPn_2Br_3$ $2H_2O$	$NiPn_1Br_3$	$NiPn_2Cl_2Br$	$NiPn_2Cl_2$ $12H_2O$	$NiPn_2I_3$	$NiPn_2$ Br_2	$NiPn_2Cl$ $(ClO_4)_2$	$NiPn_2Cl_2$ (ClO_4)
8,800	8,900	9,000	9,000	9,000	8,900	8,300	8,600	8,000	8,800
						11,500	11,800	11,700	
14,000	14,000	14,000	14,000	14,000	14,400		14,000	14,400	14,600
16,500	16,000	16,900	16,100	16,100		16,000	16,100	16,000	16,600
		20,000	18,600) 20,200)	20,000	19,400	19,400	19000		
26,800	26,000	26,800	26,800	26,800	26,800	26,800		26,800	27,000
38,000	31,660	38,000	38,000	38,000	31,000	32,000	38,000	38,400	38,400
44,500	37,800	44,000	44,000	44,300	38,000	38,000	45,000	45,000	44,500
	44,000				44,800	45,000			

TABLE 13(b)

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type $NiPn_2X_3$ (continued)

$NiPn_2Cl_2(HSO_4)_2$	$NiPn_2Cl_2(HSO_4)$	$NiPn_2Cl(NO_3)_2$	$NiPn_2Cl_2(NO_3)$
8,000	8,000	8,000	9,000
11,500		12,000	
14,300	14,500	14,200	14,200
		16,800	16,100
19,900	19,400		19,000
26,000	26,000	27,000	26,800
40,800	40,600	40,200	38,000
45,200	45,500	47,000	46,000

TABLE 14

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type $Ni(AA)_3X_3$ where AA = (en) and (Pn)

$Nien_3Cl_3$, $3H_2O$	$Nien_3Cl_3$, $HCl,2H_2O$	$Nien_3Br_3$, $2H_2O$	$Nien_3Br_3$, $HBr,2H_2O$	$Nien_3I_3$	$Nien_3I_3$, $HI2H_2O$	$NiPn_3Cl_3$	$NiPn_3Cl_3$, $2H_2O$	$NiPn_3Br_3$	$NiPn_3Br_3$, $2H_2O$	$NiPn_3I_3$
								9,000	9,000	6,800
13,000	13,100	13,000	13,000	11,800	11,600	11,800	11,700	11,700	12,000	11,000
				14,000	14,100		14,000		14,000	14,000
16,400	16,800	15,700	16,100	16,000	16,100	16,000	16,000	16,000		
				19,800	19,400	19,400		18,600	19,600	19,400
26,000	26,800	26,800	26,800			26,000	26,000	26,200	26,200	26,000
				31,000	31,800	32,200	32,000			33,500
36,500	37,200	38,500	37,000	38,300	39,200	38,000	37,800	38,300	38,000	38,600
46,000	45,800	46,200	45,900	46,200	46,000	44,200	44,000	45,000	45,200	45,600

TABLE 15(a)

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type $Ni(AA)_2X_3$ where AA = (N-eten), (N,N'-2eten), (N,N-2eten)

$Ni(N\text{-}eten)_2Cl_3$	$Ni(N\text{-}eten)_2Br_3$	$Ni(N\text{-}eten)_2I_3$	$Ni(N,N\text{-}2eten)_2Cl_3,2H_2O$	$Ni(N,N\text{-}2eten)_2Br_3,2H_2O$	$Ni(N,N\text{-}2eten,Br_3\frac{1}{2}H_2O$	$Ni(N,N'\text{-}2eten)Br_3HBr, 2H_2O$
	8,400	8,000	8,000	7,800	7,600	7,600
		11,700		11,800	11,800	11,800
14,000	14,600	14,800	14,700	14,800		14,800
		16,800	16,800		16,800	16,100
18,600	18,600	19,400		19,500		
26,000	26,500	26,500	26,100	26,500	26,500	26,000) 26,500)
32,000			31,500			
	37,300	37,800	37,800	38,000	37,800	37,600
44,500	45,000		43,800	44,800	45,000	44,500
46,200	47,000	46,800				

TABLE 15(b)

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type $Ni(AA)_2X_3$ where AA = (N-eten), N,N'-2eten), (N,N-2eten) (continued)

$Ni(N,N\text{-}2eten)_2I_3HI, 2H_2O$	$Ni(N,N\text{-}2eten)_2I_3$	$Ni(N,N'\text{-}2eten)_2Cl_3, 2H_2O$	$Ni(N,N'\text{-}2eten)_2Br_3, 2H_2O$	$NiN,N'\text{-}2eten)_2I_3\ 2H_2O$
7,600	7,600	8,000	8,000	7,000
11,800	11,800		12,000	11,800
	14,800	14,800	14,800	14,800
16,800	16,500	16,000	16,100	17,000
		19,500		
26.100	26,000	26,500	26,500	
38,200	37,900	38,200	37,800	38,000
45,200	45,200	44,300	45,000	45,000

TABLE 16(a)

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type Ni(AA)$_2$X$_3$ where AA = (N-meen), (N,N'-2meen), (N,N-2meen)

Ni(N-meen)$_2$Cl$_3$, 2H$_2$O	Ni(N-meen)$_2$Br$_3$	Ni(N-meen)$_2$I$_3$	Ni(N,N-2meen)$_2$Cl$_3$ HCl,2H$_2$O	Ni(N,N-2meen)$_2$Cl$_3$ 2H$_2$O	Ni(N,N-2meen)$_2$Cl$_3$
	8,000	7,800	8,000	8,200	7,000
11,700	12,000	11,800			11,800
		14,800	14,800	14,800	14,800
16,000) 16,800)	16,800		16,800	16,800	
		18,600			18,600
26,000	26,200	26,500	26,500	26,500	26,200
33,000		33,200	33,800	33,600	
37,800	38,000	38,000	36,500	36,00	38,000
44,000	45,200	46,000	43,000	43,000	45,000

TABLE 16(b)

Reflectance Spectra (room temperature) - Band Positions in cm^{-1}

Compounds of the type $Ni(AA)_2X_3$ where AA = N=meen), (N,N'-2meen), (N,N-2meen) (continued)

$Ni((N,N\text{-}2meen)_2Br_3$ $2H_2O$	$Ni(N,N\text{-}2meen)_2I_3$	$Ni(N,N'\text{-}2meen)_2Cl_3$ $2H_2O$	$Ni(N,N'\text{-}2meen)_2Br_3$ $2H_2O$	$Ni(N,N'\text{-}2meen)_2I_3$ $2H_2O$
7,800	8,000	8,000	8,200	8,000
11,800	11,800	11,800	11,800	11,800
	14,800	14,800	14,800	14,800
16,800	16,800		16,100	16,800
19,400			19,800	19,800
26,800	26,800	26,500	26,00	26,800
		34,000		
38,000	38,800	36,800	38,800	38,800
44,800	46,000	43,200	46,000	46,000

Diffuse Reflectance Spectra (Room Temperature)

FIGURE:- 10

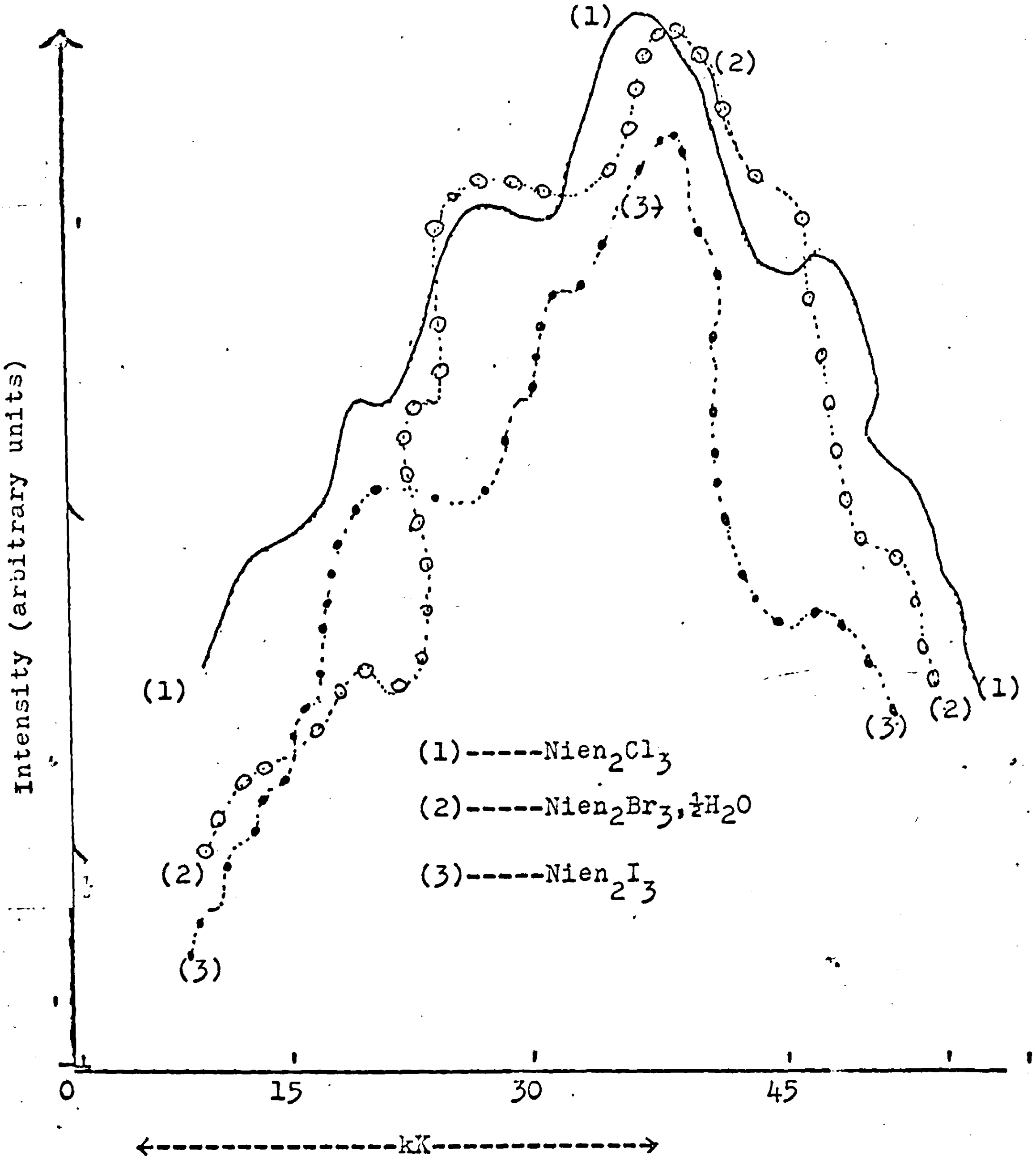


FIGURE:- 11 Visible Absorption Spectra of Solids (Room Temperature)

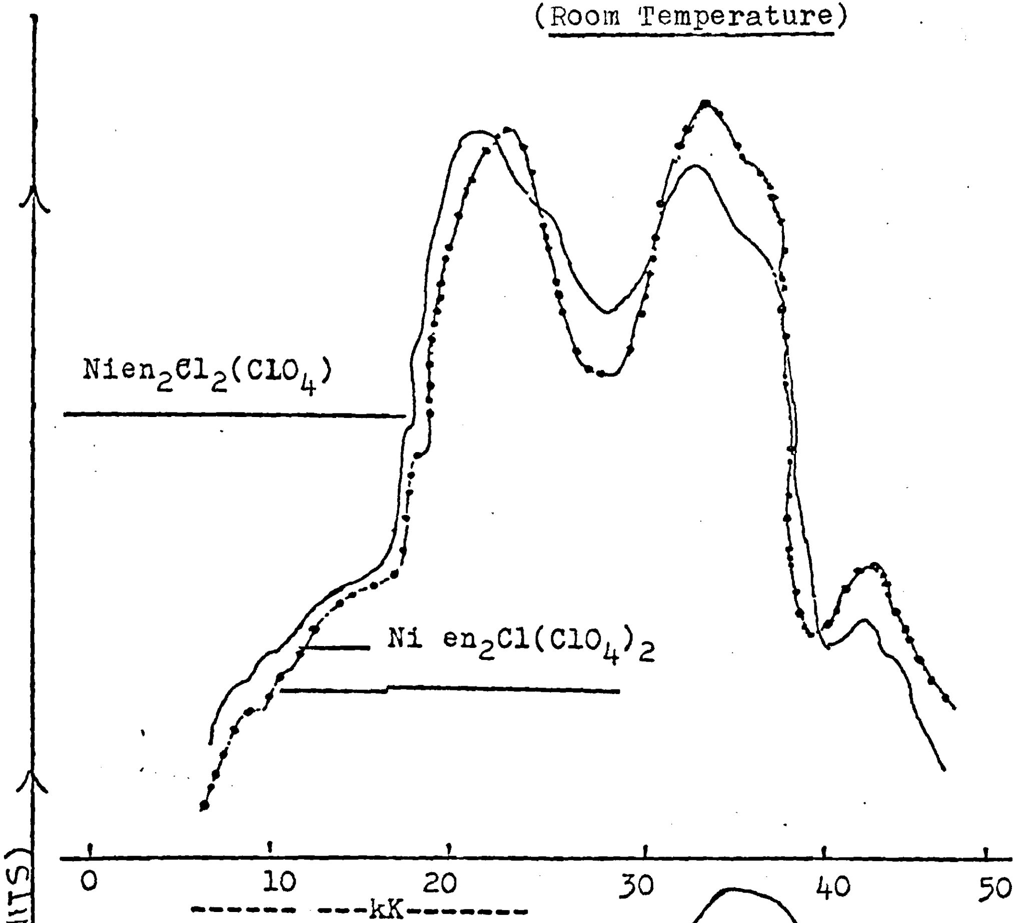
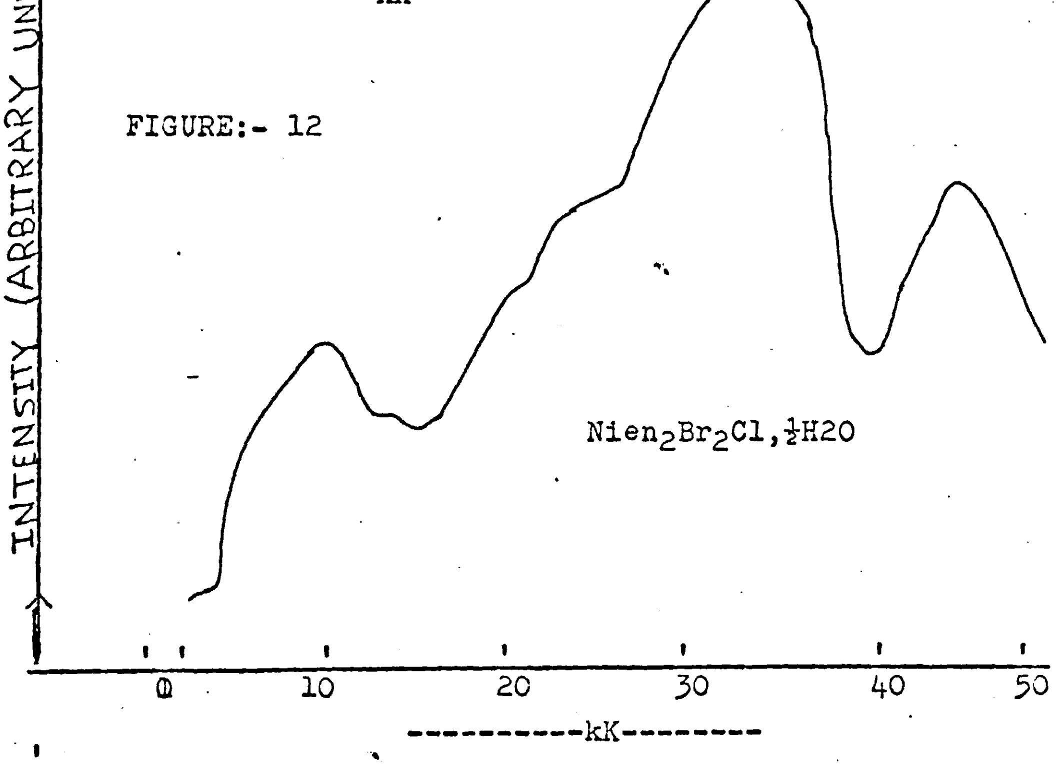


FIGURE:- 12



Visible Absorption Spectra of Solids (Room Temperature)

FIGURE-13

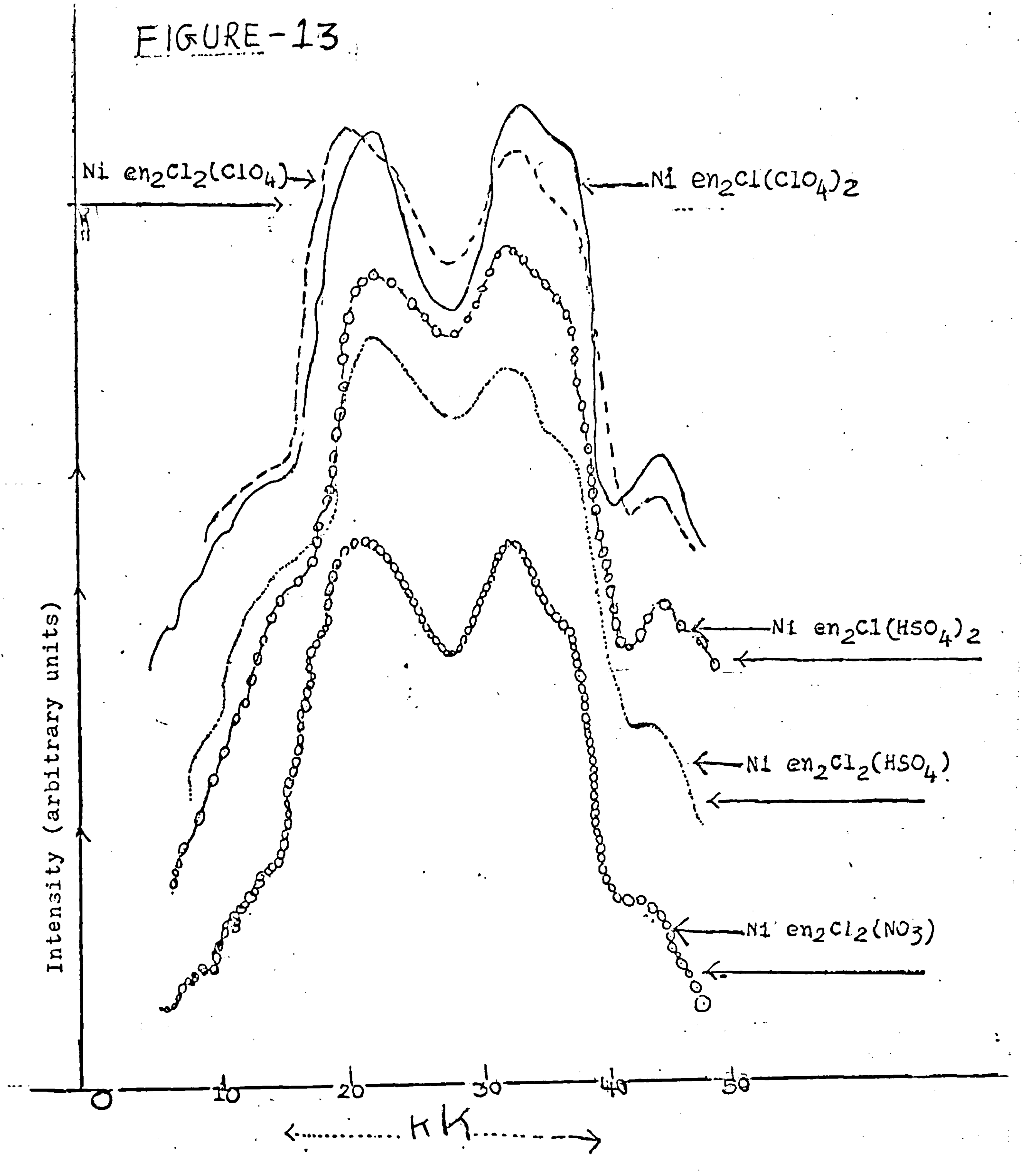


FIGURE:- 14

Visible Absorption Spectra of Solids (Room Temperature)

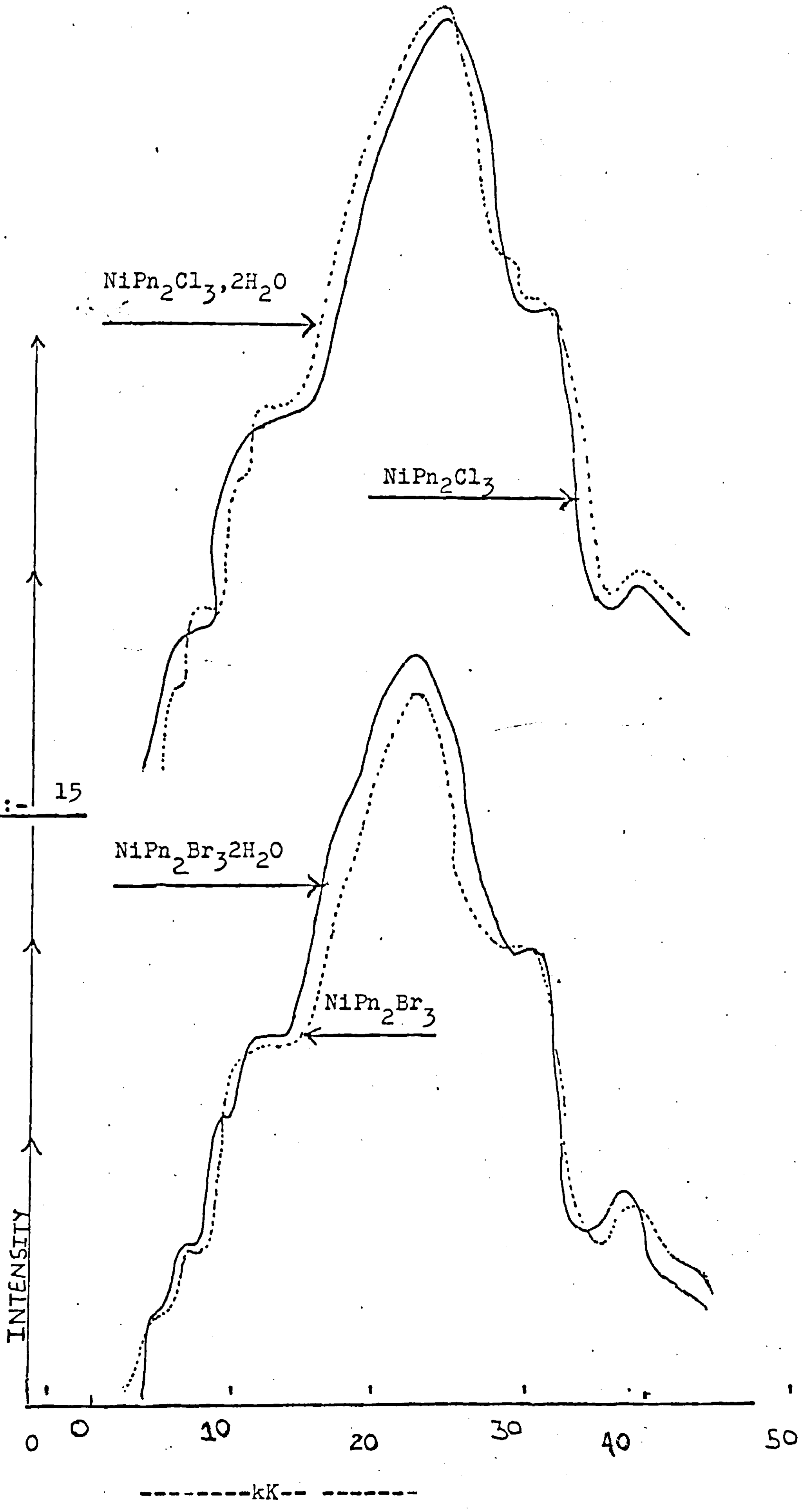


Figure:- 15

FIGURE:- 16

Visible Absorption Spectra of Solids (Room Temperature)

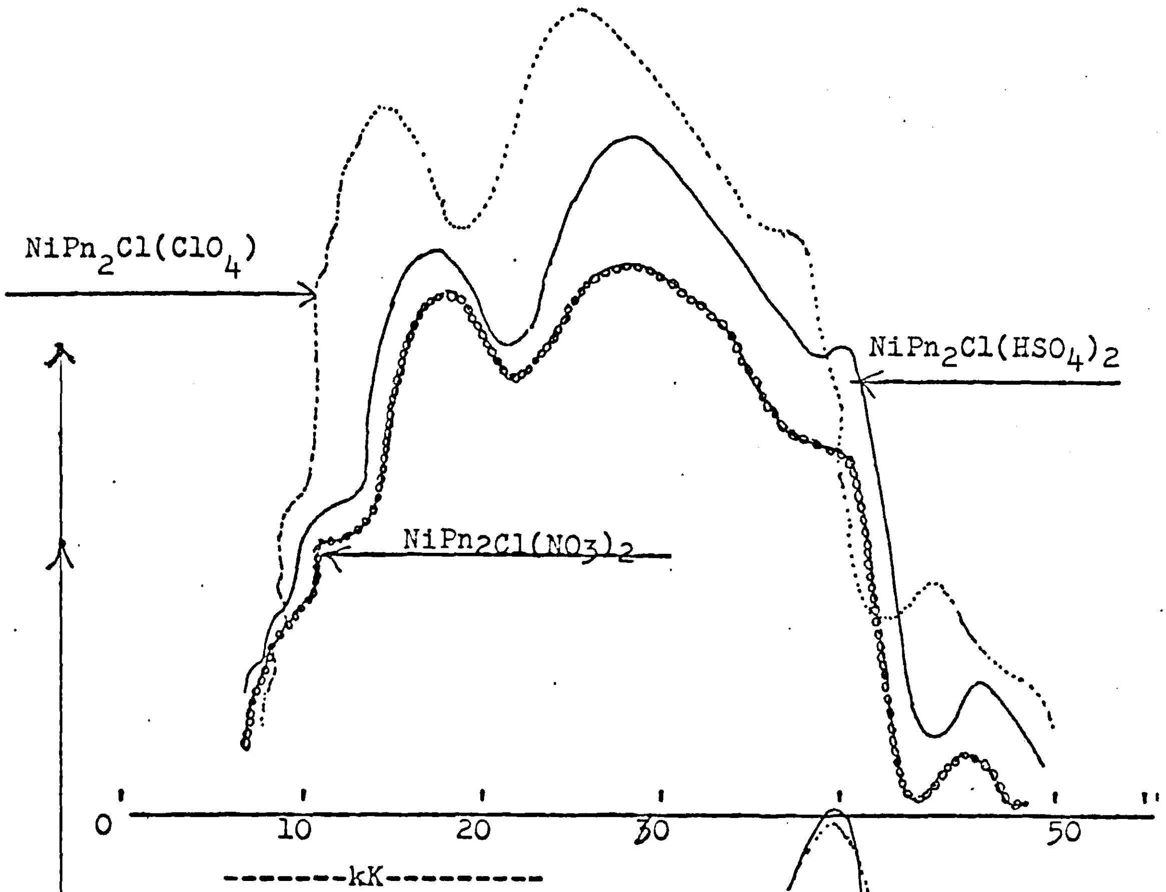


FIGURE:- 17

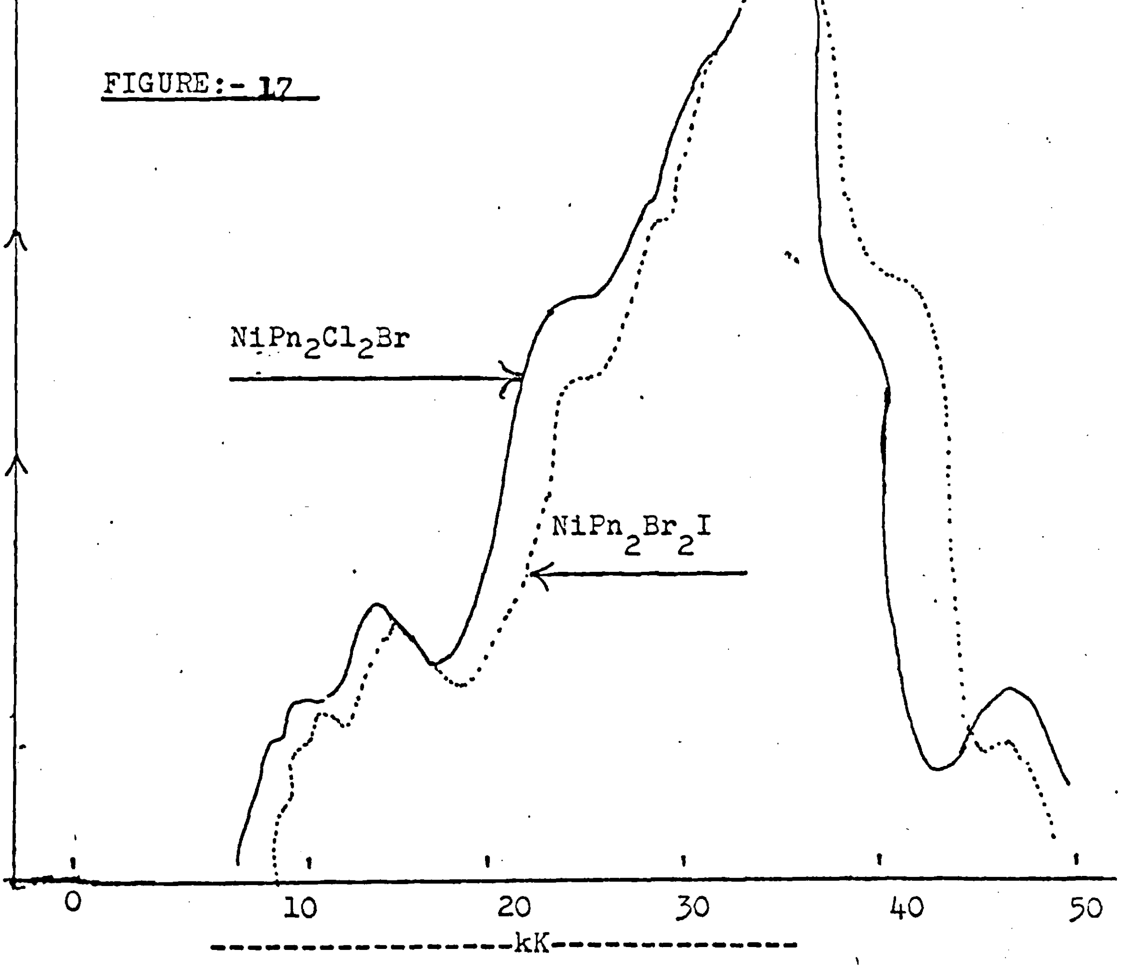
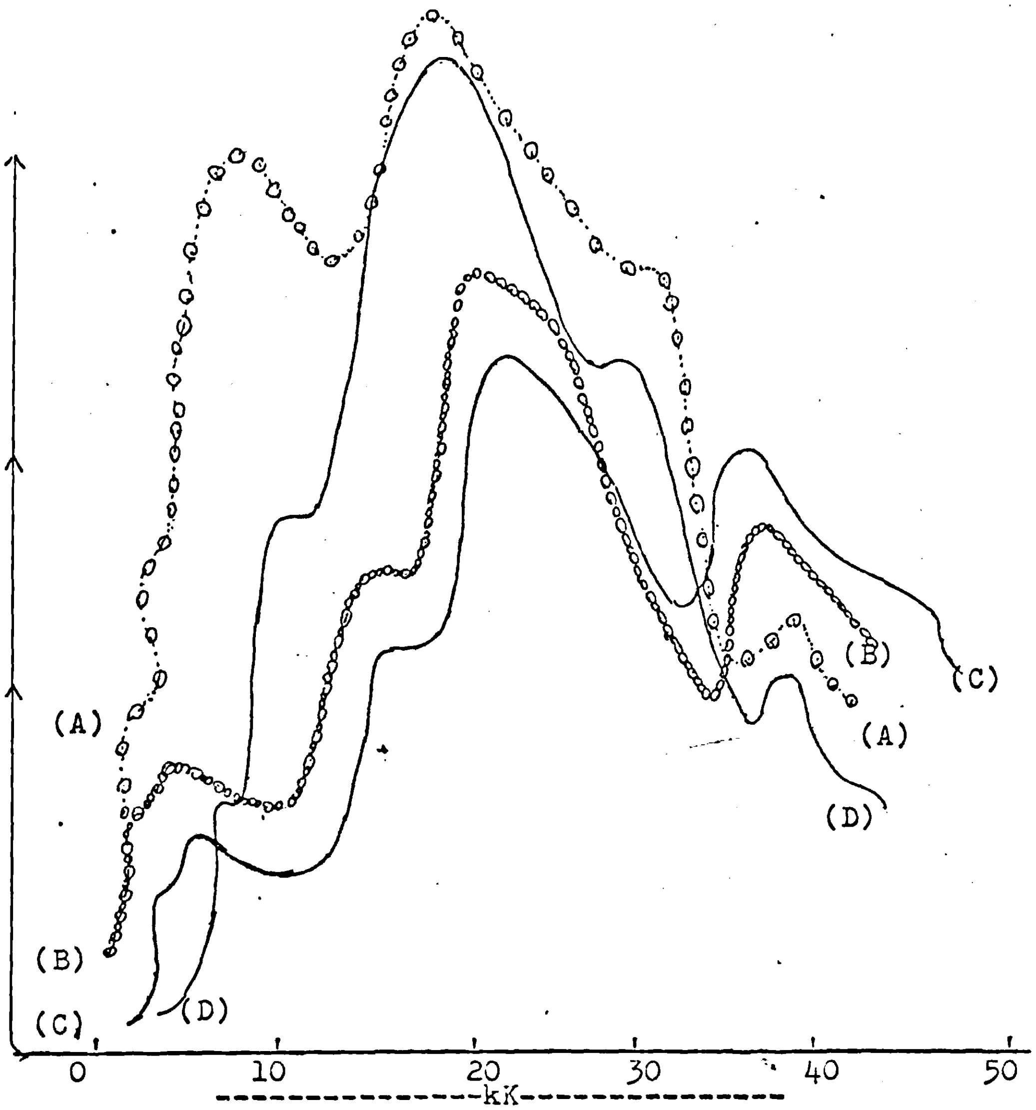


FIGURE:- 18

Visible Absorption Spectra of Solids (Room Temperature)



(A) -------- $NiPn_2Cl_2(ClO_4)$

(B)---------$NiPn_2Cl_2(NO_3)$

(C)-------- $NiPn_2Cl_2(HSO_4)$

(D)--------$NiPn_2Cl(ClO_4)_2$

FIGURE:19 Visible Absorption Spectra of Solids (Room Temperature)

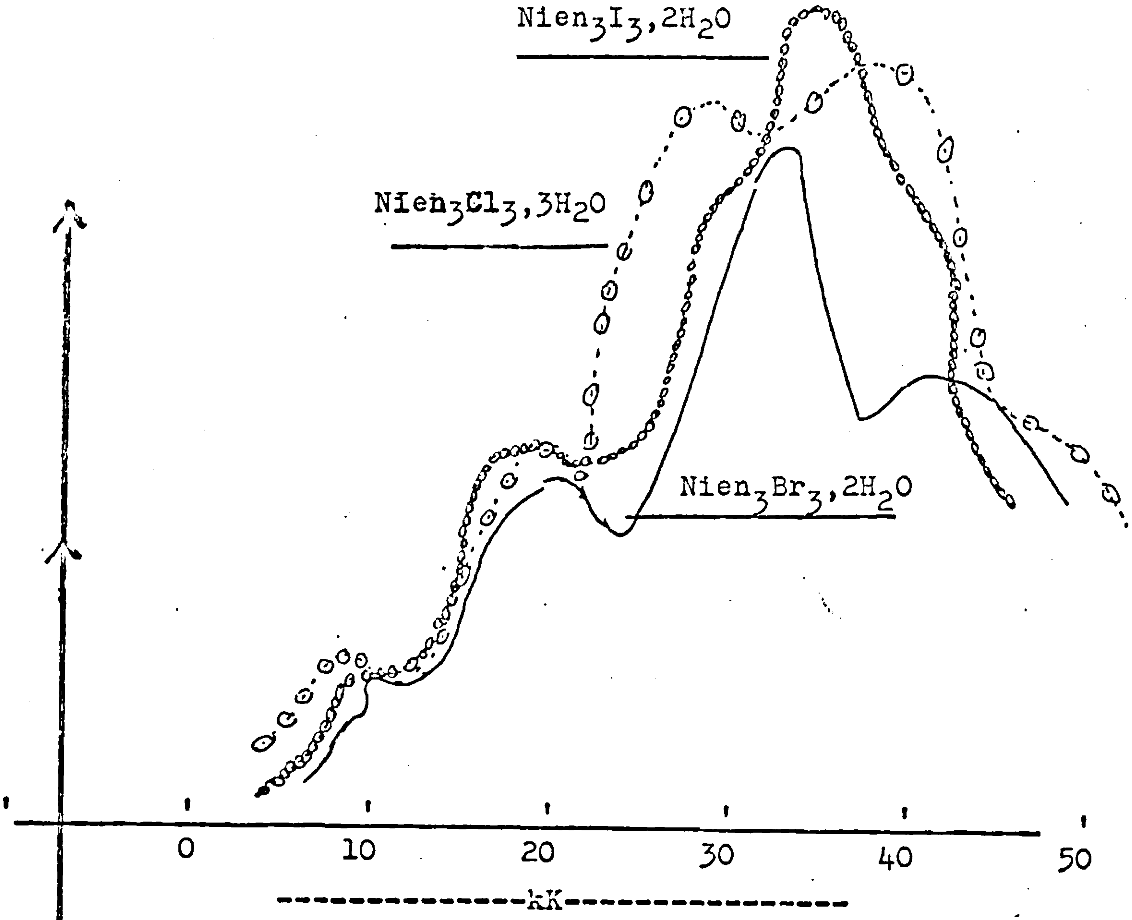
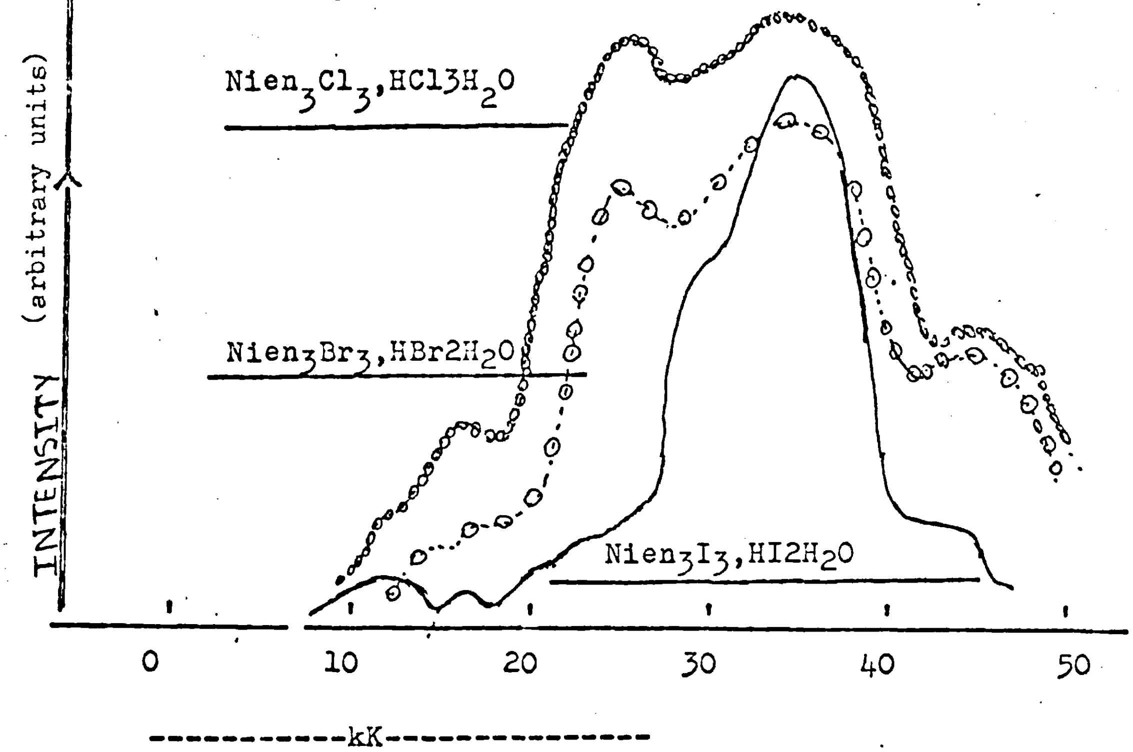


FIGURE:20



Visible Absorption Spectra of Solids (Room Temperature)

FIGURE:- 21

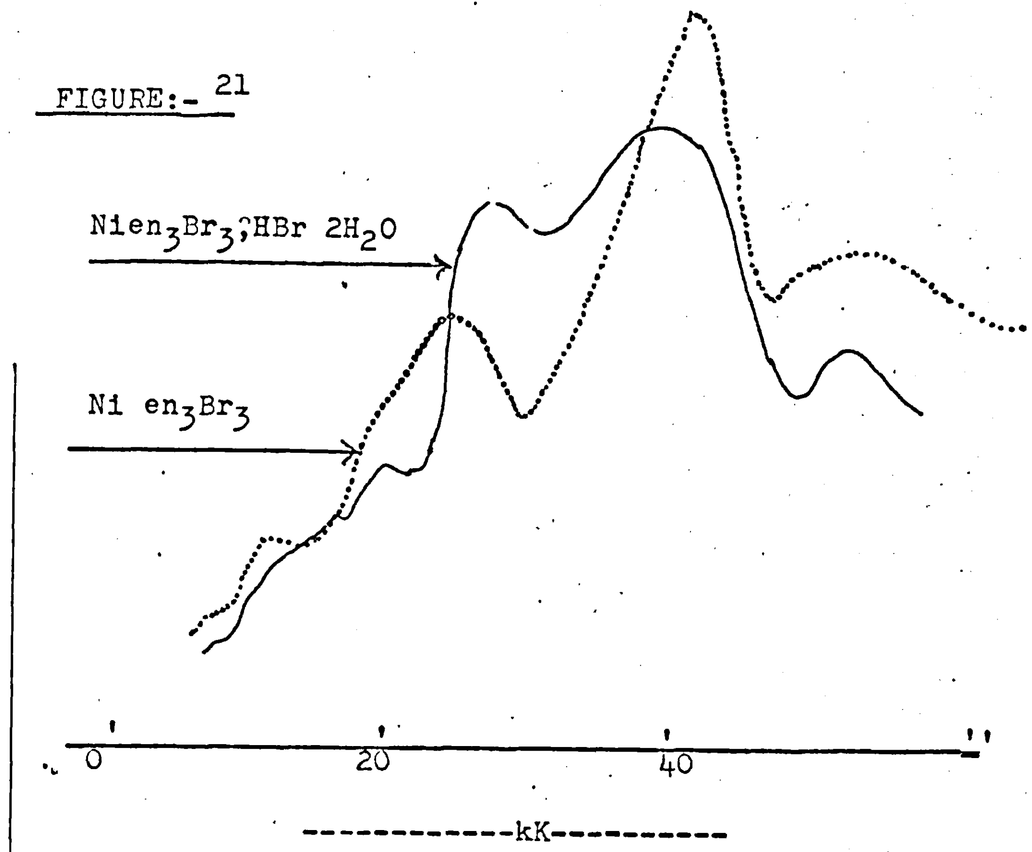
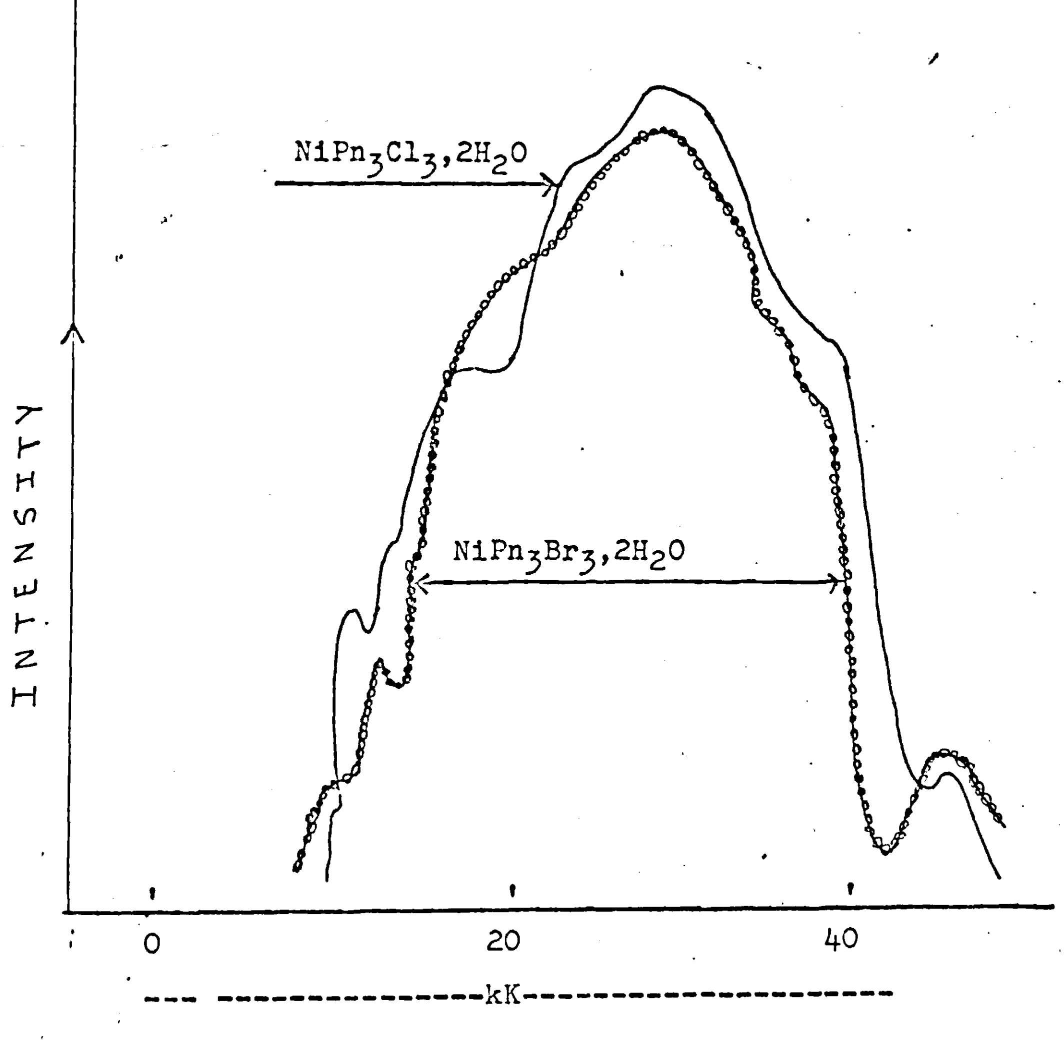
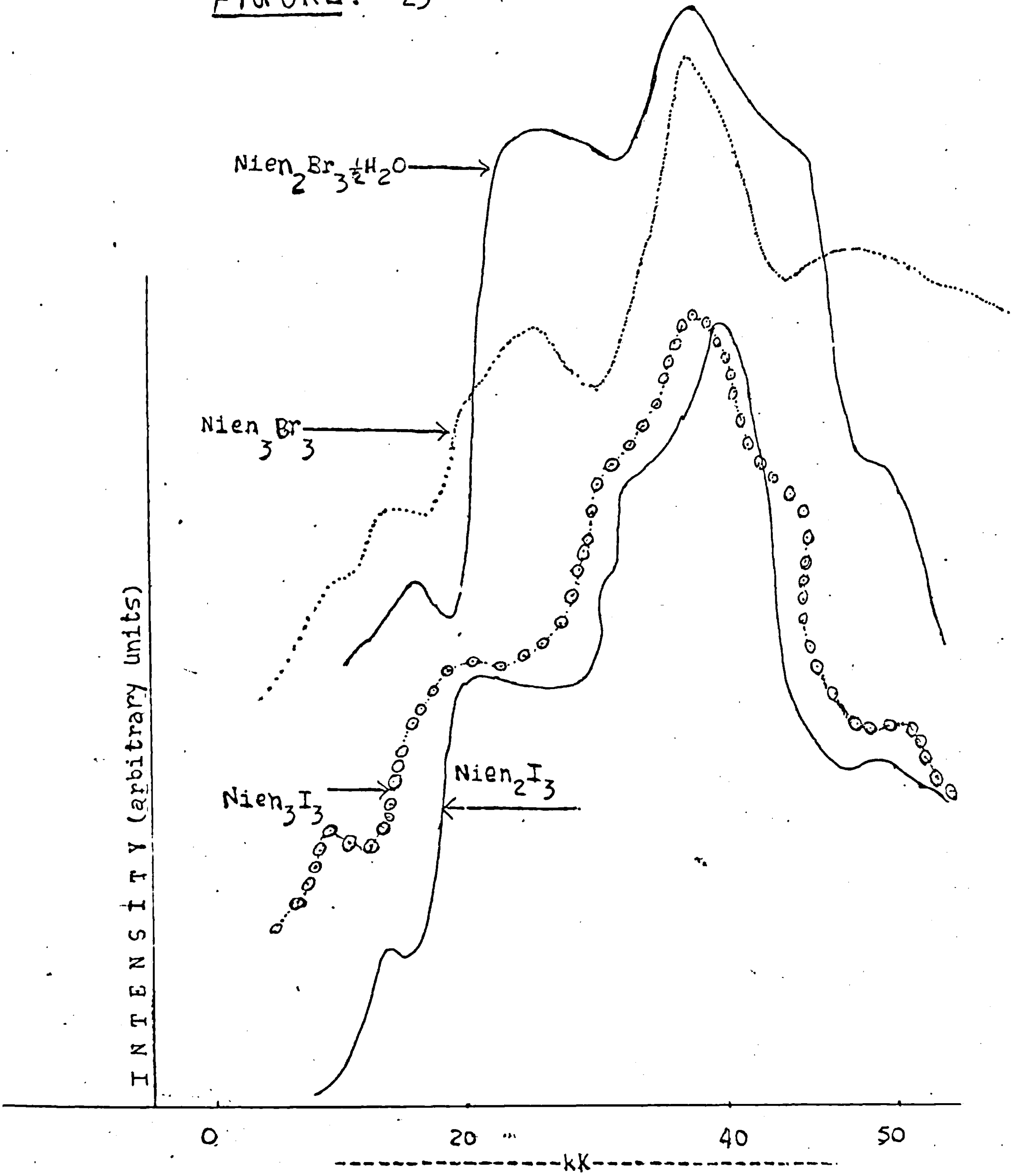


FIGURE:-22



Visible Absorption Spectra of Solids (Room Temperature)

FIGURE:- 23



Visible Absorption Spectra of Solids (Room Temperature)

FIGURE:- 24

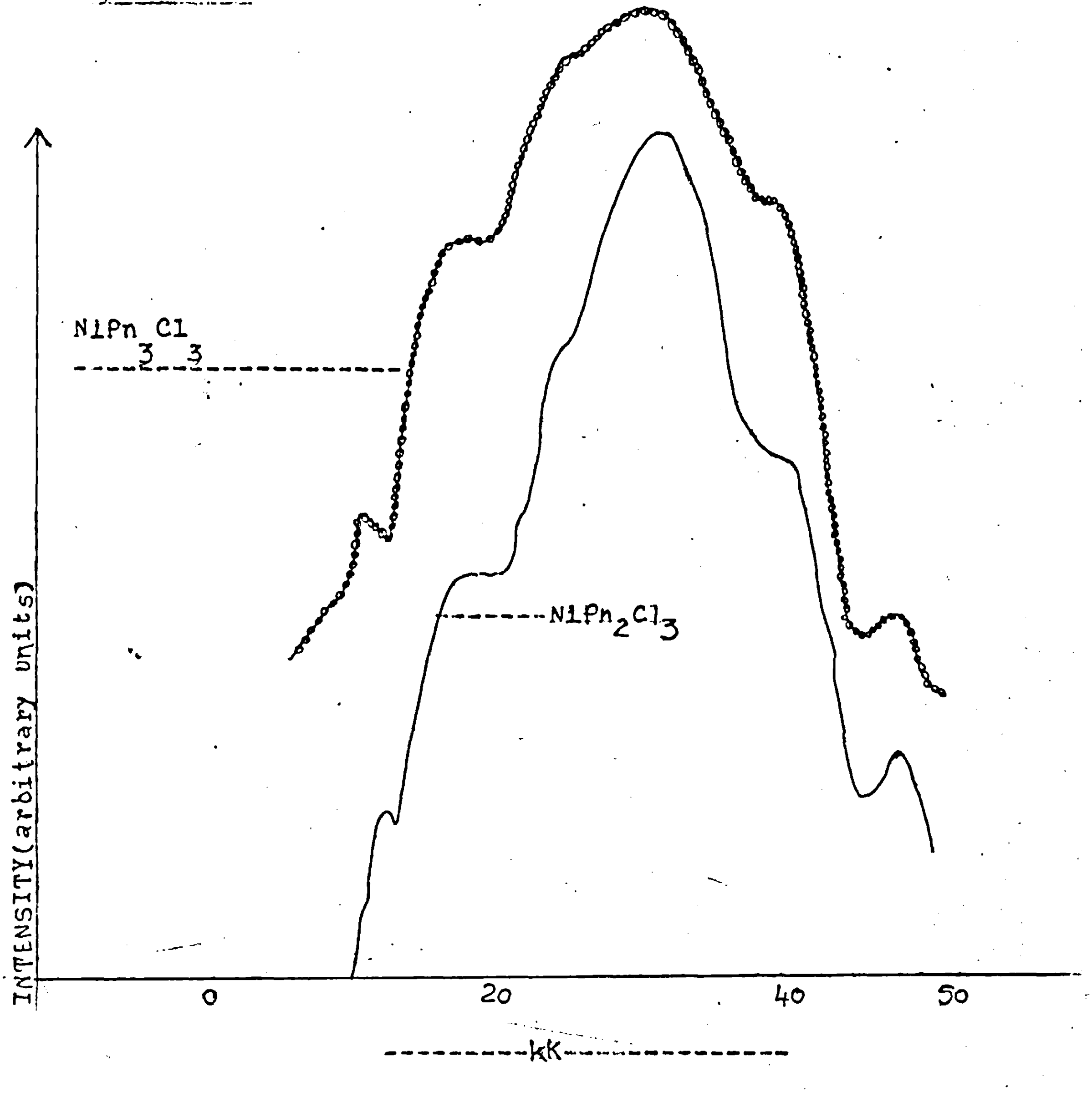


FIGURE 25

Visible Absorption Spectra of Solids (Room Temperature)

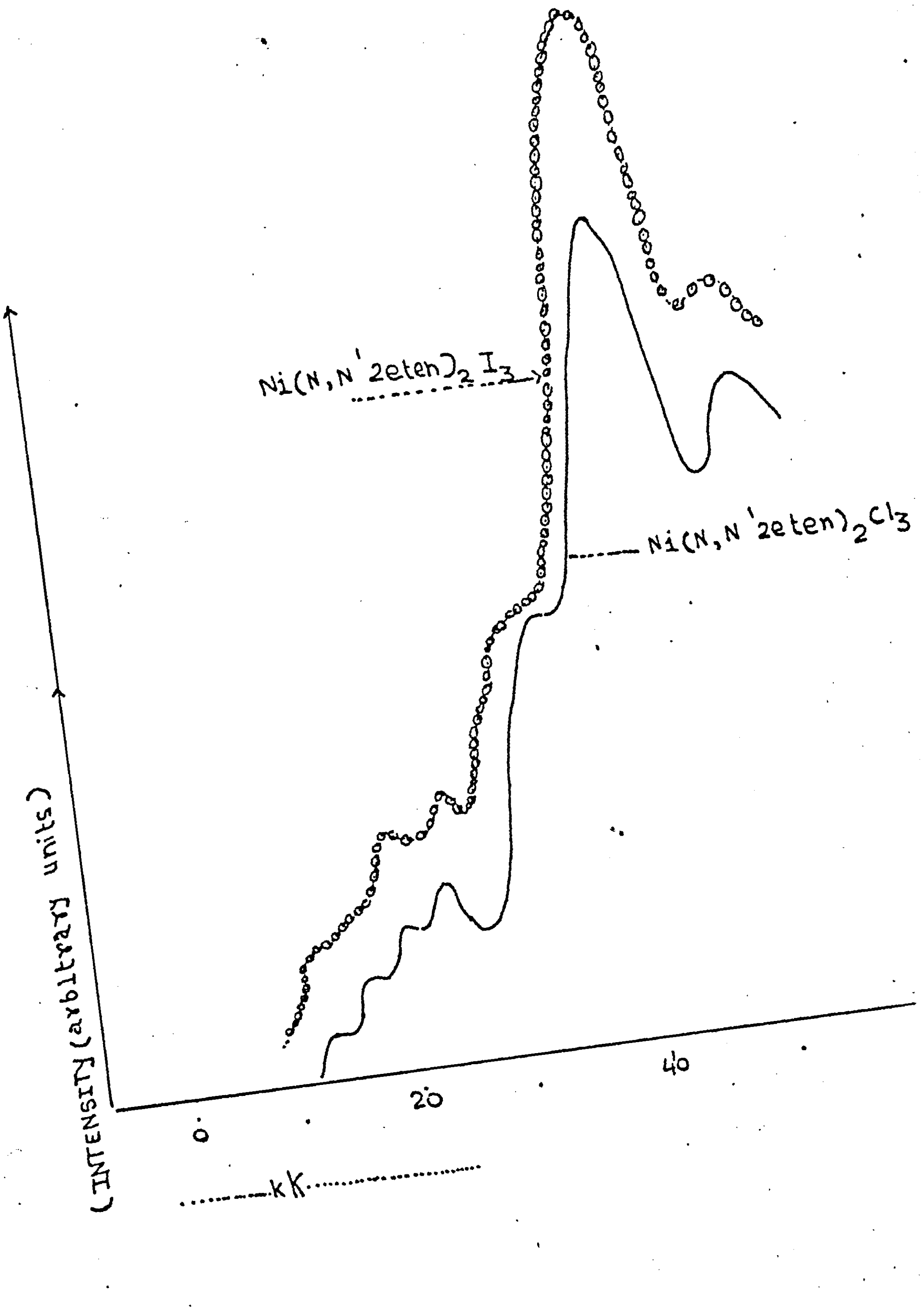
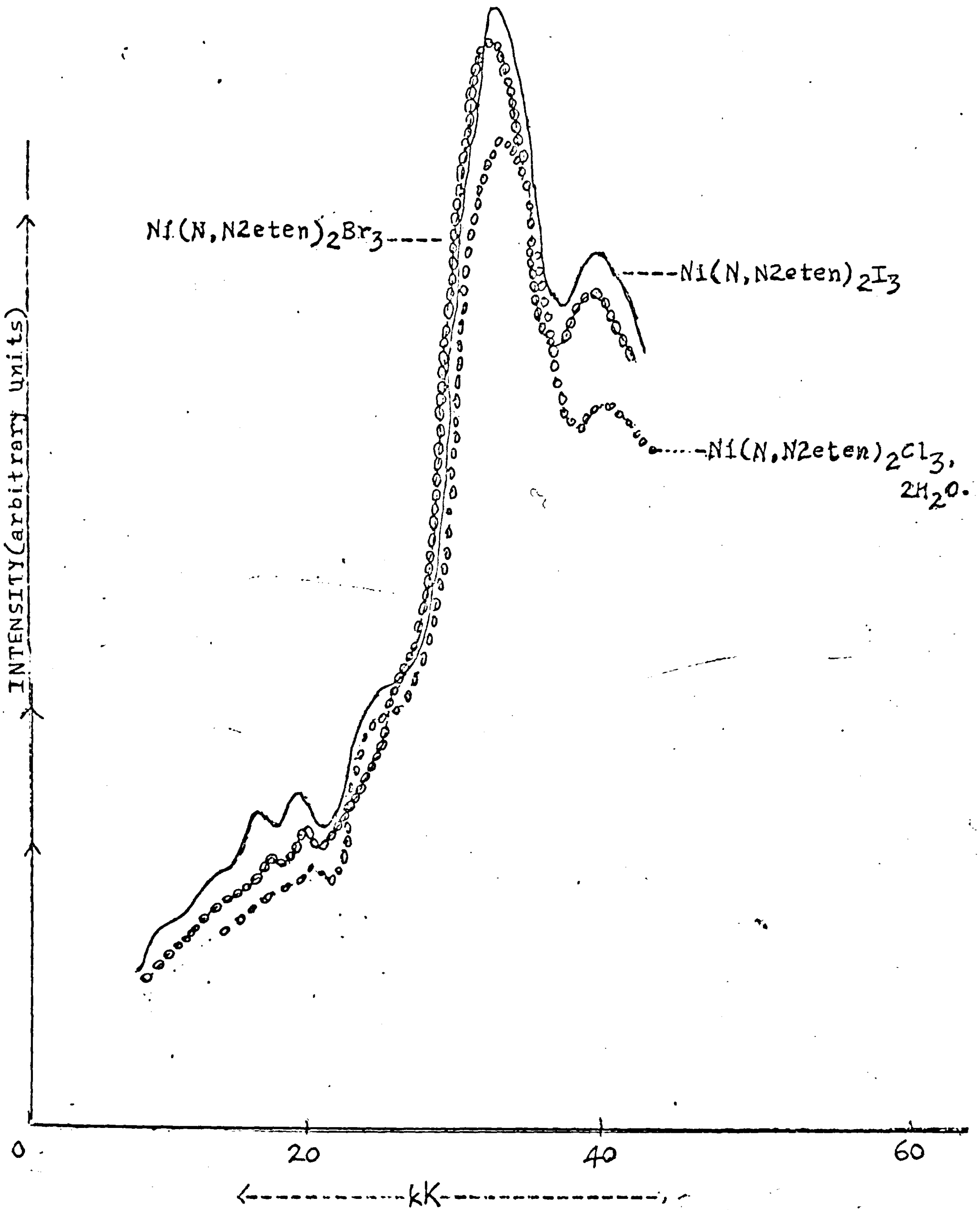


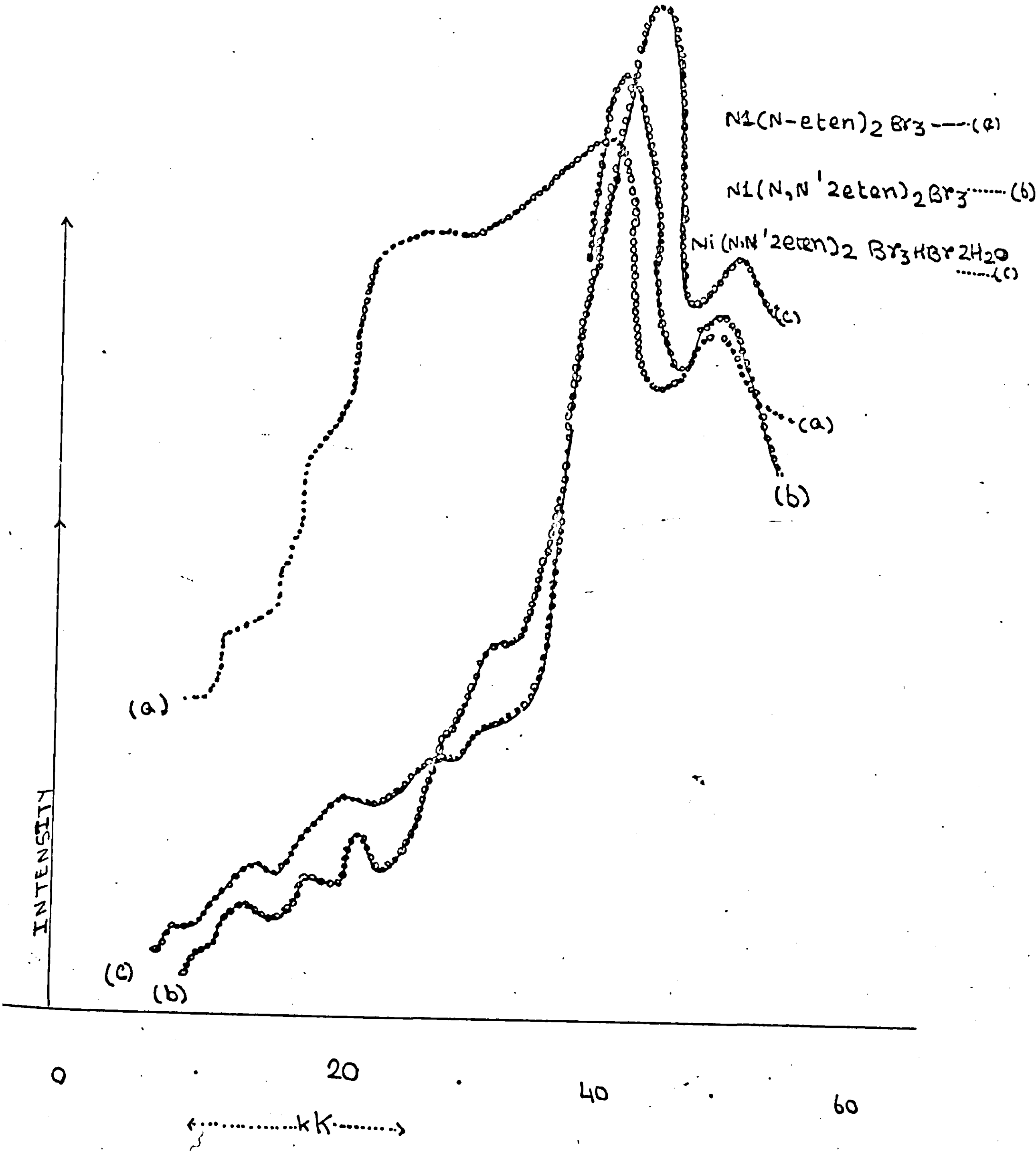
FIGURE 25(a)

Visible Absorption Spectra of Solids (Room Temperature)



Visible Absorption Spectra of Solids (Room Temperature)

FIGURE:-26



Visible Absorption Spectra of Solids(Room Temperature)

FIGURE 27

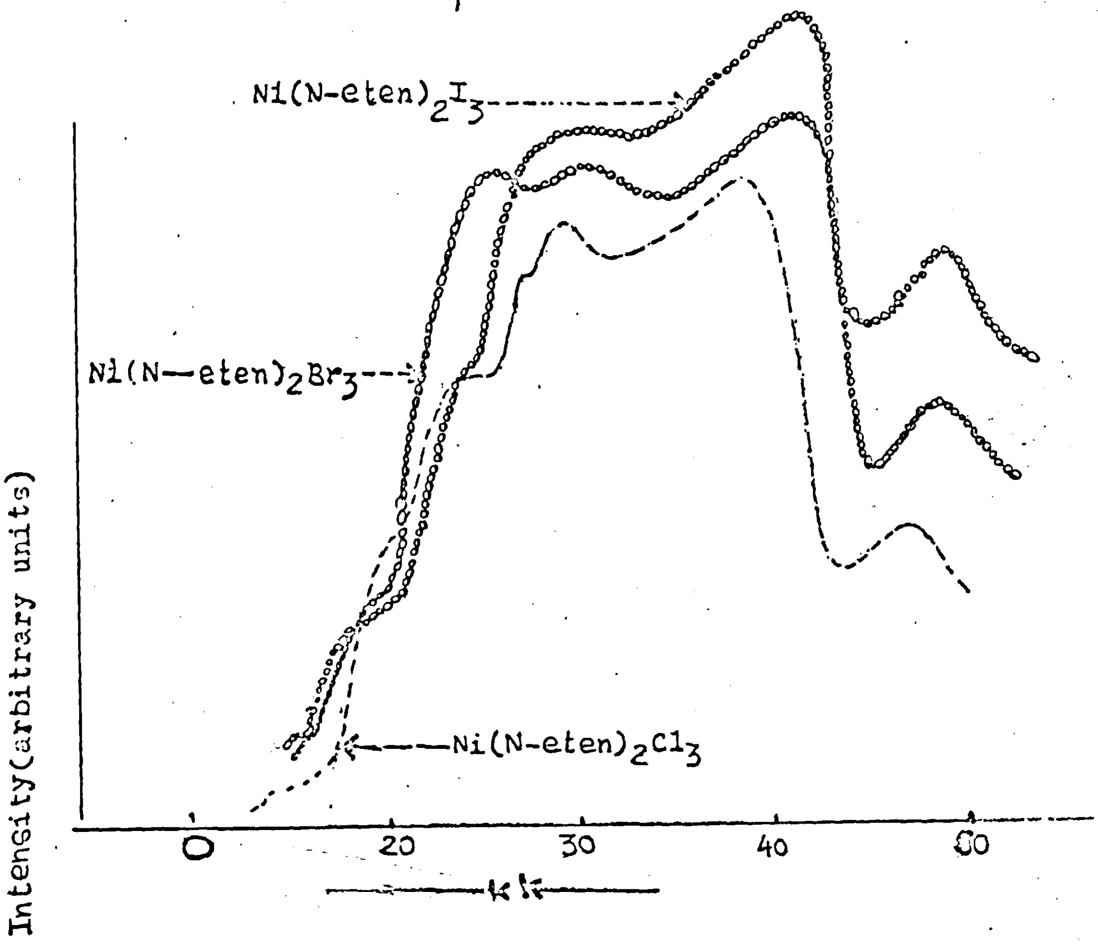


FIGURE:- 28' Visible Absorption Spectra of Solids (Room Temperature)

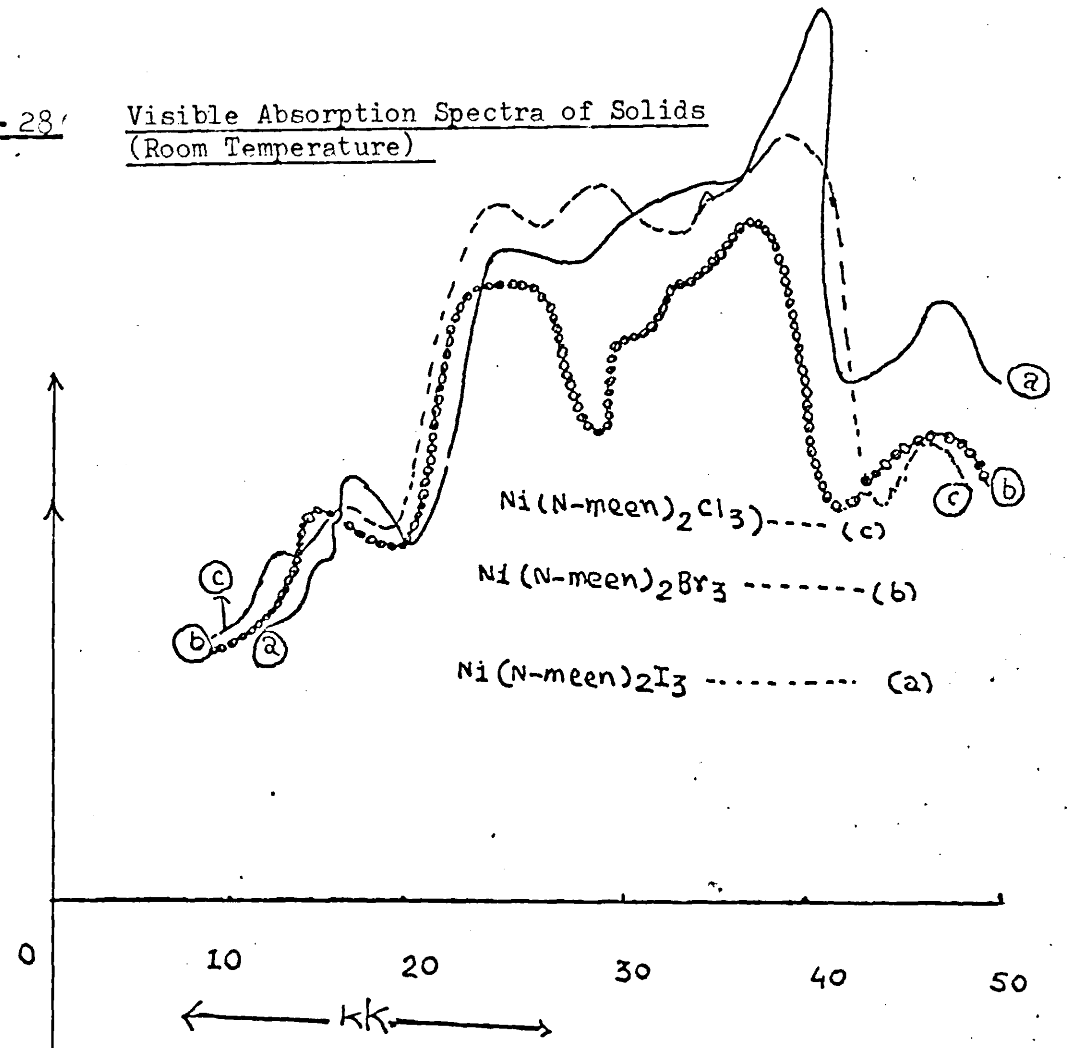


FIGURE:- 29

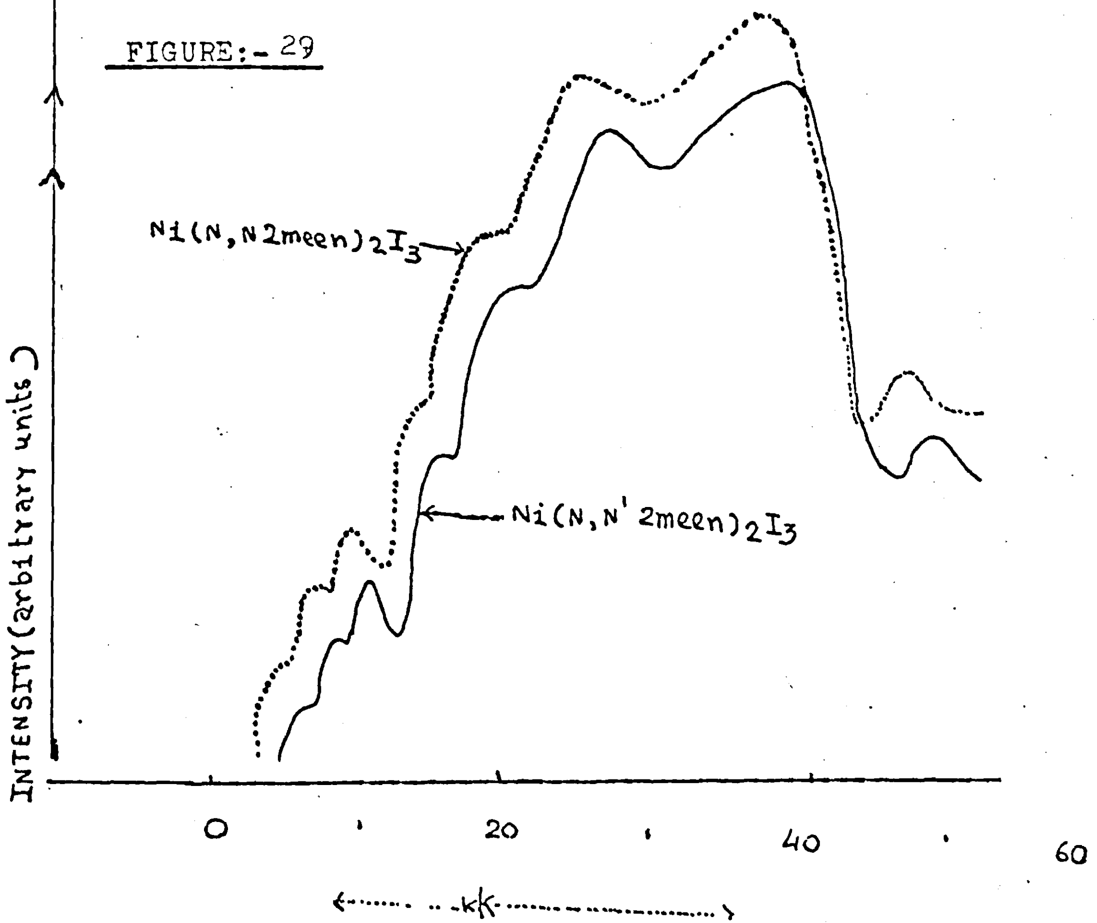


FIGURE:- 30

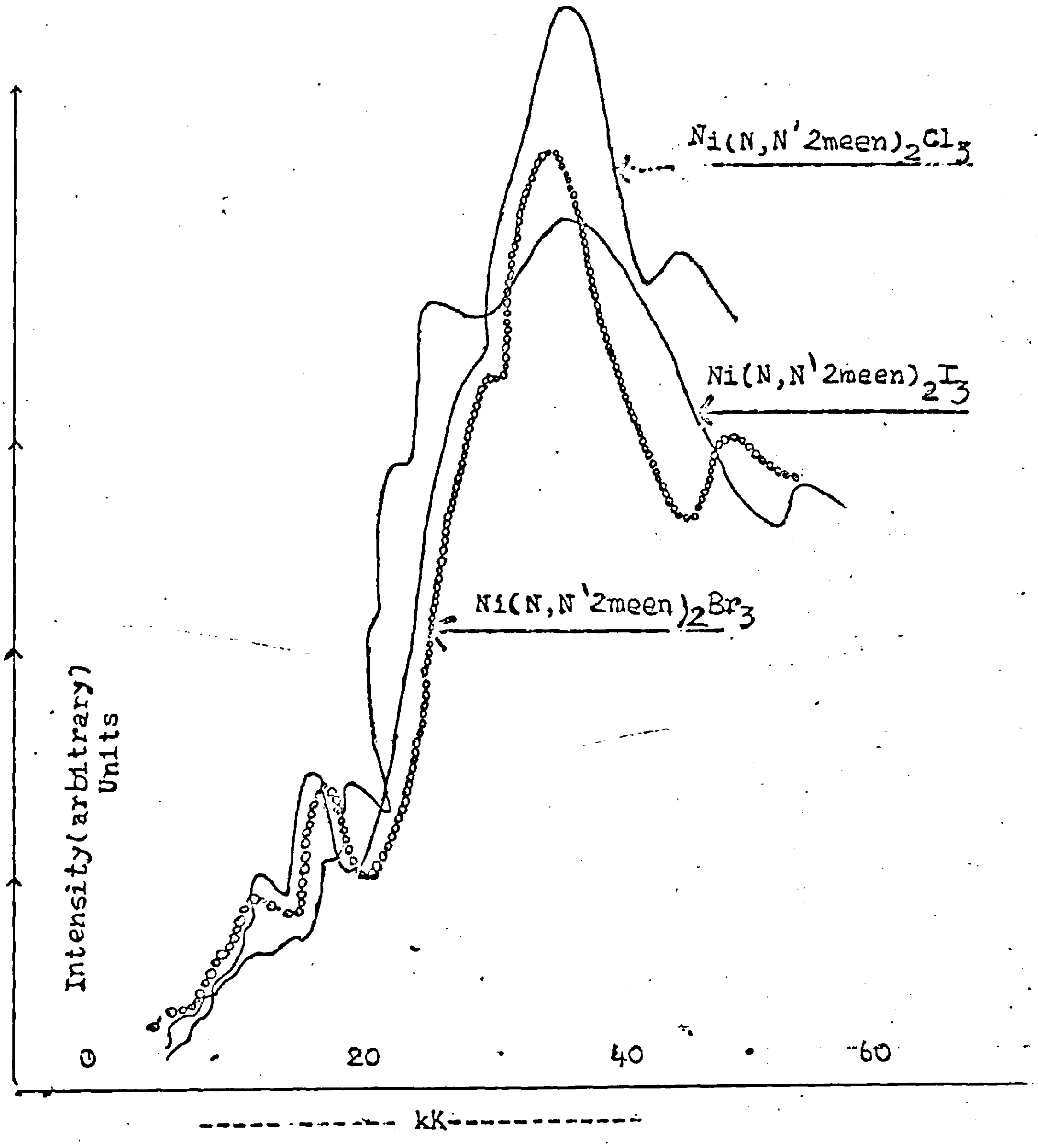
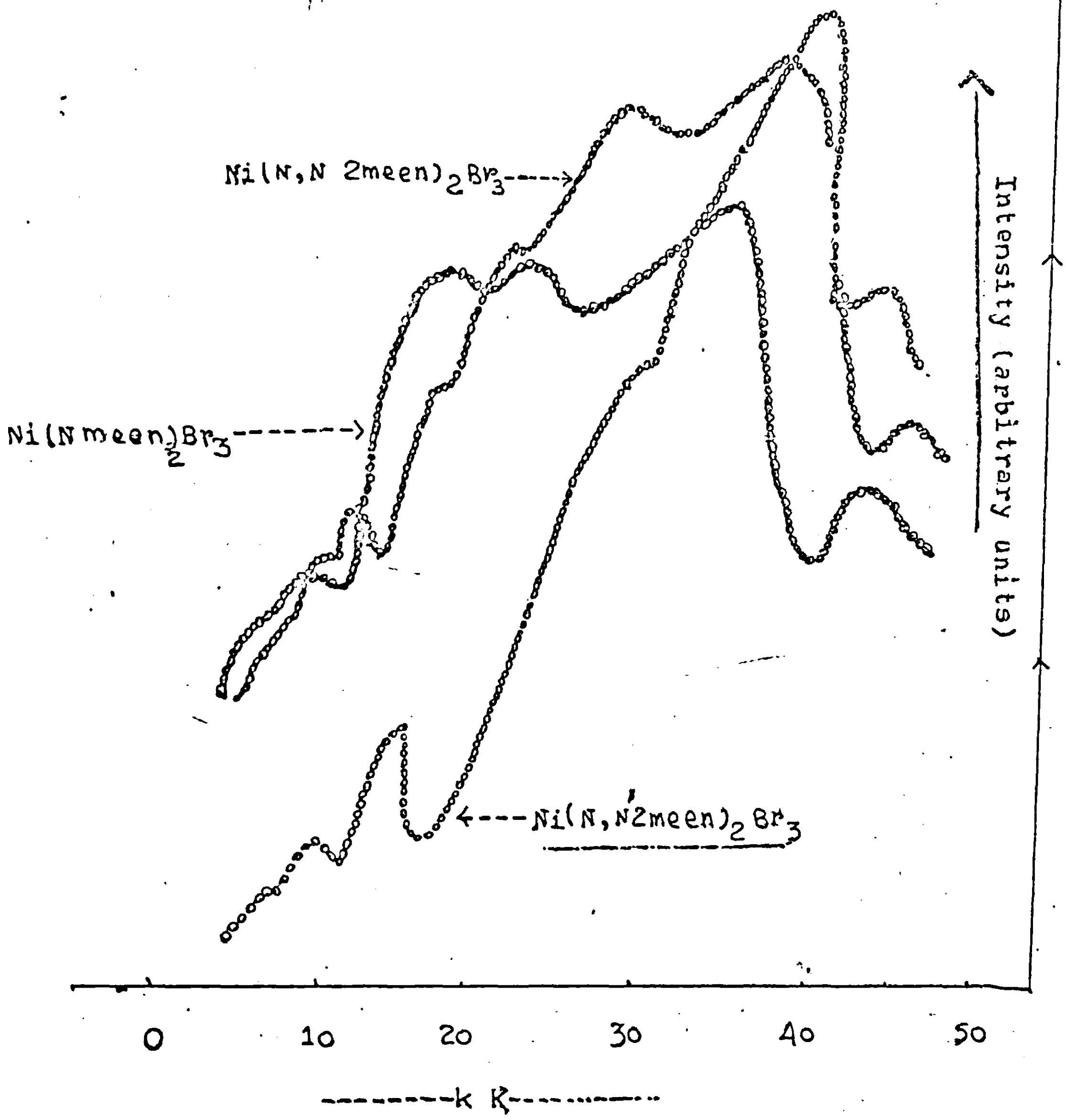

$Ni(N,N'2meen)_2Cl_3$
$Ni(N,N'2meen)_2I_3$
$Ni(N,N'2meen)_2Br_3$
Intensity(arbitrary) Units
0
20
40
60
kK

FIGURE 31

Visible Absorption Spectra of Solids
(Room Temperature)



Discussion of Visible and Ultraviolet Spectra

The diamine complexes of nickel(III) have complex spectra and an attempt is made here to analyse them in terms of $t_{2g}^6\ eg^1$ low spin ground state in which appreciable tetragonal Jahn-Teller[63] distortion occurs. The four bonds in the plane are shorter than the two in the axial direction. Hence the symmetry changes from Oh in the regular octahedron to D_4h in the tetragonal complexes. This lowering of the symmetry results in ^2A_1g ground terms and a splitting of the observed bands. The effect of reducing the symmetry on the several states is shown below:

	Oh	D_4h	D_3
(1)	Eg	$A_1g + B_1g$	E
(2)	T_2g	$A_2g + E_g$	$A_2 + E$
(3)	T_1g (G)	$B_2g + E_g$	$A_1 + E$
(4)	T_1g (H)	$A_2g + E_g$	$A_2 + E$

^2T_1g (G) and ^2T_2g are likely to be very close (see diagram Fig5.7+9). In pure Oh symmetry it seems possible that only two bands may occur. It is difficult to determine therefore which transition $^2E \longrightarrow {}^2T_1$(G) or $^2E \longrightarrow {}^2T_2$ be lower. Allen and Warren[21] indicate that the ^2T_1g state is slightly lower and assignemtnts will be given on thid basis. The energy level diagram (pages 97,102) for a D_4h field indicates that the quartet/doublet cross-over point the $^2A_2$ and 2_E terms are very close although at higher ligand fields these diverge and 2_E moves towards the 2_A term.

Allen and Warren[21] calculate that the bands for the various transitions in the NiF_6^{-3} ion would be at the following wave numbers.

Band Position, KK		Assignment [*]
Observed	Calculated	
6.8	6.7	$^2A_1 \longrightarrow {}^2B_1$
12.3	11.7	$^2A_1 \longrightarrow {}^2E$
	14.0	$^2A_1 \longrightarrow {}^2A_2$
15.7	16.1	$^2A_1 \longrightarrow {}^2E$
	16.8	$^2A_1 \longrightarrow {}^2B_2$
19.2	18.6	$^2A_1 \longrightarrow {}^2A_2$
	19.4	$^2A_1 \longrightarrow {}^2E$
	26.1	$^2A_1 \longrightarrow {}^2E$
	26.2	$^2A_1 \longrightarrow {}^2B_2$
32.0	--	π - eg
37.0	--	π - eg

Dq = 1620 cm^{-1}, B = 703 cm^{-1}, DS/Dt = 3.0 and Dt = 423 cm^{-1}.

[*] The symmetry tables for the ligand field bands relate to D_4 symmetry and the charge transfer bands to Oh symmetry.

The symmetry of the cis and of the tris complexes is formally D_3, but it seems unlikely from e.s.r. measurements that the E ground state is retained and it seems reasonable to discuss all the complexes in terms of a virtual D_4 symmetry. Ballhausen[44] expects a trans complex to exhibit a tetragonal splitting which is twice that of a cis complex. The difference in appearance of the absorption spectra in solution of the cis and the trans forms has been used as an empirical rule by Lewis,[38] in the Co(III) complexes to assign the symmetry when the complexes are non-labile and retain their configurations.

The tris ethylenediamine and propylenediamine nickel complexes pages 107, 118 for Tables and diagram) give almost the same spectra with different anions whether or not containing acid of crystallisation or water molecules. Magnetic evidence indicate that these complexes are almost always magnetically dilute. Thus they are most likely to be tris chelated octahedral. The visible spectra show fewer bands and less splitting then the bis analogues, indicating that the distortion from octahedral are considerably less than that in the case of the bis complexes.

We expect the following transitions in Oh symmetry (see page 129).

$^2E_g \longrightarrow {}^2T_2g$

$^2E_g \longrightarrow {}^2T_1g$ (G)

$^2E_g \longrightarrow {}^2T_1g$ (H)

and on the whole for the compounds of the type $[Ni(AA)_3]X_3$ where AA = ethylenediamine and propylenediamine (see Table 14 page 107) three bands are observed.

On Oh symmetry these may be assigned

Band 1 $^2E_g \longrightarrow {}^2T_2g$ near 13,000 cm^{-1}

Band 2 $^2E_g \longrightarrow {}^2T_1g$ (G) near 17,000 cm^{-1}

Band 3 $^2E_g \longrightarrow {}^2T_1g$ (H) near 27,000 cm^{-1}

Alternatively if the 27,000 cm^{-1} band is a charge transfer band then Band 1 should be assigned to both the $^2E \longrightarrow {}^2T_2g$ and the $^2E \longrightarrow {}^2T_1g$ transitions. The Oh symmetry may be reduced to D_3 or D_4 in which we expect the following six or seven transitions respectively.

D_3

$^2E \longrightarrow A_2$

$E \longrightarrow E$

$E \longrightarrow A_1$

$E \longrightarrow A_1$

$E \longrightarrow E$

$E \longrightarrow E$

$^2E_g \longrightarrow {}^4T_1g$ With a spin forbidden transition (transition expected for D_4h symmetry are shown on page 129).

In some of the tris complexes considerable splitting of the bands is observed, particularly in the case of the iodide salts;

Band 1	near 9,000 cm^{-1}
	near 12,000 cm^{-1}
Band 2	near 16,000 cm^{-1}
	near 19,000 cm^{-1}
Band 3	near 26,000 cm^{-1}
	near 33,000 cm^{-1}

Electronic transitions involving molecular orbitals mainly localised on different atoms are called charge transfer transitions. The charge transfer absorption bands which result from such transitions usually occur at higher energies than the d-d bands, and thus found mainly in the ultra-violet region of the spectrum. The charge transfer processes are of two types, the transfer of an electron from an orbital mainly localised on the ligand(s) to an orbital mainly on the metal, abbreviated ligand ⟶ Metal or L ⟶ M; and the transfer of an electron in opposite direction i.e. from an orbital mainly based on the metal to an orbital situated on ligand(s) abbreviated metal ⟶ ligand or M ⟶ L.

On the basis of IR and magnetic parameters (see pages 73), most of the bis complexes are believed to have cis dimeric structures, and the bands of the spectra of these complexes may be assigned for D_4h symmetry. In this symmetry (D_4h) we would expect at least seven bands in the spectra corresponding to the spin allowed transitions are assigned as follows.

$^2A_1g \longrightarrow {}^2B_1g$

$^2A_1g \longrightarrow {}^2E_g\ (G)(T_1)$) These transitions are likely to be
) very close see diagram 9 page 102
)
$^2A_1g \longrightarrow {}^2A_2g\ (G)$)

$^2A_1g \longrightarrow {}^2E_g\ (G)\ (T_2)$)
)
)
$^2A_1g \longrightarrow {}^2B_2g\ (G)$)

$^2A_1g \longrightarrow {}^2A_2g\ (H)$

$^2A_1g \longrightarrow {}^2E_g(H)$)
)
) Close
$^2A_1g \longrightarrow {}^2B_2$)

The bands for the various transitions in the nickel(III) bis complexes may be assigned to the following transitions.

Assignments	Frequencies cm^{-1}
$^2A_1g \longrightarrow {}^2B_1g$	7,000 - 8,000
$^2A_1g \longrightarrow {}^2E_g(G)(T_1)$	11,000 - 13,000
$^2A_1g \longrightarrow {}^2A_2g\ (G)$	12,000 - 15,000
$^2A_1g \longrightarrow {}^2E_g(G)T_2$	16,000 - 17,000
$^2A_1g \longrightarrow {}^2B_2g\ (G)$	17,000 - 17,500
$^2A_1g \longrightarrow {}^2A_2g\ (H)$	18,000 - 19,000
$^2A_1g \longrightarrow {}^2E_g(H)$ or $^2A_1g \longrightarrow {}^2B_2g$	26,000 - 27,000
Charge-transfer bands to Oh symmetry	
π - eg π - eg π - eg	36,000 - 45,000 (two to three bands)

The visible spectra of the halide of N,N'-2eten complexes show the same characteristics as those of the unsubstituted complexes. The trans tetragonal structure is ruled out because of the steric hinderance of the ethyl groups.

In comparing the spectra of the complexes with different substituents on the diamine the absorption peaks shift to lower wavenumbers with increased substitution on the nitrogen of the diamine, however with increasing substitution on the carbon atom there is a move to higher wavenumbers.

CHAPTER V

MAGNETISM

Magnetism in transition metal complexes

Chemical substances may be classified by their behaviour when placed in a non-uniform magnetic field. Those substances which tend to move from a stronger part to a weaker part of the field are termed as diamagnetic and those which move from the weaker to the stronger part are paramagnetic. The extent to which the material becomes magnetised is measured by its magnetic moment per unit volume, called intensity of magnetisation I. If a substance is placed in a magnetic field of a strength H Gauss, then the magnetic induction B in a substance is given by $B = H + 4\pi I$, where I is the intensity of magnetisation, B is the magnetic induction or the density of lines of force within the substance and H is the applied field.

$$\therefore \quad \frac{B}{H} = 1 + \frac{4\pi I}{H}$$

$$\text{i.e. } \mu = 1 + 4\pi K$$

where μ is the magnetic permeability of the material (not to be confused with μ for magnetic moment) and K is the volume susceptibility of the material. A more convenient quantity than K is χ, which is the susceptibility per gram, which is given by $\chi = {}^{K}/_{d}$ where d is the density of the material. The molecular susceptibility is $\chi_M = \chi \times M$ where M = molecular weight. Atomic and ionic susceptibilities can be similarly defined.

Substances are broadly divided into two categories; diamagnetic and paramagnetic.

Diamagnetism[44,67]

For diamagnetic substances I, K and χ are negative, $\mu < 1$, and they experience a force in the opposite direction to the magnetic field gradient. The value of χ is of the order of +1 to 10^{-6} c.g.s. e.m.u. and is independent of H and the temperature. An electron moving in a closed orbit can be considered as an electric current. Application of an external magnetic field causes a precession of the orbit (the Larmor precession) which produces a magnetic field directed against the applied field (Lenz's law).[44,46] Classical mechanics gave as the expression for the susceptibility

$$\chi_A = \frac{-Ne^2}{6Mc^2} \sum \bar{Y}^2$$

where $\bar{Y}^2$ is the mean of the squares of the radii of the projections of the orbits perpendicular to the field;
e is the electronic charge
M is the mass of the electron
and c is the velocity of light.

A similar expression results from the quantum mechanical treatment. It indicates that all atoms have a characteristic property of diamagentism even though this may be swamped by a larger paramagnetism. From the formula given above it follows that diamagnetism, being only dependent on the effective radii of the electronic orbits, is independent of temperature. For the precise measurement of the paramagnetic susceptibility of an ion, the diamagnetism of the ligands must be accounted for. The diamagnetism arising from the paramagnetic ion should also be considered, but this is difficult to estimate and being comparatively small ($\sim 20 \times 10^{-6}$ c.g.s. e.m.u.) for the transition metal ions) is frequently neglected.

Pascal[38] showed empirically that

$$\chi_M = \sum n_A \chi_A + \lambda$$

where χ_M is the molecular susceptibility
n_A is the number of atoms of susceptibility
χ_A is the molecule, and
λ is the constitution correction, dependent on the nature of the bond in the molecule. From the published values of χ_A and λ[38] it is thus

possible to calculate the diamagnetic susceptibilities of anions and organic ligands present in compounds. Diamagnetic corrections are usually small compared with the paramagnetic susceptibilities of complexes. However, in certain complexes of low paramagnetic susceptibilities, the diamagnetic correction makes a major contribution to the total susceptibility.

Paramagnetism

For paramagnetic substances, I, K and χ are positive $\mu > 1$ and they experience a force in the same direction as the magnetic field gradient. The value of χ is of the order of +1 to 10^{-4} c.g.s. e.m.u. It is independent of H but dependent on the temperature. The susceptibility of a number of paramagnetic substances varies inversely as the absolute temperature (Curie's Law)[46]

$$\chi = {}^{C}/T \qquad (1)$$

only a few substances obey this Curie Law very rigidly and very large deviations frequently occur. Weiss[44,46] improved the Curie Law by introducing a correction θ:

$$\chi = {}^{C}/T + \theta \qquad (2)$$

This is so called the Curie-Weiss Law and has a wide applicability. Weiss interpreted θ on the basis of "molecular field" though it is perhaps best considered merely as a measure of deviation from the ideal behaviour. In practice the use of the formula $\mu = 2.84\sqrt{\chi(T + \theta)}$ for the calculation of magnetic moments is quite common, though its use is rarely theoretically justified.

Paramagnetism is exhibited by atoms, ions or molecules having unpaired electrons, and hence possessing a permanent magnetic moment. The magnetic properties may be developed upon the supposition that each atom or molecule possesses the properties of the magnetic dipole i.e. it acts as if it were a microscopic magnet. In the presence of the applied field the magnetic dipoles are quantized so that they point either in the direction of the applied field or against it. The process of magnetic polarization then involves the tendency of the magnetic dipoles to achieve the lower energy state of alignment with the applied field. This tendency is counter acted by the randomizing effect of thermal energy kT. The magnetic properties of a substance will depend on the thermal population of different energy levels. Three distinct types of behaviour arise depending on the relative magnitudes of kT and the multiplet widths. The multiplet widths may be large or small compared to kT or they may be of comparable size. The multiplet widths may be wide, narrow or comparable to kT.

Assuming that each atom of a paramagnetic substance behaved independently as a small permanent magnet or μ Langevin[45] deduced an expression for the susceptibility, which accords with Curie's Law.[46]

$$\chi_A = \frac{N\mu^2}{3kT} \qquad (3)$$

van Vleck[42,43] used a quantum mechanical treatment and deduced a similar equation:

$$\chi_A \quad \frac{N\overline{\mu^2}}{3kT} + N\alpha \qquad (4)$$

where Nα is the temperature independent contribution of the high frequency elements to the paramagnetic moment. In this case $\overline{\mu^2}$ is the magnetic moment averaged over time and over the various levels, weighed according to a Boltzmann distribution.

Nowadays magnetic moments are expressed in β, Bohr magnetons (B.M.). β is the magnetic moment of an electron possessing only one unit of spin angular momentum. It is equal to $\frac{eH}{4\pi mc}$ and evaluated as 0.927×10^{-20} ergs gauss^{-1}. Substituting the value of β in the equation (4), the Langevin-Debye equation is obtained.

$$\chi_A = \frac{N\mu^2\beta^2}{3kT} + N\alpha \qquad (5)$$

where μ is the magnetic moment expressed in Bohr magnetons. The second term is small compared with the first, i.e. the Curie Law is obeyed plus a small constant term (Temperature Independent Magnetism), (T.I.P.). However, in practice χ_A is the quantity measured in order to derive μ so that, rearranging (5) and neglecting $N\alpha$, we get

$$\mu e = \sqrt{\frac{3k.\chi_A.T}{N\beta^2}} \quad \text{where}$$

μe = the effective magnetic moment

k = Boltzmann constant

N = Avogadro number

T = absolute temperature

χ_A = is the susceptibility per atom or ion; (including diamagnetic correction).

The above theoretical expressions assume magnetic dilution, i.e. they assume the complete absence of any form of interaction between neighbouring paramagnetic atoms or ions. This assumption is justified in the case of paramagnetic gases (providing the temperature is well above the critical temperature) and is indeed also justified in many solids providing the paramagnetic ions are well shielded from each other by diamagnetic ions or ligands. When shielding is imperfect and interaction between paramagnetic ions occurs, the substance is said to be 'magnetically concentrated', and the phenomena of ferro- and antiferro-magnetism occur.

From the Langevin-Debye equation, van Vleck[42] distinguished three separate cases according to the relative sizes of the spin multiplet widths, $h\upsilon$ of the atoms ground state and the thermally available energy kT.

(i) Multiplet intervals small compared to kT; $h\upsilon \ll kT$

(ii) Multiplet intervals large compared to kT; $h\upsilon \gg kT$

(iii) Multiplet intervals comparable to kT.

Multiplet intervals small compared to kT

Under these conditions the coupling of L and S may be neglected and they are considered to react separately with the applied field. The moment $\mu = \sqrt{4S(S + 1) + L(L + 1)}$ where $4S(S + 1)$ gives the spin contribution, and $L(L + 1)$ the orbital contribution. Thus for an atom is an S state i.e. $L = 0$, $\mu = \sqrt{4S\ (S + 1)}$, but $S = \frac{n}{2}$ where n is the number of unpaired electrons

$$\therefore \quad \mu = \sqrt{n(n + 2)}$$

This is the 'spin only' moment giving values of 1.73, 2.83, 3.87, 4.90, 5.90 Bohr magnetons for 1, 2, 3, 4, and 5 unpaired electrons. This explains many of the moments of first-row transition metals even when the ground state is not an S state (Table below).

TABLE- 17

Magnetic Moments of Spin-free Transition Metal Ions

No. of d electrons	Ion	$\mu=[4S(S+1)$ $L(L+1)]^{\frac{1}{2}}$	$\mu=[4S(S+1)]^{\frac{1}{2}}$	μ_e B.M. observed
d^1	T_1^{3+},V^{4+}	3.00	1.73	1.73 to 1.8
d^2	V^3	4.47	2.83	2.8 to 3.1
d^3	Cr^{3+} Mn^{4+}	5.20	3.87	3.7 to 4.0
d^4	Mn^{3+},Cr^{2+}	5.48	4.90	4.8 to 5.1
d^5	Fe^{3+}	5.92	5.92	5.7 to 6.1
d^6	CO_3^+	5.43	4.90	5.1 to 5.7
d^7	CO_2^+,(Ni(III)	5.20	3.87	4.3 to 5.2
d^8	Ni^{2+}	4.47	2.83	2.6 to 3.5
d^9	Cu^{2+}	3.0	1.73	1.7 to 2.2
d^{10}	Zn^{2+}	0	0	diamagnetic

The "quenching" of the orbital contribution is caused by the crystal field in a manner which will be discussed later. (Page144). Providing the system is magnetically dilute the Curie Law should hold in this case.

Multiplet widths large compared to kT; $h\upsilon >> kT$

In this case only the energetically lowest J value is thermally populated. This type of behaviour is shown by rare earths except Sm(III) and Eu(III) and $\mu = g\sqrt{J(J+1)}$ where g = Lande splitting factor which is equal to $g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}$

The Curie Law should again hold in this case.

Multiplet intervals comparable to thermal energy; $h\upsilon$ comparable to kT

In this case, it will be necessary to take into account a Boltzmann distribution between various J values. Examples of these type are Sm(III) and Eu(III) and No. The expression for the moment is rather complicated and large departures from the Curie Law are observed. Besides normal paramagnetism further sub-divisions are ferro and antiferromagnetism.

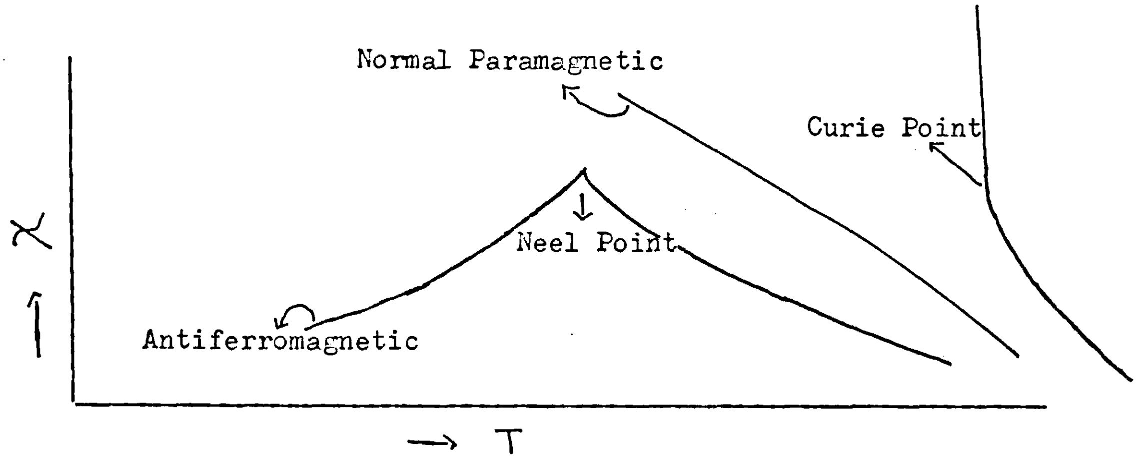
Ferromagnetism [37, 46]

For ferromagnetic substance χ is +ve, 10^{-2} to 10^{4} c.g.s. e.m.u. dependent on both H and T. This corresponds to the parallel alignment of electron spins between adjacent paramagnetic ions so that the moments of the separate ions reinforce one another. According to Heisenberg's theory of ferromagnetism it arises from a positive exchange interaction between adjacent paramagnetic ions, the exchange interaction being expressed by $\Delta E = Jsisj$ (where J is the exchange integral and not to be confused with the quantum number J). Below the Curie temperature the susceptibility increases much more rapidly with decreasing temperature than expected from the Curie Law, while above the Curie temperature, thermal energies are more or less able to randomize the orientations and the substance obeys the Curie or Curie-Weiss Law.

The susceptibilities are very large and field dependent. Thus determinations of the susceptibilities of paramagnetic materials at several field strengths allows the detection of ferromagnetic impurities, even though the concentrations of these impurities may be too low for detection by normal analytical methods.

Antiferromagnetism

For antiferromagnetic substance χ is +ve, 1 to 10^{-4} c.g.s,e.m.u., dependent on T and sometimes H. J is negative, the lowest state is that with spin-paired, correspond to an antiparallel alignment of the adjacent spins. This spin-pairing causes reduction in the moments and susceptibilities, and where interaction is direct, is the phenomenon of covalent bonding. As the temperature is raised a point is reached when the thermal energy is sufficient to overcome the magnetic interaction of whichever kind it happens to be. This is known as the Curie temperature or in antiferromagnetism, more usually Neel temperature. At much higher temperatures where the interaction is negligible compared to kT, normal paramagnetic behaviour occurs and χ is independent of field and follows the Curie-Weiss Law (see below). Fig-33



In many cases of antiferromagnetism, the distance between paramagnetic ions is too great for direct interaction of the unpaired electrons, instead these are coupled through intervening negative ions such as halide or oxide. This phenomenon is known as "super-exchange". Two types of antiferromagnetism may be distinguished, (i) inter molecular, where the interactions extend through the crystal (lattice), and (ii) intra molecular, where the interactions are confined within the molecule.

Two methods are commonly used to detect antiferromagnetism in the coordination compounds. Dissolution; by surrounding the complex species with solvent molecules and thus separating the interacting ions should destroy the interaction. The difficulties with this method are: (i) the compounds are insoluble or considerably changed by dissolution and (ii) the experimental errors in measuring χ if the solution is very dilute, may be greater than the effect being observed.

The second method is dilution in a solid diamagnetic isomorphous compound. The difficulties here are of finding a suitable host material and of measuring a probably very small susceptibility.

Intra molecular antiferromagnetism in which the intervening ions are present within single molecule in which dilution or dissolution has no effect on the interaction unless the complex is broken by the solvent. In such polynuclear complexes mathematical treatment has been developed.

Quenching of Orbital Contribution

For an electron to have orbital angular momentum about a given axis it must be possible to transform the orbital which it occupies into an exactly equivalent and degenerate orbital by a rotation about the axis. For a free ion, a rotation about axis through 45^o converts the dx^2-y^2 orbital into the dxy orbital, while t2g orbitals are interconvertible by 90^o rotations. In an octahedral complex the d orbitals are split into t2g and eg levels, thus removing the degeneracy of the dx^2-y^2 and dxy orbitals and eliminating their contribution to the orbital angular momentum. However, dxy and dyz are still equivalent and capable of giving an orbital contribution. As eg orbitals cannot be transformed into each other by a rotation about an axis, an electron occupying them cannot contribute to the orbital angular momentum (the eg orbitals are thus known as a non-magnetic doublet). If there is an electron in each of the t2g orbitals, each with the same spin, generation of orbital angular momentum is also not possible. In an octahedral complex, the following configurations are expected to have all orbital contribution to the moment quenched.

Spin-paired - d^6 ($t2g^6$) and d^7 ($t2g^6$ eg^1)
Spin-free - d^3 ($t2g^3$), d^4 ($t2g^3$ eg^1), d^9 ($t2g^6$ eg^3)

Configurations which will give some orbital contribution are:

Spin-free d^1, d^2, d^6 and d^7
Spin spaired d^4 and d^8

Alternatively, in the weak field case spin only values may be expected for ions in S states and when a doublet from D term or singlet from a F term lies lowest. But orbital contribution is expected when orbital triplets from D and F terms lie lowest. However, divergences from the spin only value when no orbital contribution would be expected are often noted because of spin-orbit coupling. This causes a "mixing in" to the ground state of some of the higher levels with orbital angular orbital momentum. For efficient mixing these higher levels must have the same multiplicity (S value) as the ground state. This effect is encountered in the following equation $\mu_e = \mu_o (1 - \alpha \frac{\lambda}{\Delta})$ where

μ_e = the observed magnetic moment
μ_o = the spin only moment
Δ = the energy separation to the nearest level of the same multiplicity.
α = constant. Its value 4 for F terms.
ξ or λ = spin-orbital coupling constant.

TABLE 18

FREE IONS VALUES (cm^{-1}) OF THE FIRST ROW TRANSITION METAL IONS

ground term weak	λ	ground term strong	λ	ion	ζ	No. of d electrons
$^4t_{1g}$	-238	^2e_g	-715	Ni^{3+}	715	7
$^5t_{2g}$	-145	$^1A_{1g}$	-	Co^{3+}	580	6
^5e_g	+89	$^3t_{1g}$	-178	Mn^{3+}	355	4

Determination of Susceptibility

Methods for the measurement ofmagnetic susceptibility may be divided into two basic categories, according to whether the magnetic induction in or the force exerted on a body in a magnetic field is the quantity determined. Normally the magnetic induction is detected by electronic means and the force exerted on a body by a mechanical means. Methods involving the use of the magnetic induction type include various forms of induction bridges, oscillators and a specially applied nuclear resonance phenomenon. Among methods of the force type, the Gouy and Faraday are closely related methods.

The simple and convenient method of Gouy[38] was used for magnetic susceptibility determinations for solids and liquids. It consists esssentially of the suspension of a cylindrical sample of the substance in question in a non-homogonous magnetic field and measurement, by a conventional weighing technique of the force extended on it. A uniform cylindrical column of the material whose magnetic susceptibility is required (at room temperature) to suspend vertically so that the lower end is in a maximum homogenous magnetic field and the upper end is in a region of effectively zero field theoretically in a region of a minimum field. If F_s = Force on a cylinder of material in dynes, which is a vertical pull of a paramagnetic material which as above tends to set itself with the maximum length in the region of maximum field. A vertical thrust on a diamagnetic material which tends to set itself with the minimum length in the region of maximum field.

Since $F_s = I \times A$ at any point in the field where

A = area of the cross-section of a material betweem the magnetic poles at that point in the field and I is the intensity of magnetisation, i.e. Force/unit area.

$$\beta = \mu H = H + 4\pi I$$

$$= \mu H - H = 4\pi I$$

$$\therefore I = H\frac{(\mu-1)}{4\pi} \qquad (1)$$

This gives the intensity of magnetisation I at any point in terms of the field strength H and the permeability of the medium μ. Substituting the value of I from equation (1) we get

$$F_s = \frac{H\ (\mu-1)}{4\ \pi} \times A$$

gives the force at any point on a piece of material cross-section A when field strength is H. When in a differential field varying between a maximum H_1 and a minimum of H_2, the total force is given by the integral

$$F_s = \frac{A\ (\mu-1)}{4\ \pi} \int_{H_2}^{H_1} H.2\ell$$

$$\therefore\ F_s = \frac{A\ (\mu-1)}{8\ \pi}\ (H_1^{\ 2} - H_2^{\ 2}) \qquad (2)$$

This gives the force on a cylinder of material of permeability μ suspended in a vacuum. If however the material is suspended in air, or some material whose permeability is not unity then we could say

μ_1 = the permeability of the material

μ_2 = the permeability of the medium (usually air or nitrogen)

$\therefore$ the equation (2) can be

$$F_s = \frac{\mu_1 - \mu_2)A(H_1^{\ 2} - H_2^{\ 2})}{8\ \pi}$$

$$\therefore\ F_s = \tfrac{1}{2}(K_1 - K_2)A(H_1^{\ 2} - H_2^{\ 2})$$

($\therefore\ \mu = 1 + 4\ \pi\ K$ general expression for a volume susceptibility)

Where K_1 and K_2 are volume susceptibilities of the material and medium

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

$$\therefore\ K_1 = \frac{2F_s}{A(H_1^{\ 2} - H_2^{\ 2})} + K_2 \qquad (3)$$

If the material is sufficiently long, H_2 may be neglected thus integration over a whole length of the specimen from $H_1 = H_2$ at zero length to

H_1 at length = ℓ, i.e. H_2 is arranged to be zero which can be readily provided by a sufficient length of the material is used.

$$\therefore \quad K_1 = \frac{2F_s}{A(H_1^2)} + K_2 \qquad (4)$$

The mass susceptibility $\chi = K/_P$ where P = density.

$$\therefore \quad \chi \times M = K \times V \quad \left(P = {}^M/V = \frac{W_s}{\ell A} \right.$$

where M = mass
V = volume
W_s = wt. of a sample)

$$\therefore \chi \times P = K = \frac{2F_s}{A(H_1^2)} + K_2$$

$$\therefore \frac{\chi \times W_s}{1 \times A} = \frac{2F_s}{A(H_1^2)} + K_2 \quad (P = W_{s/\ell A})$$

$$\therefore \quad \chi = \frac{2F_s \times 1}{W_s \; H_1^2} + \frac{K_2 \, \ell A}{W_s} \qquad (5)$$

Since $21/_{H_1^2}$ is constant for a given length of material and constant field, it is customary to write equation (5) as

$$\chi = \frac{\alpha F_s}{W_s} + \frac{V K_2}{W_s}$$

where $\alpha = 2\ell/_{H_1^2}$ which is also known as a 'Balance constant'

Under standard conditions, the thrust or pull F_s may be measured by attaching the suspended cylinder to the pan of an accurate analytical balance.

W_s = weight of a sample (material)

V = volume of the material gives the magnetic mass susceptibility X

K_2 = volume susceptibility of air = + 0.029×10^{-6} c.g.s. e.m.u.

if nitrogen is used = 0.0004×10^{-6} c.g.s. e.m.u.

In practice for most of the paramagnetic and diamagnetic species, pulls or thrusts are of the order of a few milligrams, so it is usually to replace dynes to milligram by wg. $\delta \ell$ in cm.

and

$$\therefore \chi = \frac{K_2V + (\frac{2g\ell}{H^2}) \times F_s}{W_s} = \frac{(\frac{2g\ell}{H^2}) \times F_s}{W_s} + K_2V$$

$$= \frac{\alpha \times Fs}{W_s} + K_2V \quad \text{where } \alpha = \frac{2 \times g\ell}{H^2}$$

$$\therefore \chi = \frac{2 \times g \times \ell}{W_s \times H^2} \times F_s$$ (if nitrogen is used K_2V = zero negligible) (6)

$$\chi_M = \frac{\alpha F_s}{W_s} \times M$$ where M = molecular weight of a sample

and α = balance constant

$= 2 \times g \, \ell / H^2$

χ_M is known as a molecule susceptibility

Single temperature measurements are generally carried out under air so the correction for air 'K_2V' is applied in the equation

$$\chi = \frac{2 \times g \times \ell \times F_s}{W_s \times H^2} + K_2V$$

Single temperature measurements were carried out at room temperature using the apparatus illustrated in Fig. 34 page 151. and the results were satisfactory.

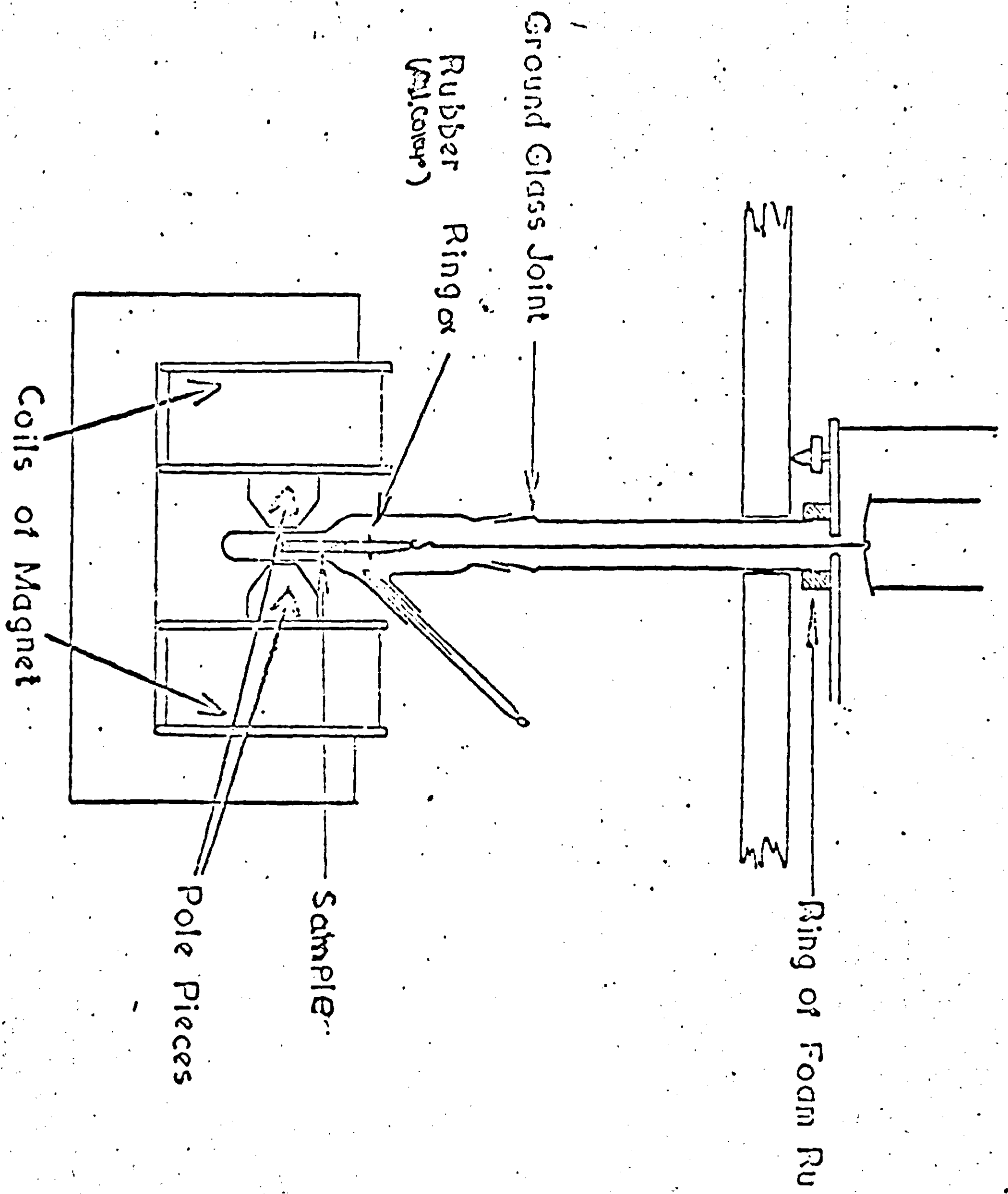
A Temperature Variable Gouy Balance

Measurements at low temperatures are generally of greater interest to coordination chemists and most attention has therefore been given to ways of cooling below rather than heating above room temperature.

In magneto chemical investigation, temperature dependent studies are essential, not only to show the existence of, but also to measure the magnitude of departures from ideality. The principle is precisely the same as for single temperature measurements, but with some modification of the apparatus. The significant difference is that in

FIGURE 34

SINGLE TEMPERATURE GOUY BALANCE



this case the specimen was surrounded by a rather bulky cryostat to maintain the temperature at any predetermined value. This is necessary to use the pole gaps of up to 6 cm with a pole force diameter of about 10 cm as illustrated in Fig. 35 page 153 To maintain a reasonable field with such dimensions the Humpry's Sucksmith type electromagnet, capable of a field variation up to about 10,000 oersteds was selected. Variable field strength measurements allow to detect ferromagnetic impurities is also an additional advantage over a permanent magnet. The current has been used through rectified mains to obtain the necessary constancy in voltage.

Specimen and Suspension

The specimen was powdered into fairly small and roughly uniform particles and was carefully packed into a glass tube. Owing to the traces of ferromagnetic impurities in the glass its diamagnetic correction varies appreciably with temperature. As the compounds were hygroscopic sealed glass tubes were used.

Cryostat:

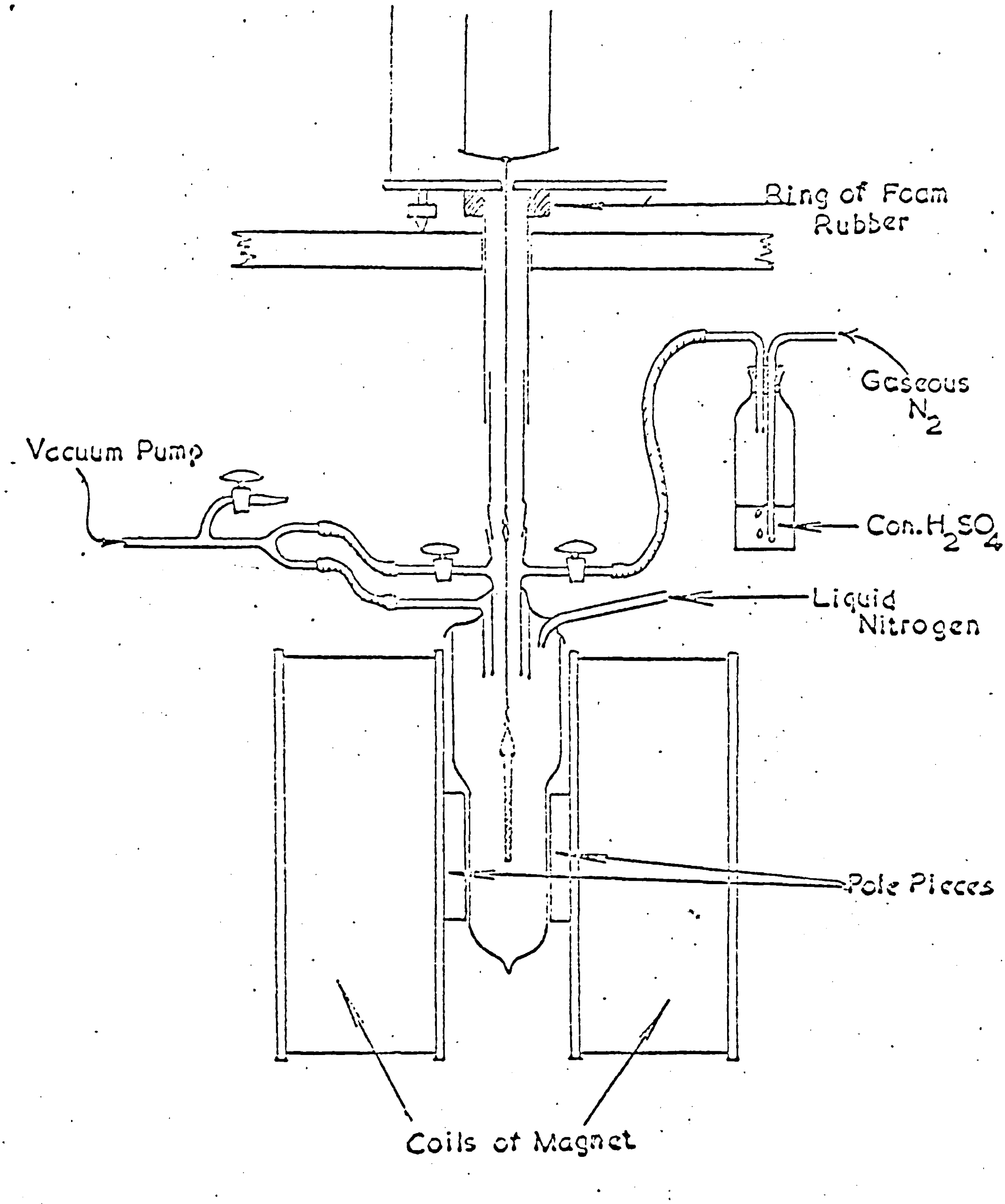
The cryostat was shown in Fig.36 page 154 It is very similar to that used by Earnshaw,[45] Figgis and Nyholm.[44] In order to take satisfactory readings with the specimen at predetermined but variable temperatures, four things are essential.

(1) A method for cooling the system.
(2) A method for heating the system.
(3) A thermostatic arrangement to ensure that (1) and (2) balance.
(4) A means of measuring the temperature.

The cryostat itself incorporates (1) and (2).

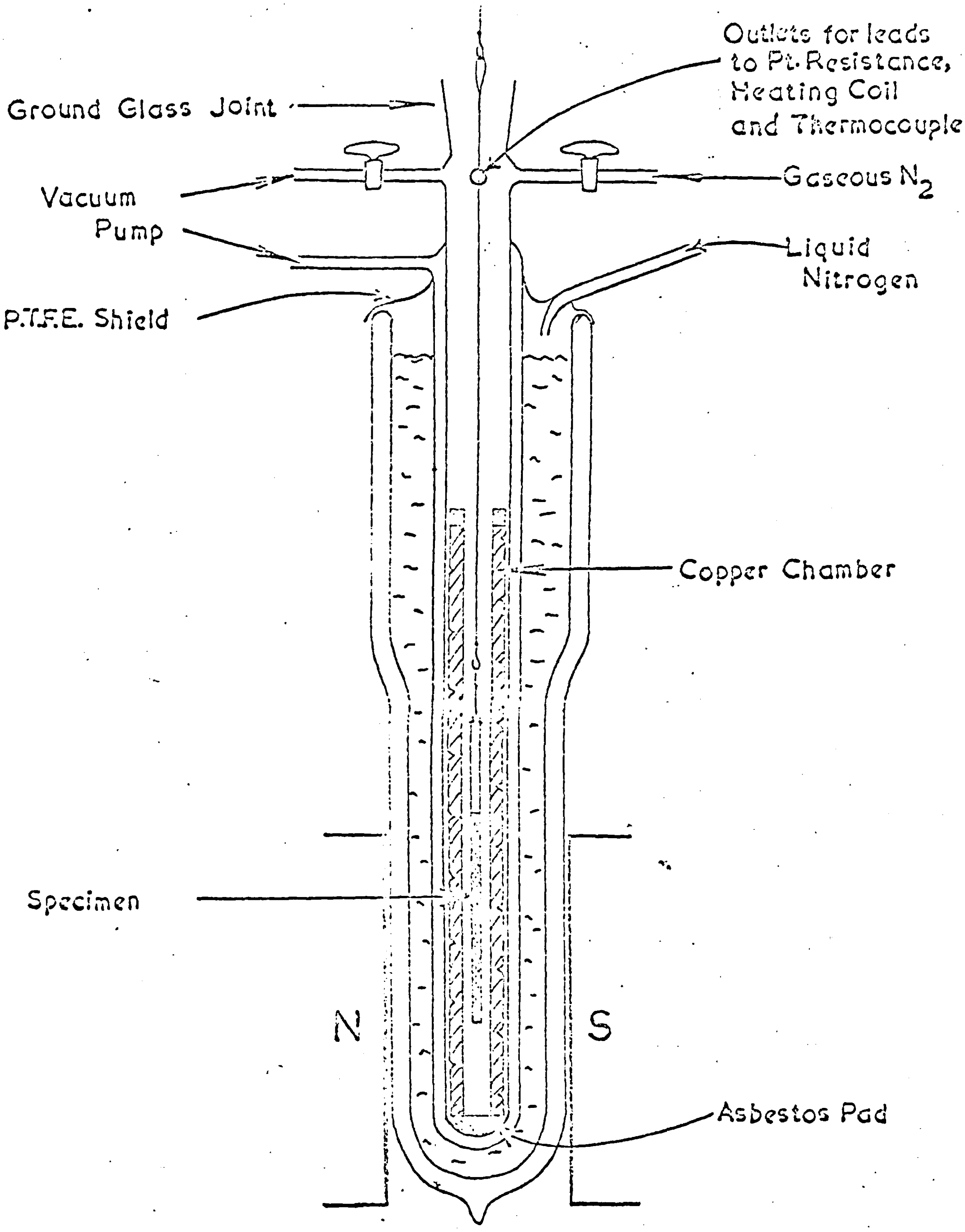
(1) Liquid nitrogen was used as the coolant. The specimen suspended inside the copper chamber was heated electrically and the heat lost from the copper to liquid nitrogen was reduced by interposing variable vacuum between them. The coolant was contained in the outer dewar which was

FIGURE;-35


Ring of Foam Rubber
Gaseous N_2
Vacuum Pump
Con. H_2SO_4
Liquid Nitrogen
Pole Pieces
Coils of Magnet

A CRYOSTAT ALLOWING AUTOMATIC TEMPERATURE CONTROL FOR A GOUY BALANCE

FIGURE[3] :-36



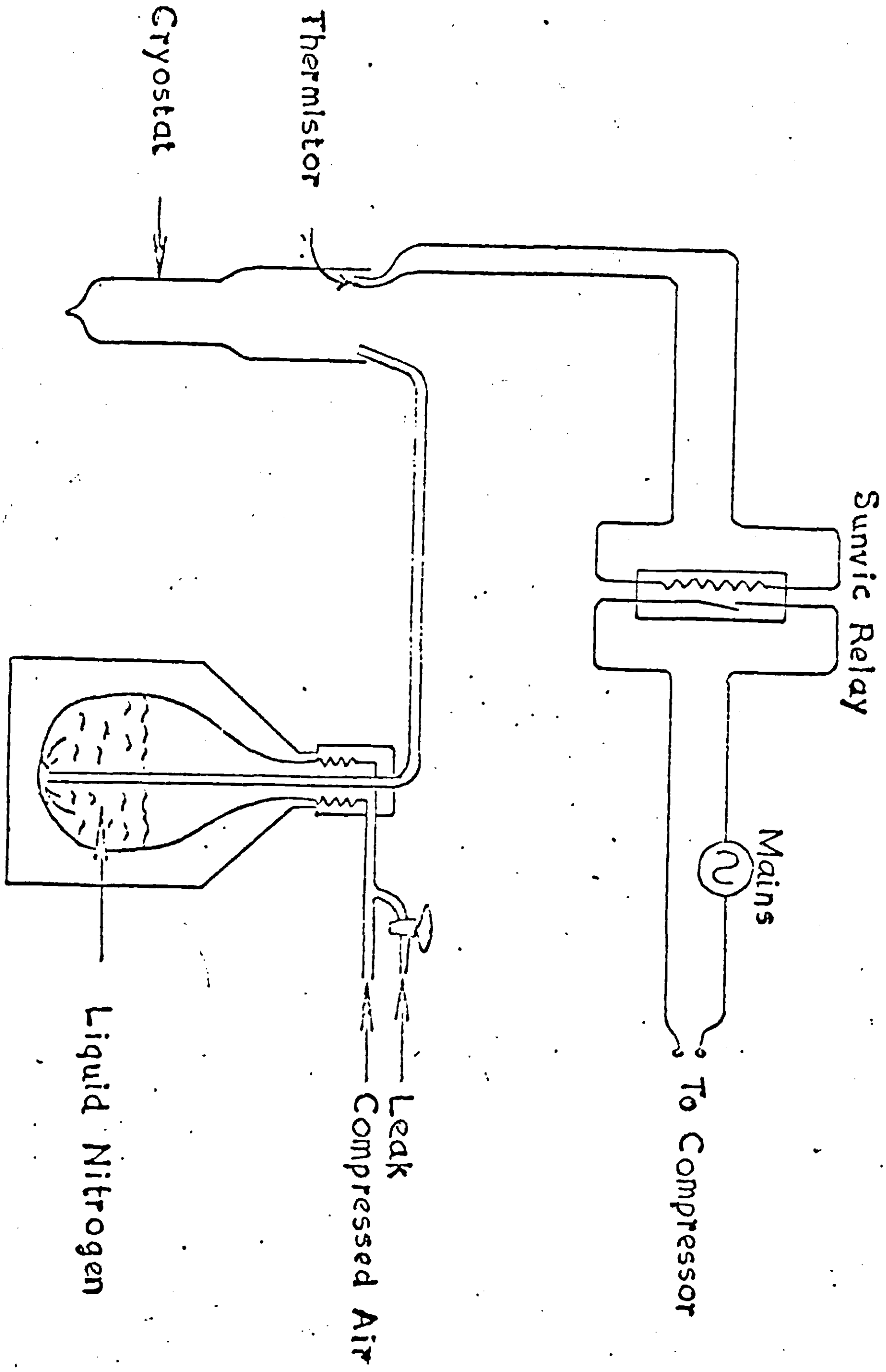
clamped permanently in position between the pole pieces of the magnet. The level of the liquid nitrogen was maintained automatically by a method illustrated in Fig.37 page 156. The coolant was forced into the dewar by the compressed air from the 1/4 h.p. compressor. It was operated by a Sunvic relay type F 102/3 M, in conjunction with thermistor 4000 ohms at room temperature. The thermistor was situated just inside the top of the dewar so that when the level of the coolant fell the resistance of the thermistor decreased sufficiently to cause the relay switch to close, thereby starting the compressor and forcing the coolant into the cryostat. With the increase of the level of the coolant, the thermistor resistance was increased and the compressor was turned off. In this way the level of the coolant was maintained in the dewar as long as the reservoir contained an adequate supply.

(2) The copper chamber was heated electrically by passing a current up to one ampere through a 54 ohms nichrome coil wound around the copper chamber. The strength of the current was regulated with the help of a variac and the current was controlled by a hot wire switch which was in turn operated by a thermostatic control.

(3) A temperature control was esentially a bridge system. One arm of which was a platinum resistance and the other a variable resistance. The platinum wire is 0.005 inch diameter with a resistance of about 20 ohms at room temperature and is around the copper chamber in a similar way to the nichrome coil from which it was insulated by a thin sheet of P.T.F.E. After the variable resistances had been set at an appropriate value, cooling of the system below the corresponding temperature produced and out of balance voltage on the bridge because of the fall in the resistance of the platinum. This out of balance voltage was used to operate a relay which switched on the heating current and restored the balance. Heating was therefore intermittent but because of the heat

FIGURE 37

CONTROL OF THE LEVEL OF LIQUID NITROGEN BY SUNVIC RELAY



capacity of the copper chamber this effect was smoothed out (detected by 'off and on' of green and red lights), and the specimen suspended in the middle attained an effectively constant temperature. The heat loss from the copper to the liquid nitrogen was reduced by interposing a vacuum between them. To avoid condensation of oxygen at the lower temperatures, it was necessary to evacuate the inside of the cryostat and to fill with nitrogen. This had also an additional advantage that no correction for the volume of the specimen was needed because of the very low susceptibility of the nitrogen ($\sim -0.0004 \times 10^{-6}$) displaced by the specimen.

(4) The temperature was measured accurately by means of a nichrome constantan thermocouple. The 'hot' junction was spot welded and the 'cold' junction silver soldered to copper leads and immersed in ice water bath. The e.m.f. was measured on a Tinsley potentiometer type 3387B with an accuracy of ± 0.000005 volts. The nichrome constantan junction was inserted half way down a narrow hole bored vertically down the wall of the copper chamber, and the temperature so measured was taken as that of the specimen itself. This was justifiable provided sufficient time was allowed for thermal equilibrium, because of the method of calibration of the thermo couple and also because of the conductivity of the copper.

Field and specimen length calibrations

Numerous substances are available as calibrants.[48, 47] Among solid calibrants, $Hg[Co(CNS)_4]$ $X_g = 16.44 \times 10^6$ at 20°C (decreasing approximately 0.05×10^{-6} per degree Centograde rise) and $[Ni(en_3)]S_2O_3$ with $X_g = 11.04 \times 10^{-6}$ at 20°C (decreasing by approximately 0.04×10^{-6} per degree Centigrade rise) are common.

Calibrations for Gouy Balance

1. The optimum position for the base of the tube between the poles of a magnetic.

By altering the suspension length on the tube the height of the base was altered relative to the centre of the poles of the magnet. Once the length was known it could easily found the optimum position for the base of the tube between the poles of a magnet.

(A) The suspended length from the hook to the centre of the poles of a magnet was shown in the form of graph of Pull or Force = F_s (versus) against length. (See fig. 38 page 159).

(B) The sensitivity of a magnet between the poles of a magnet by plotting a graph of Pull against distance from the poles was found (see fig.39 page159).

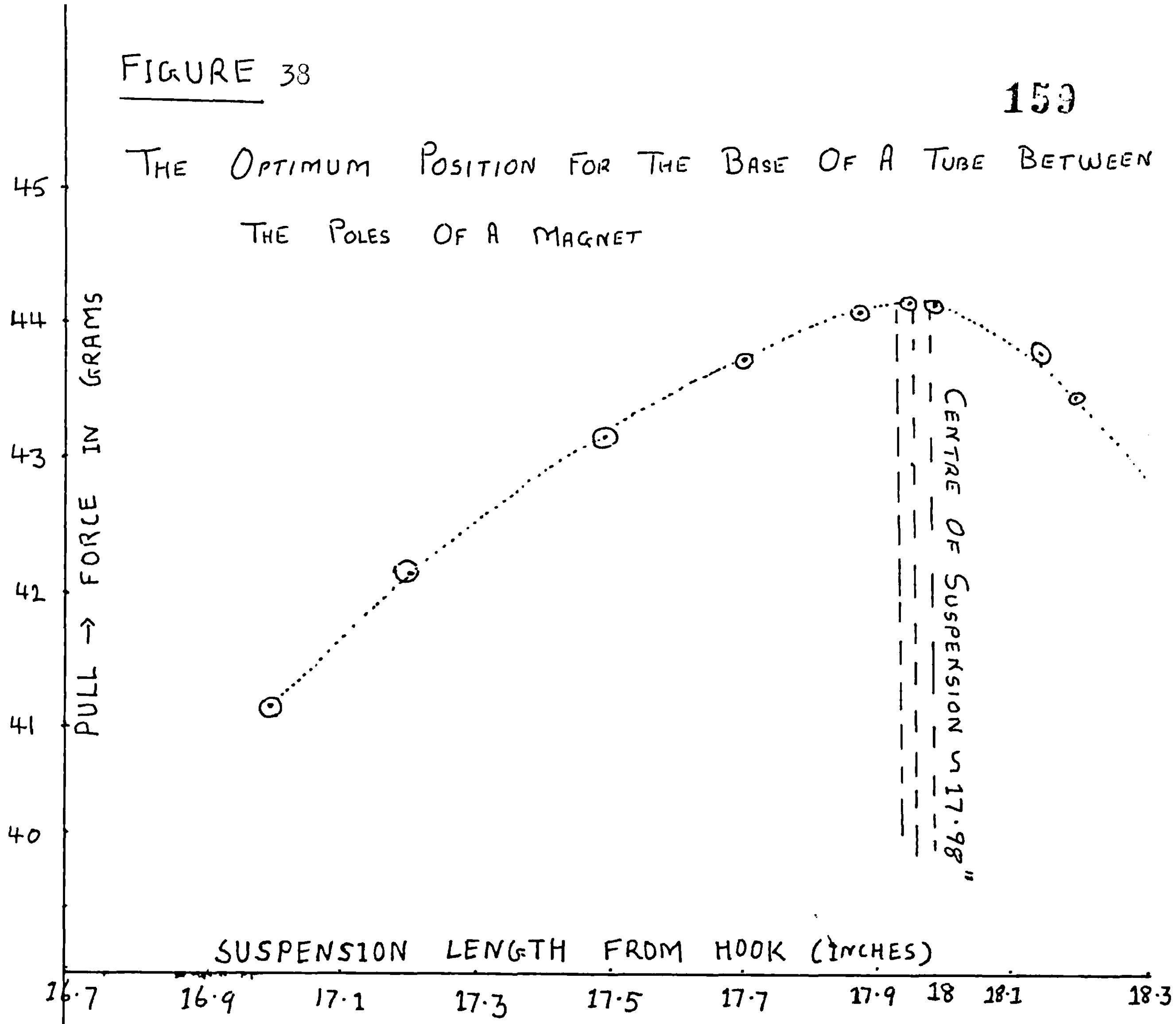
2. Effect of altering length of a specimen and current was found by plotting graphs of length "l cm" ⟶ (Pull F_s) in grams. The results were shown in the form of graphs (Fig.40).

From the graphs we could say that a minimum length of a specimen > 8.0 cm for 8 amp and 10 amp current. If the current was increased for the same length of the specimen, the pull was also increased respectively. Similarly for the constant current (same amps) if the length was decreased the pull exerted on a specimen was also decreased. The specimen used for the above experiment was ($Nien_3S_2O_3$) and the temperature was maintained at 26°C.

3. Field calibration

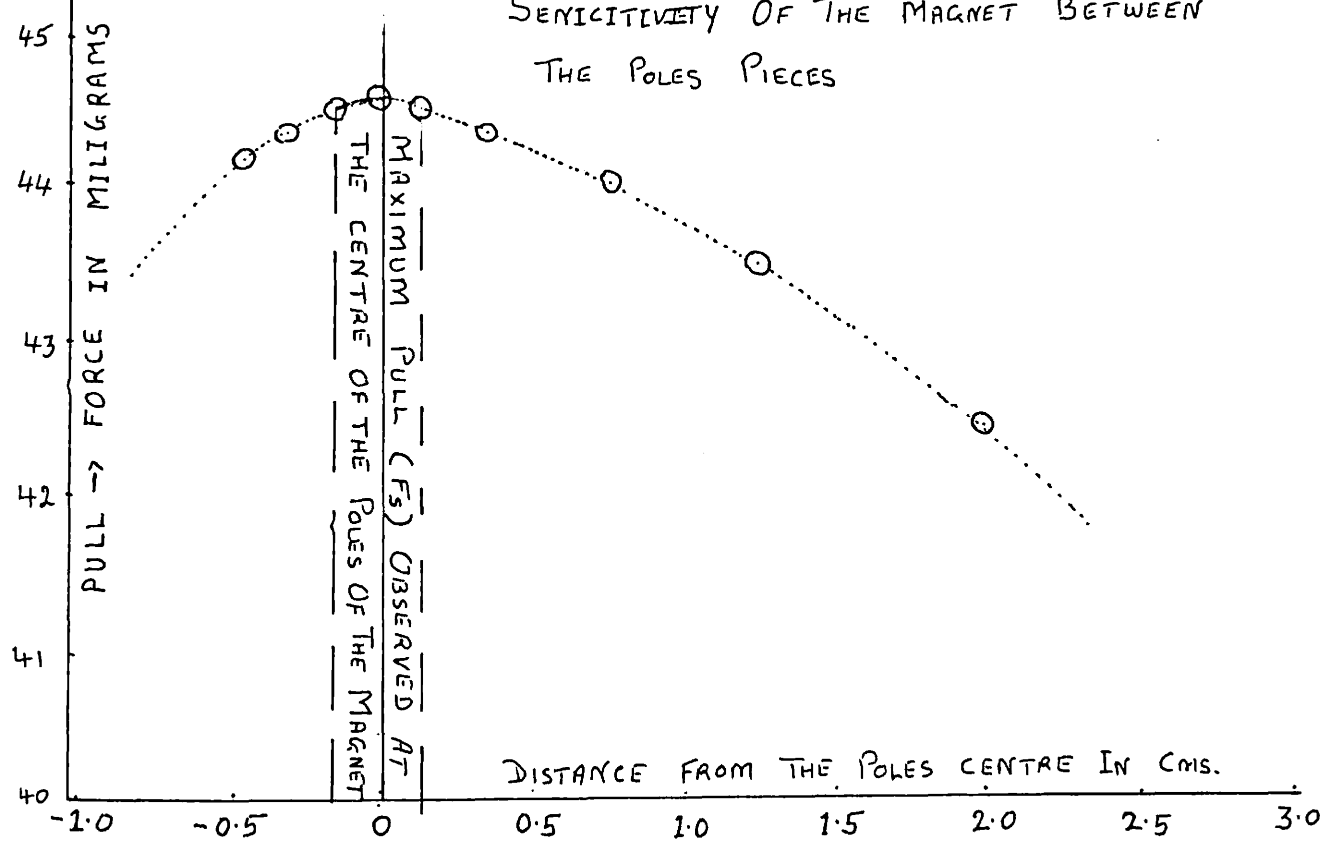
Determination of the field strengths were carried out as for a permanent magnet. The determination of a field strength was repeated for a range of different magnetic currents. The calibrants generally[47,48] used were: (1) nickel chloride solution; (2) $Hg[CO(CNS)_4]$; (3) $Nien_2(S_2O_3)$.

FIGURE 38



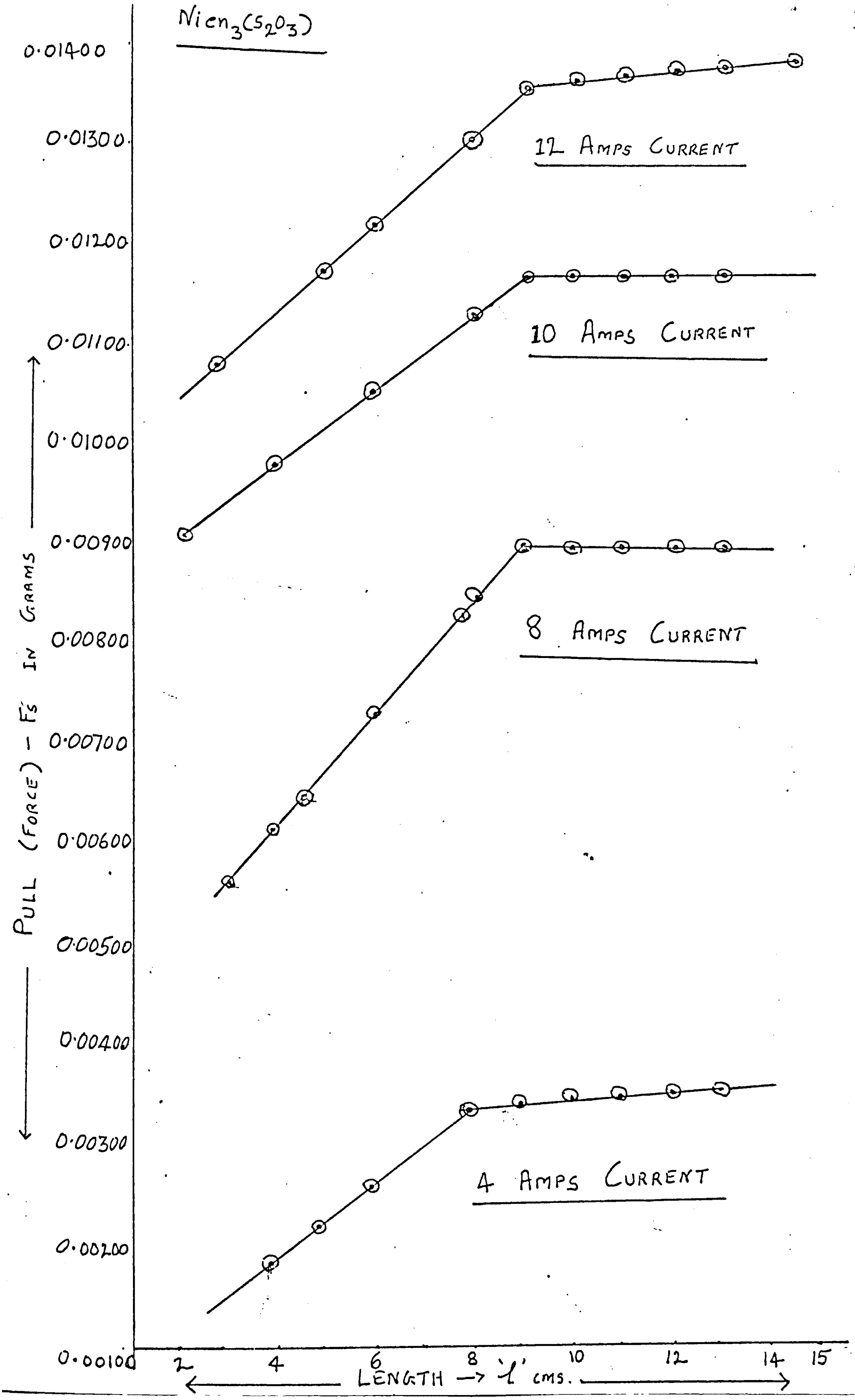
The Optimum Position For The Base Of A Tube Between The Poles Of A Magnet

Figure:-39



Senicitivety Of The Magnet Between The Poles Pieces

FIGURE-40. EFFECT OF ALTERING LENGTH OF SPECIMEN AND CURRENT ON $Nien_3(S_2O_3)$



Using the equation (of the susceptibility) where

F_s = Pull in dynes/mg

W_s = Weight of a substance in g

ℓ_s = Length of a substance in cm

g = Gyromatic constant = 98

χ_c = Susceptibility of a (calibrant) substance

$$\chi_c = \frac{2 \times F_s \times \ell_s \times g}{W_s\, H^2}$$

$$= \frac{2 \times g \times \ell_s}{H^2} \times \frac{F_s}{W_s} = \alpha \frac{F_s}{W_s}$$ where α = balance constant

$$= \frac{2 \times g\, \ell_s}{H^2}$$

$$\therefore\ H^2 = \frac{2 \times g \times \ell}{\chi_c \times W_s} \times F_s$$

The results were plotted in the form of graph of log H^2 ⟶ specimen length (ms) and hence the graphical values of log H^2 were used in calculating for log α and α.

Field calibrations were carried out at 2 amps, 3 amps, 4 amps, 5 amps, 10 amps (see Figs. 41, 42 pages 162, 163).

FIGURE 41

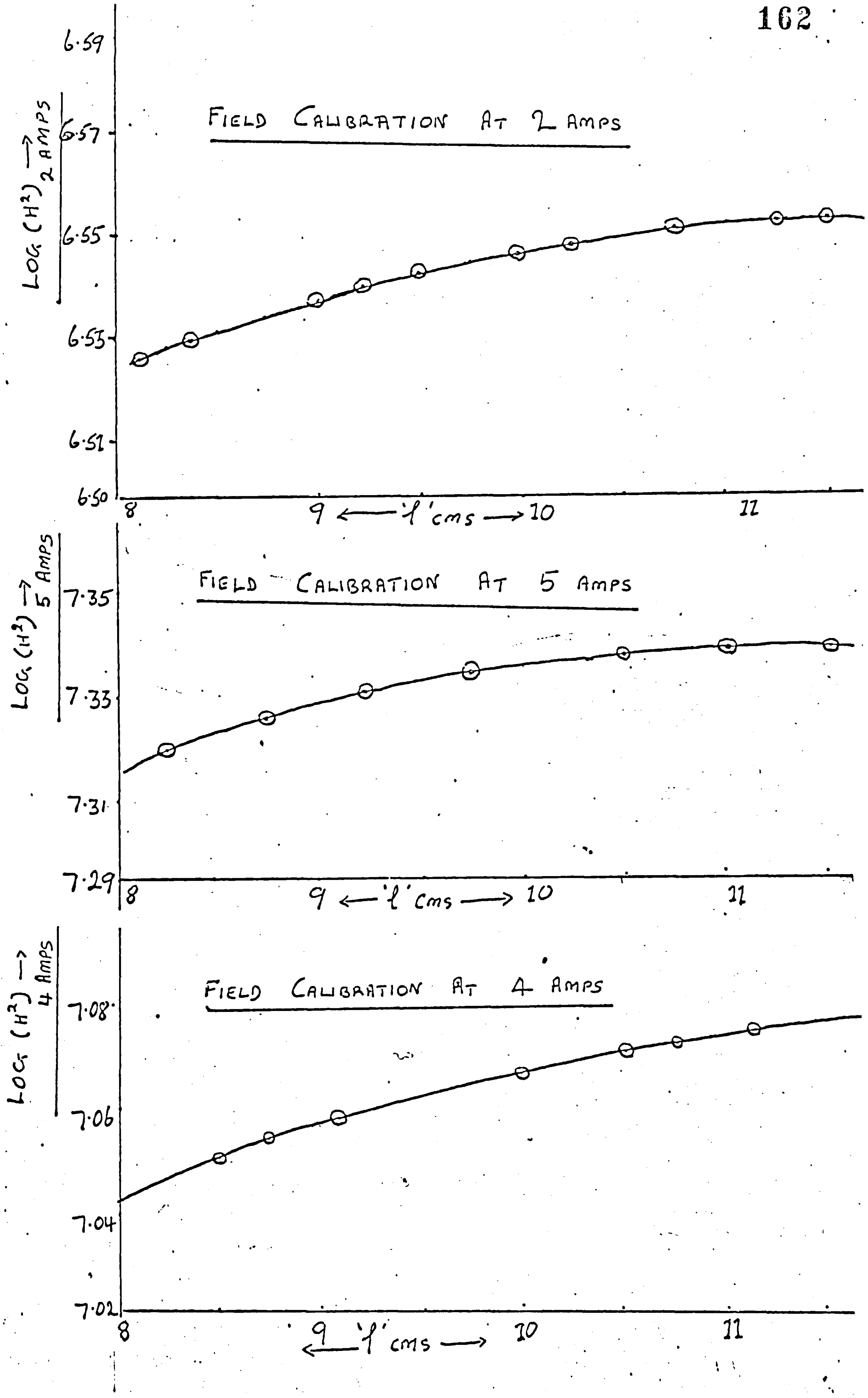

FIELD CALIBRATION AT 2 AMPS
LOG (H²) → 2 AMPS
6.59
6.57
6.55
6.53
6.51
6.50
8
9 ← 'l' cms → 10
11
FIELD CALIBRATION AT 5 AMPS
LOG (H²) → 5 AMPS
7.35
7.33
7.31
7.29
8
9 ← 'l' cms → 10
11
FIELD CALIBRATION AT 4 AMPS
LOG (H²) → 4 AMPS
7.08
7.06
7.04
7.02
8
9 ← 'l' cms → 10
11

FIGURE:-42

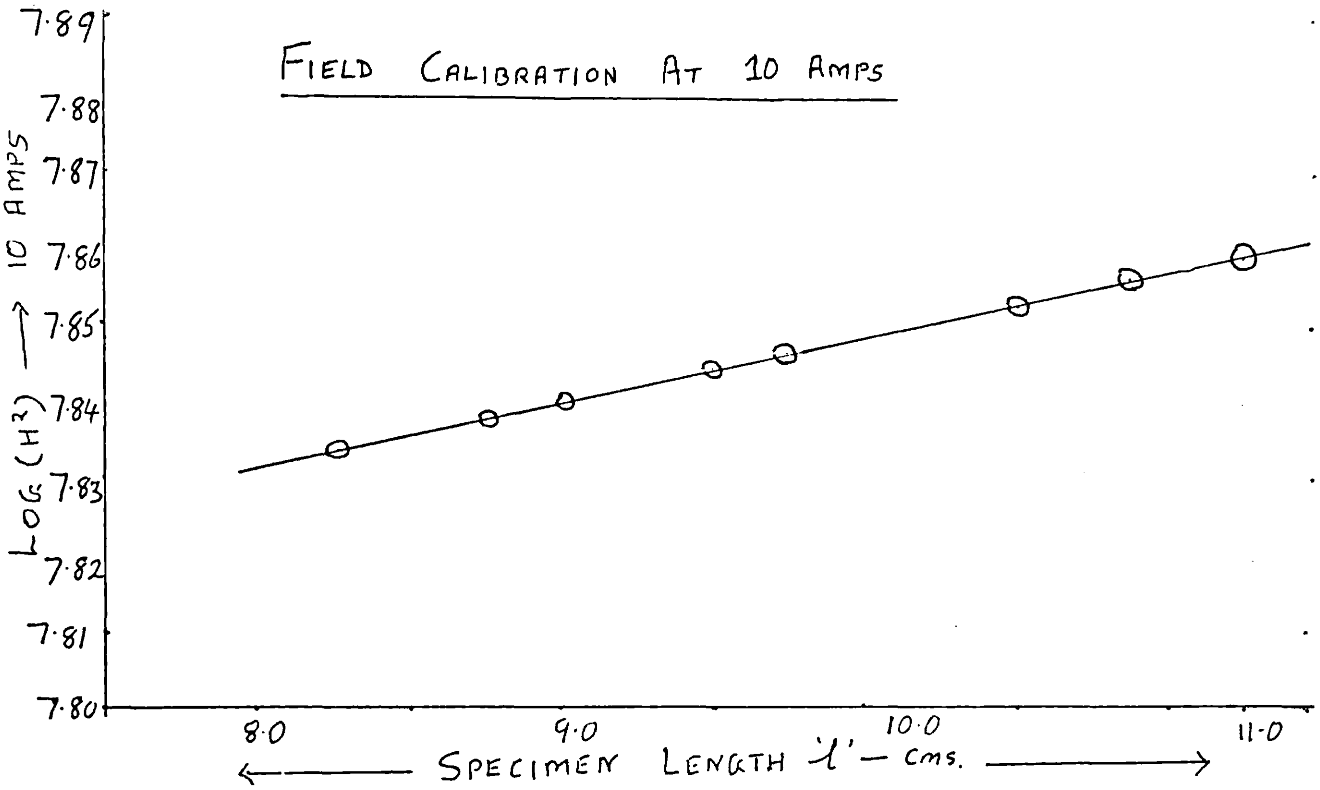
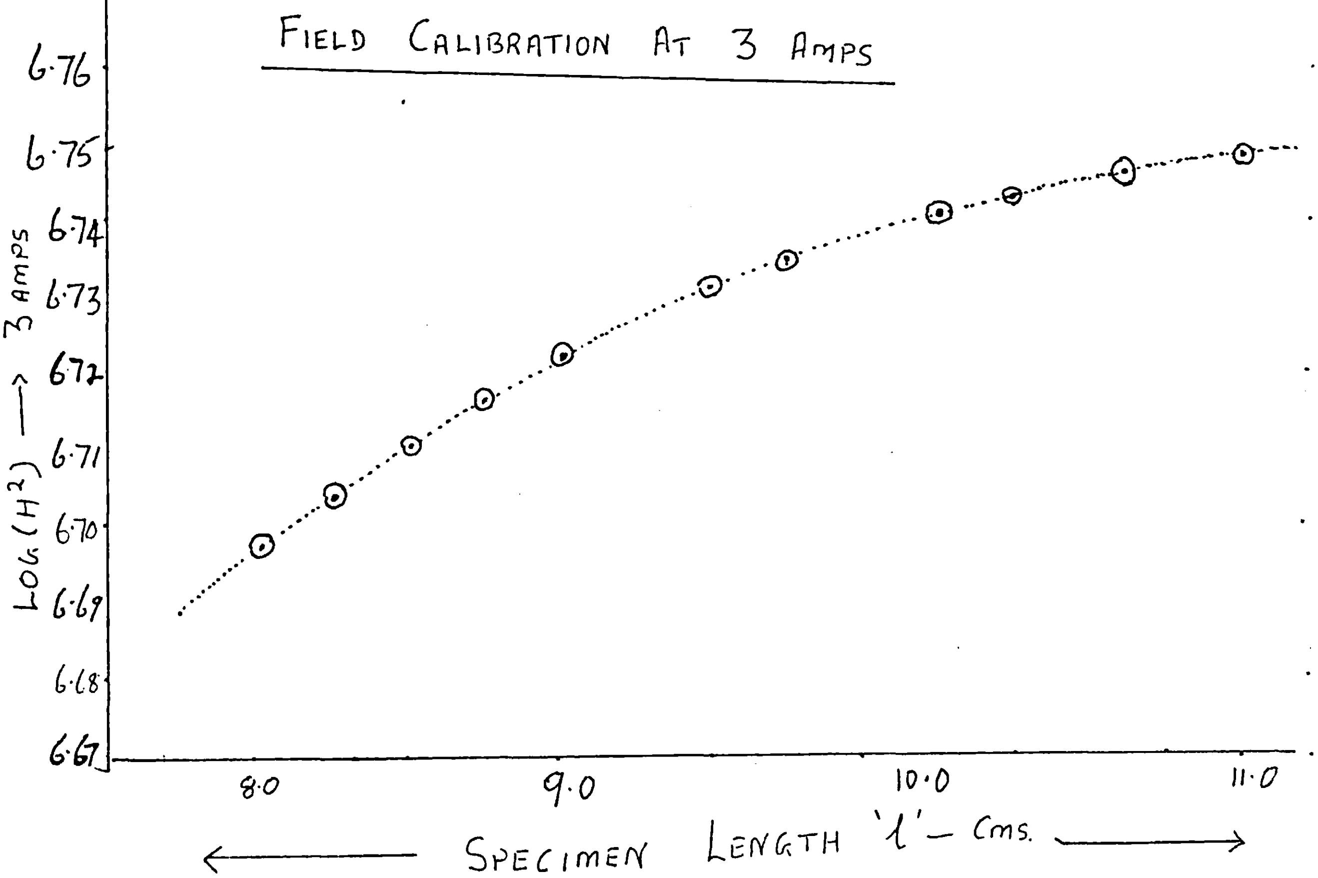


FIGURE:- 43



Results and Discussion of Magnetic Susceptibility Measurements

The variation with temperature in the range 80-300°K of X_A and μeff of the diamine complexes are shown in Tables 19 - 39. The reciprocals of their magnetic susceptibilities decrease linearly with temperatures down to liquid nitrogen temperatures as shown in Figs.

The Curie-Weiss constants are given in Tables 19 - 39. Magnetically normal low spin nickel(III) complexes should have spin only magnetic moments 1.7 - 1.8 B.M. for one unpaired electron. The nickel(III) ion has the d^7 configuration and the present magnetic measurements suggest low spin $t_{2g}^6 e_g^1$ ground state, although the temperature dependence magnetic moment is surprising for an E_g level.

The magnetic moments are significantly above the spin-only value and a thermal equilibrium between low and high spin configurations seems possible, implying that the value of Dq/B lies only slightly beyond the ^4T_1g - ^2Eg cross over point. For ^2Eg ($t_{2g}^6 e_g^1$) ground state we have a single electron in a doubly degenerate 'σ' level which would give rise to substantial Jahn-Teller configurational instability. The inclusion of spin-orbit coupling does not affect this conclusion since ^2Eg ground state is not a Kramer's doublet and can therefore split by Jahn-Teller distortion. It has been found by Figgis[67] that a tetragonal distortion is expected to lead a variation of magnetic moments with temperatures. The complexes investigated do so decreasing magnetic moments with decreasing temperatures.

Trew[116] et. al. have suggested a small magnetic coupling between two nickel ions in the binuclear complex $[Ni_2en_4Cl_2]Cl_2$. Porai-Koshits[117] found that this compound was in fact a cis-dimer by crystallographic analysis.

Compounds which show antiferromagnetic interactions are discussed later in page 194.

Thus the following possibilities exist for the magnetic behaviour.

(1) There is a marked deviation from octahedral - due to the Jahn-Teller effect.

(2) There is metal-metal interaction brought about by dimerisation or polymerisation.

(3) The individual Ni atoms in the polymers have tetragonal environments.

The only other explanation for a temperature dependent moment is that the compound is tetrahedral. Molecular weight determinations and magnetic susceptibilities measurements in solutions are desirable to determine whether the polymeric nature of the compounds persists in solution, but because of their limited solubility in organic solvents and unstable nature, these are not possible.

TABLE 19

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

Compound $\mathrm{Nien_2Cl_3}$, Field 5 amps

Temp °K	$X'_M \times 10^6$	$X'_A \times 10^6$	$^1/_{X'_A} \times 10^{-2}$	μeff B.M.
297.1	1434.0	1596.2	6.264	1.955
284.5	1505.0	1667.2	6.000	1.955
269.1	1592.0	1754.2	5.700	1.952
242.0	1787.0	1949.2	5.130	1.951
221.7	2066.0	2128.2	4.700	1.946
180.3	2463.0	2625.2	3.810	1.954
142.7	3116	3278.2	3.050	1.942
126.1	3528	3690.2	2.710	1.936
107.0	4148	4310.2	2.320	1.929
86.0	5030	5192.2	1.926	1.893

$\theta = -5^\circ$ Dia. corrn. x 10^6 = -162.2

Compound $\mathrm{en_2Br_3\frac{1}{2}H_2O}$ Field 5 amps

Temp °K	$X'_M \times 10^6$	$X'_A \times 10^6$	$^1/_{x'_A} \times 10^{-2}$	μeff B.M.
296.1	1408	1610.3	6.21	1.96
282.0	1690	1892.3	5.91	1.961
269.1	1552	1754.3	5.701	1.949
240.8	1758	1960.3	5.102	1.952
221.0	1906	2128.3	4.70	1.947
183.0	2362	2564.3	3.900	1.945
144.1	3045	3247.3	3.079	1.943
126.1	3502	3704.3	2.70	1.941
111.0	4053	4255.3	2.35	1.943
88.0	4926	5128.3	1.95	1.907

$\theta = -10^\circ$ Dia. corrn. x 10^6 = -202.3

TABLE 20

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

* Compound en_2ICl_2 Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.8	1398	1587.4	6.30	1.949
280.7	1477	1666.4	6.0	1.942
244.0	1722	1916.4	5.22	1.941
224.3	1890	2079.4	4.81	1.939
210.3	2009	2198.4	4.55	1.931
180.3	2369	2558.4	3.91	1.929
140.6	3089	3278.4	3.05	1.928
110.0	3978	4167.4	2.40	1.923
88.0	4938	4927.4	2.03	1.849

θ = -8°

Dia. Corrn. x 10^{-6} = -189.4

* Compound en_2IBr_2 Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.3	1422.0	1623.8	6.162	1.970
280.1	1544.0	1745.8	5.731	1.950
234.0	1799.0	2000.8	5.00	1.943
201.3	2119.0	2320.8	4.31	1.941
173.0	2487.0	2688.8	3.72	1.936
107.0	4128.0	4329.8	2.31	1.933
86.0	5062.0	5263.8	1.900	1.910

θ = -12°

Dia. Corrn x 10^{-6} = -201.80

TABLE 21

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

Compound $Nien_2Cl_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
297.0	1285	1473.3	6.799	1.878
282.1	1350	1538.3	6.503	1.869
270.3	1404	1592.3	6.281	1.863
245.0	1566	1754.3	5.701	1.862
210.0	1853	2041.3	4.91	1.858
171.0	2312	2500.3	4.0	1.857
145.8	2669	2857.3	3.50	1.846
110.0	3488	3676.3	2.720	1.805
88.2	4276	4464.3	2.240	1.782

$\theta = -12°$

Dia. Corrn. x 10^{-6} = -188.28

*

Compound $en_2Br_2Cl,\frac{1}{2} H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
296.3	1347.0	1538.10	6.503	1.921
280.1	1427	1618.1	6.182	1.912
263.0	1533	1724.1	5.801	1.911
243.0	1668	1859.1	5.379	1.865
210.3	1959	2150.1	4.651	1.864
172.0	2309	2500.1	4.00	1.862
136.9 (137.0)	2934	3125.1	3.20	1.859
110.3	3874	4065.1	2.46	-
86.0	4736	4927.1	2.030	1.848

$\theta = -8°$

Dia. Corrn. x 10^{-6} = -191.10

Reciprocal magnetic susceptibility against temperature and magnetic moments against temperature for:-

FIG. 44

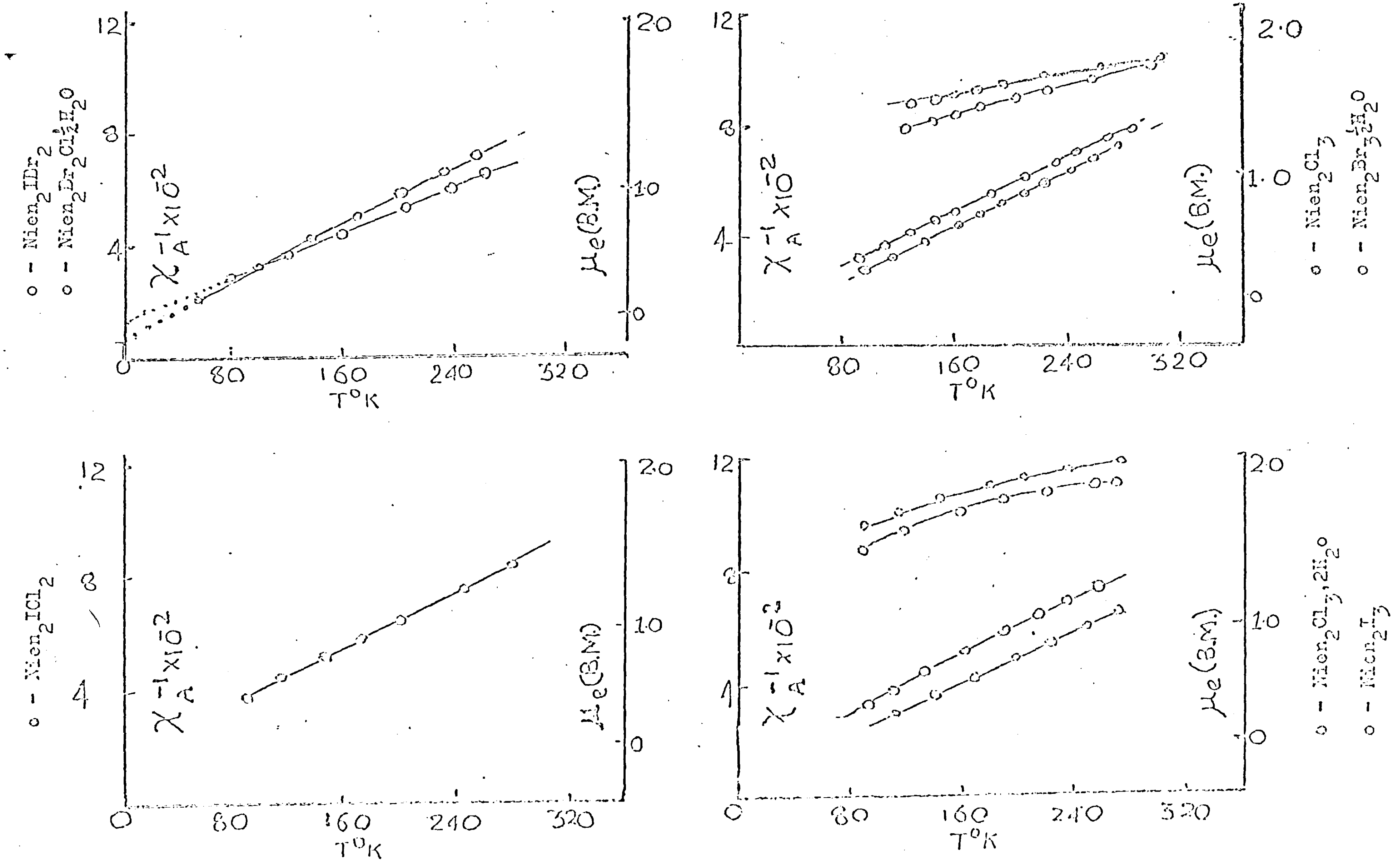


TABLE 22

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound en$_2$Cl$_2$(ClO$_4$) Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.0	1391	1539	6.498	1.92
282.1	1455	1603	6.239	1.914
272.8	1518	1666	6.002	1.914
244	1690	1838	5.441	1.902
222.5	1893	2041	4.900	1.90
196.1	2161	2309	4.332	1.90
150.0	2855	3003	3.33	1.893
126.8	3398	3546	2.82	1.891
112.8	3852	4000	2.50	1.884
88.0	4716	4864	2.056	1.852

$\theta = -12°$ Dia. Corrn. x 10^{-6}=-148

*

Compound en$_2$Cl$_2$(NO$_3$) Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.0	1380	1515	6.602	1.920
282.0	1452	1587	6.300	1.912
272.3	1504	1639	6.102	1.900
243.8	2107	2242	4.460	1.898
223.8	2107	2242	5.00	1.898
196.6	2135	2270	4.405	1.897
153.0	2808	2943	3.397	1.894
128.2	3327	3462	2.888	1.892
112.0	3787	3922	2.550	1.882
88.0	4673	4808	2.080	1.847

$\theta = -10°$ Dia. Corrn. x 10^{-6}=-135.0

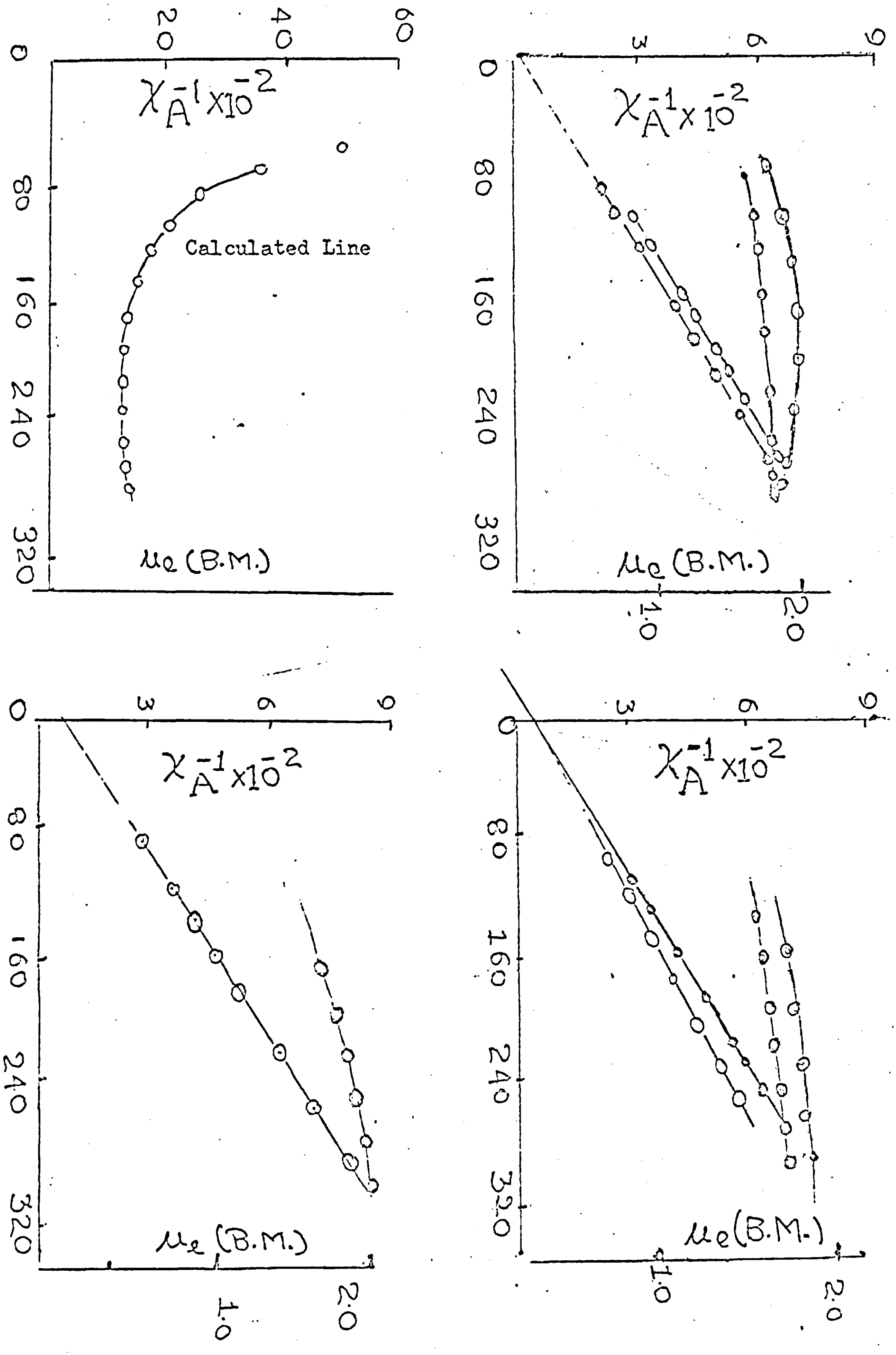
FIG. 45

Reciprocal magnetic susceptibility against temperature and magnetic moments against temperature for:-

o - $Nien_2Cl_3$

o - $Nien_2Cl_2(ClO_4)$

o - $Nien_2Cl_2(NO_3)$



o - $NiPn_2BrCl_2$

● - $NiPn_2Br_3$

o - $NiPn_2Cl_3$

TABLE 23

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

Compound $Nien_2I_3$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/X'_A x10^{-2}$	μeff B.M.
297.1	1263	1506	6.638	1.902
284.5	1344	1587.8	6.30	1.901
269.1	1396	1639.8	6.11	1.901
242.0	1579	1822.8	5.489	1.891
221.7	1979	2222.8	4.50	-
176.0	2257	2500.8	4.00	1.884
142.7	2881	3124.8	3.21	1.884
126.1	3293	3546.8	2.82	1.883
107.0	3739	4082.8	2.45	1.869
86.0	4707	4950.8	2.024	1.852

$\Theta = -12^\circ$

Dia Corrn. x $10^{-6} = -243.80$

TABLE 24

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound Pn_2Cl_3 Field 5 amps

Temp °K	$X'_M \times 10^6$	$X'_A \times 10^6$	$^1/_{X'_A} \times 10^{-2}$	μeff B.M.
298.0	1286.0	1473.08	6.789	1.881
280.0	1361	1548.08	6.461	1.870
246.1	1568	1755.08	5.698	1.866
210.0	1841	2028.08	4.931	1.853
182.0	2138	2325.08	4.301	1.848
144.3	2670	2857.08	3.50	1.824
110.2	3465	3652.08	2.738	1.801
90.3	4076	4263.08	2.346	1.761

$\theta = -18^\circ$ Dia. corrn. x $10^{-6} = -187{,}08$

*

Compound Pn_2Br_3 Field 5 amps

Temp °K	$X'_M \times 10^6$	$X'_A \times 10^6$	$^1/_{X'_A} \times 10^{-2}$	μeff B.M.
296.1	1328	1548.7	6.461	1.923
280.3	1406	1626.7	6.151	1.918
244.1	1621	1841.7	6.432	1.904
207.0	1926	2146.7	4.66	1.902
1803	2231	2451.7	4.08	1.889
146.3	2783	3003.7	3.33	1.882
110.2	3597	3817.7	2.62	1.842
88.4	4350	4570.7	2.188	1.803

$\theta = -22^\circ$ Dia. corrn x $10^{-6} = -220.68$

TABLE 25

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*Compound Pn_2BrCl_2 Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/X'_A x10^{-2}$	μeff B.M.
296.1	1415.0	1613.3	6.20	1.961
280.1	1497.0	1695.3	5.899	1.954
244.3	1726	1924.3	5.199	1.947
210.1	2024	2222.3	4.50	1.940
180.0	2366	2564.3	3.90	1.931
144.2	2917	3115.3	3.21	1.904
110.0	3786	3984.3	2.51	1.881
90.0	4466	4664.3	2.144	1.820

$\theta = -20^\circ$ Dia. corrn. x 10^{-6} = −198.28

*Compound $Pn_2ICl_2,2H_2O$

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/X'_A x10^{-2}$	μeff B.M.
298.0	1342	1577.3	6.34	1.947
279.0	1449	1684.3	5.947	1.946
268.0	1516	1751.3	5.711	1.945
244.0	1688	1923.3	5.20	1.945
210.0	1987	2222.3	4.50	1.940
180.3	2216	2451.3	4.081	1.887
142.0	2871	3106.3	3.22	1.887
110.1	3765	4000.3	2.50	1.884
88.6	4395	4630.3	2.16	1.820

$\theta = -20^\circ$ Dia. corrn. x 10^{-6} = -235.28

TABLE 26

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

* Compound $Pn_2Cl_2(ClO_4)$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.0	1370	1544	6.477	1.921
283.1	1439	1613	6.200	1.917
274.0	1493	1667	5.998	1.917
244.0	1678	1852	5.400	1.910
223.1	1851	2025	4.938	1.910
196.8	2172	2346	4.230	1.90
151.0	2711	2885	3.466	1.869
128.0	3159	3333	3.00	1.855
112.0	3585	3759	2.661	1.841
88.4	4088	4262	2.346	1.748

$\theta = -24°$ Dia. Corrn. x 10^{-6} = -174

* Compound $Pn_2Cl_2(NO_3)$ Field 5 amps

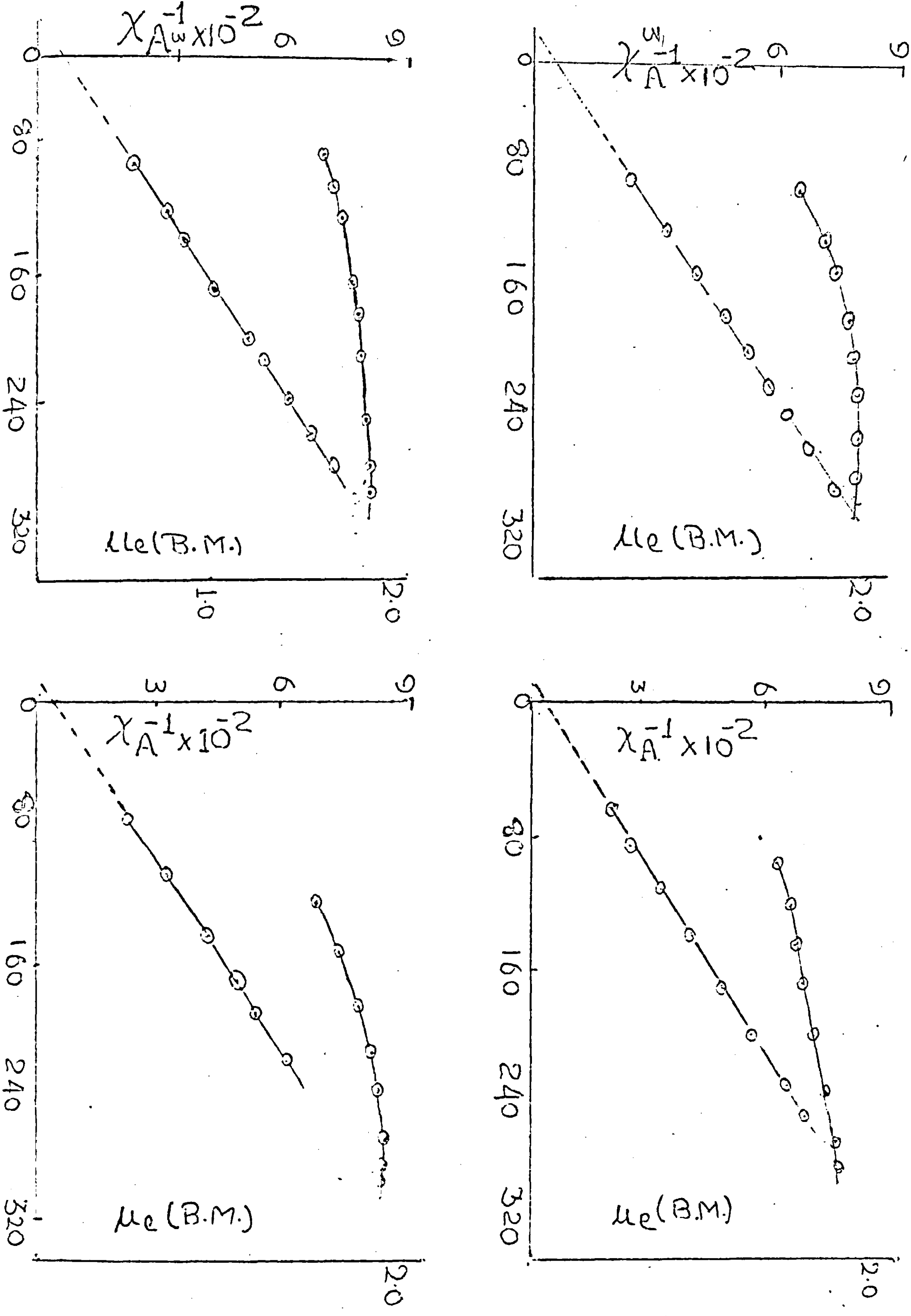
Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'} x10^{-2}$	μeff B.M.
296.0	1379	1541	6.490	1.921
283.1	1454	1616	6.189	1.928
273.8	1504	1666	6.002	1.918
244.0	1705	1867	5.356	1.917
221.3	1883	2045	4.890	1.911
196.0	2119	2281	4.384	1.900
150.0	2779	2941	3.400	1.891
125.1	3300	3462	2.888	1.868
112.0	3615	3777	2.648	1.847
85.6	4105	4267	2.344	1.716

$\theta = -22°$ Dia. Corrn. x 10^{-6} = -162.

FIG. 46

NiPn$_2$ICl$_2$,2H$_2$O

NiPn$_2$Cl$_2$(NO$_3$)



NiPn$_2$IBr$_2$

NiPn$_2$Cl$_2$(ClO$_4$)

Reciprocal magnetic susceptibility against temperature and magnetic moments against temperature for:-

TABLE 27

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

Compound $NiPn_2IBr_2$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
297.3	1361	1587.7	6.3	1.951
280.0	1423	1653.7	6.05	1.932
270.3	1489	1715.7	5.832	1.932
246.1	1682	1908.7	5.342	1.926
210.3	1942	2173.7	4.601	1.918
180.2	2274	2500.7	4.00	1.905
146.3	3758	3984.7	2.35	-
110.3	4029	4255.7	2.51	1.900
90.0	4340	4566.7	2.19	1.823

$\theta = -24^0$ Dia Corrn. x 10^{-6} = -226.68

TABLE 28

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound $en_3Cl_3,HCl,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
296.1	1212.0	1470.6	6.803	1.886
286.0	1280.0	1538.6	6.503	1.884
272.0	1355.0	1613.6	6.20	1.881
243.9	1525.0	1783.6	5.608	1.874
224.1	1665.0	1923.6	5.20	1.864
180.	2117.0	2375.6	4.21	1.857
144.2	2615	2873.6	3.48	1.828
125.3	3075	3333.6	3.90	1.824
110.0	3418	3676.6	2.720	1.806
88.0	4237.0	4495.6	2.224	1.746

$\theta = 0^o$ Dia. Corrn. x 10^{-6} = -258.6

*

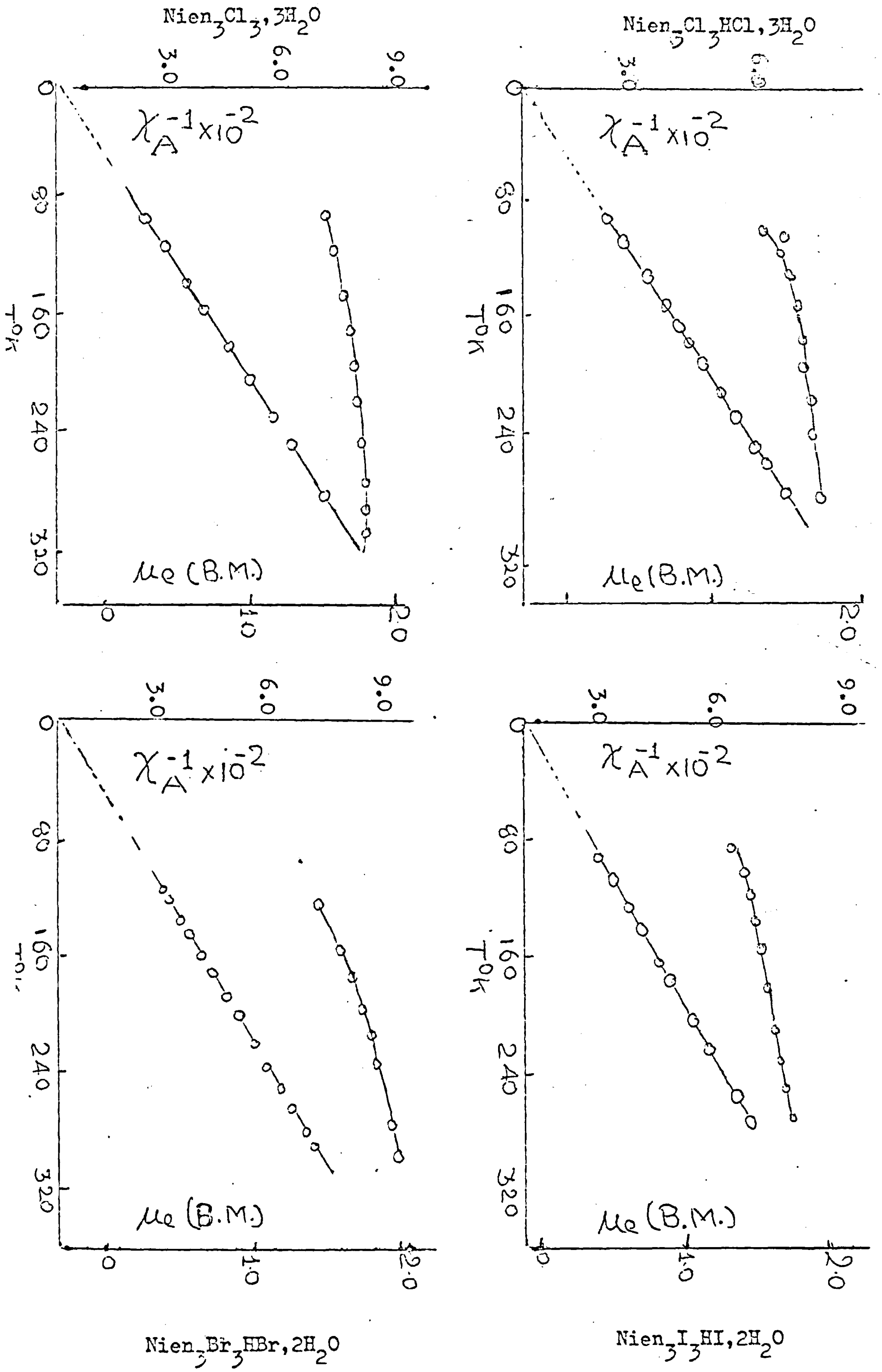
Compound $en_3Br_3,HBr,2H_2O$ Field 5 amp

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
296.0	1088.0	1391.4	7.189	1.823
280.4	1667.0	1370.4	7.299	1.760
246.3	1230	1543.4	6.481	1.751
224.1	1363.0	1666.4	6.002	1.734
180.2	1760.0	2063.4	4.847	1.732
145.3	2197.0	2500.4	4.00	-
125.4	2554.0	2857.4	3.50	1.700
110.0	2877	3180.4	3.145	1.682
90.0	3543	3846.4	2.60	1.672

$\theta = 0^o$ Dia. Corrn. x 10^{-6} = -303.4

FIG. 47

Reciprocal magnetic susceptibility against temperature and magnetic moments against temperature for:



Nien$_3$Cl$_3$,3H$_2$O

Nien$_3$Cl$_3$HCl,3H$_2$O

Nien$_3$Br$_3$HBr,2H$_2$O

Nien$_3$I$_3$HI,2H$_2$O

TABLE 29

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound $en_3I_3,HI,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
298.1	1148.0	1515.4	6.602	1.908
280.0	1113.0	1480.4	6.751	1.828
260.0	1114.0	1481.4	6.752	1.762
246.0	1195.0	1562.4	6.402	1.760
222.1	1357.0	1724.4	5.801	1.758
180.2	1716.0	2083.4	4.801	1.740
144.1	2197.0	2564.4	3.900	1.727
123.9	2574.0	2941.4	3.400	1.714
88.9	3665.0	4032.4	2.480	1.700

$\theta = 0°$ Dia. Corrn. x 10^{-6} = -367.40

*

Compound $en_3Cl_3,3H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.3	1263	1510.2	6.623	1.900
280.0	1340	1587.2	6.30	1.892
273.8	1366	1613.2	6.20	1.889
243.2	1565	1812.2	5.519	1.886
210.1	1832	2079.2	4.810	1.877
180.3	2163	2410.2	4.149	1.873
146.1	2703	2950.2	3.39	1.864
124.1	3201	3448.2	2.90	1.853
110.4	3599	3846	2.60	1.850
88.0	4340	4587	2.28	1.805

$\theta = 0°$ Dia. Corrn. x 10^{-6} = -247.2

TABLE 30

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound $en_3Br_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
296	1295	1562.8	6.402	1.932
281.6	1346	1613.8	6.20	1.915
242.1	1609	1876.8	5.33	1.914
226.3	1733	2000.8	5.00	1.911
210.	1842	2119.8	4.719	1.894
178.0	2233	2500.8	4.00	1.894
146.2	2736	3003.8	3.33	1.882
112.3	3279	3546.8	2.82	1.793
110.0	3609	3876.8	2.58	-
85.0	4385	4652.8	2.15	1.786

$\theta = 0^o$ Dia. Corrn. x $10^{-6} = -267.8$

*

Compound en_3I_3 Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
298.0	1248.0	1537.8	6.503	1.923
280.4	1203	1492.8	6.701	1.838
262.4	1248	1537.8	6.503	1.804
242.0	1377	1666.8	6.002	1.804
222.0	1503	1792.8	5.58	1.792
180.2	1884	2173.8	4.601	1.778
146.2	2343	2632.8	3.801	1.722
110.0	3144	3333.8	3.00	1.719
90.0	3743	4032.8	2.48	1.711

$\theta = -4^o$ Dia. Corrn. x $10^{-6} = -289.8$

TABLE 31

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound Pn_3Br_3 Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
297.0	1264	1543	6.481	1.923
270.0	1415	1694	5.902	1.921
246.3	1566	1845	5.420	1.914
210.0	1858	2137	4.680	1.902
180.4	2172	2451	4.080	1.888
146.1	2654	2933	3.410	1.887
107.0	3689	3968	2.520	1.879
90.0	4013	4292	2.330	1.765

$\theta = -5^o$ Dia. Corrn. x 10^{-6} = -279.12

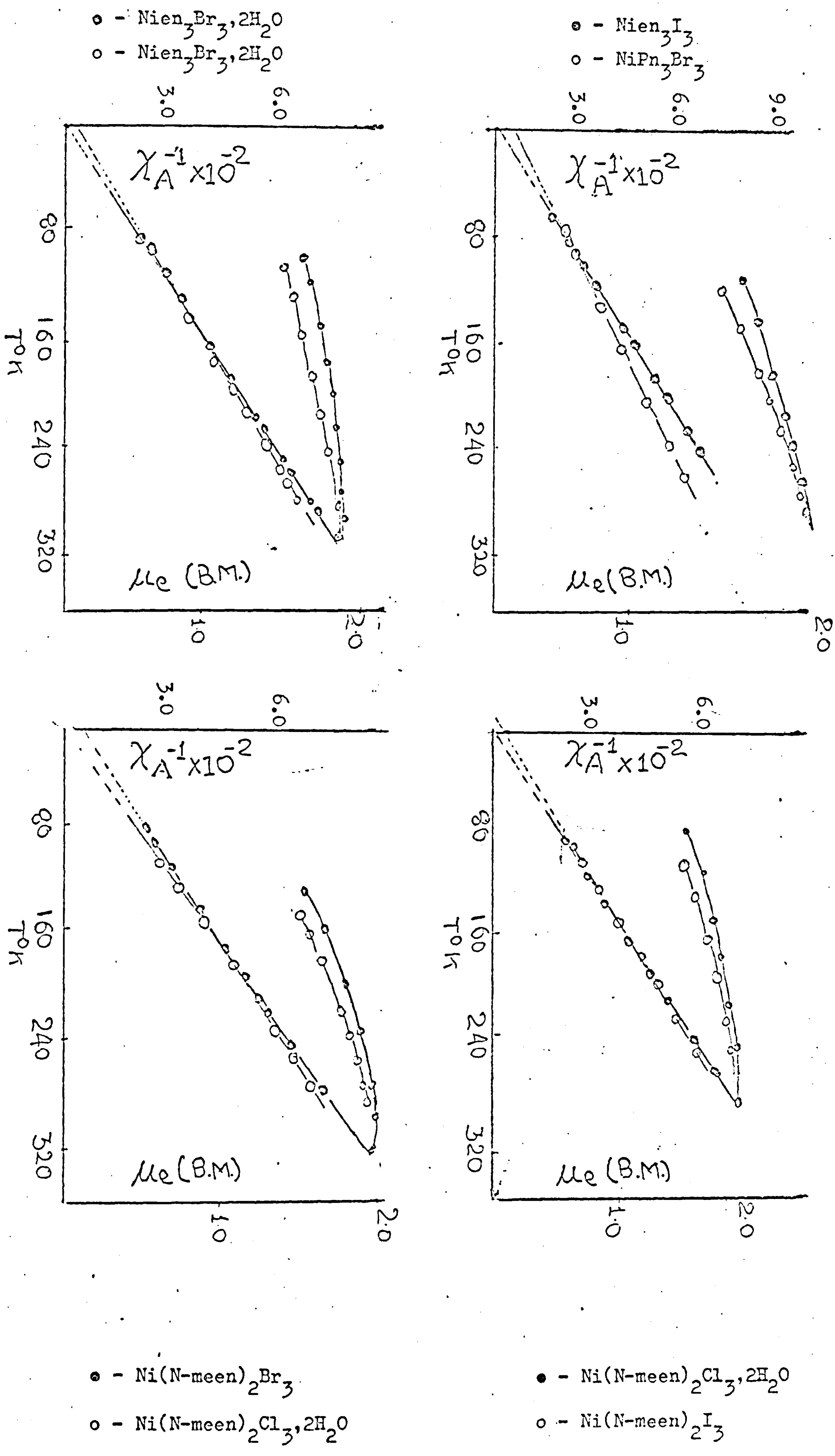
*

Compound $Pn_3Br_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
297.0	1231	1536.1	6.511	1.918
280.3	1318	1623.1	6.160	1.915
272.9	1361	1666.1	6.00	1.914
242.8	1551	1856.1	5.388	1.905
207.0	1868	2173.1	4.60	1.904
180.1	2146	2452.1	4.08	1.888
144.2	2688	2993.1	3.34	1.866
110.0	3542	3847.1	2.599	1.847
89.0	4321	4624.1	2.162	1.822

$\theta = -3^o$ Dia. Corrn. x 10^{-6} = -305.12

FIG. 48



Reciprocal magnetic susceptibility against temperature and magnetic moments against temperature for:-

TABLE 32

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300 ^{o}K)

*

Compound $(N\text{-}Meen)_2\,Cl_3,2H_2O$ Field 5 amps

Temp ^{o}K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.2	1326.0	1539.08	6.498	1.917
282.1	1400	1613.08	6.20	1.915
272.8	1454	1667.08	6.00	1.915
244.1	1635	1848.08	5.41	1.907
210.3	1888	2101.08	4.76	1.888
180.0	2226	2439.08	4.10	1.882
146.2	2720	2933.08	3.41	1.86
110.0	3591	3704.08	2.70	1.813
90.0	4097	4310.08	2.32	1.767

(Meen = Methylethylenediamine) Dia. Corrn x 10^{-6} = -213.08

$\theta = -12^{o}$

*

Compound $(N\text{-}Meen)_2Br_3$ Field 5 amps

Temp ^{o}K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
293.6	1319	1539.7	499 6.500	1.909
282.0	1372	1592.7	6.28	1.903
270.1	1447	1667.7	6.00	1.905
244.3	1598	1818.7	5.50	1.892
210.1	1859	2079.7	4.81	1.877
180.3	2161	2381.7	4.20	1.86
110.1	3430	3650.7	2.74	1.800
88.9	4128.0	4348.7	2.30	1.786

$\theta = -18^{o}$ Dia. Corrn x 10^{-6} = -220.68

TABLE 33

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound (N-Meen)$_2$I$_3$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
296	1270	1538.6	6.51	1.916
280.3	1369	1637.6	6.18	1.916
246.3	1550	1818.6	5.50	1.900
210.0	1837	2105.6	4.75	1.888
180.8	2171	2439.6	4.10	1.887
110.0	3436	3704.6	2.70	1.813
90.0	4080	4348.6	2.30	1.776

$\theta = -20^\circ$ Dia. Corrn x 10^{-6} = -268.6

*

Compound (NN-2Meen)$_2$Cl$_3$,2H$_2$O Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	µeff B.M.
296.0	1268 1270	1502.8	6.66	1.893
283.0	1321	1555.8	6.432	1.883
273.0	1377	1611.8	6.208	1.882
244.0	1550	1784.8	5.606	1.874
223.2	1700	1934.8	5.17	1.866
196.1	1931	2165.8	4.62	1.851
150.3	2485	2719.8	3.67	1.815
128.7	2841	3075.8	3.252	1.786
112.0	3181	3415.8	2.928	1.756
90.2	3933	4167.8	2.40	1.742

$\theta = -20^\circ$ Dia. Corrn. x 10^{-6} = -234.8

TABLE 34

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85- 300°K)

*

Compound $(NN\text{-}2Meen)_2Br_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.1	1231.0	1499.5	6.70	1.892
282.5	1292.0	1560.5	6.418	1.887
273.0	1348	1616.5	6.19	1.887
243.9	1513	1781.5	5.615	1.872
223	1653	1921.5	5.188	1.862
196.3	1906	2174.5	4.620	1.813
150.1	2435	2703.5	3.699	1.809
128.5	2753	3021.5	3.30	1.770
112.5	3142	3410.5	2.933	1.756
90.0	3881	4149.5	2.41	1.735

θ = -22° Dia. Corrn. x 10^{-6} = -268.48

*

Compound $(NN\text{-}2Meen)_2I_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_{A}} x10^{-2}$	μeff B.M.
296.0	1188	1504.4	6.65	1.894
283.0	1239	1555.4	6.43	1.884
273.1	1294	1610.4	6.211	1.883
244	1469	1785.4	5.602	1.874
223.1	1619	1935.4	5.168	1.866
196.0	1858	2174.4	4.600	1.854
150.0	2127	2443.4	3.645	-
128.6	2809	3125.4	3.200	1.801
112.4	3161	3477.4	2.876	1.781
90.0	3851	4167.4	2.40	1.740

θ = -22° Dia. Corrn. x 10^{-6} = -316.4

TABLE 35

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound $(N,N'\text{-}2Meen)_2Cl_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/X'_A x10^{-2}$	μeff B.M.
296.0	1281	1515.8	6.60	1.901
283.1	1329	1563.8	6.40	-
273.1	1378	1612.8	6.202	1.884
246.5	1545	1779.8	5.62	1.883
208.3	1871	2105.8	4.75	1.88
190.0	2021	2255.8	4.433	1.859
149.6	2473	2707.8	3.694	1.807
128.5	2807	3041.8	3.288	1.775
112.0	3191	3425.8	2.92	1.759
90.3	3831	4065.8	2.46	1.721

θ = -25°

Dia. Corrn x 10^{-6} = -234.8

*

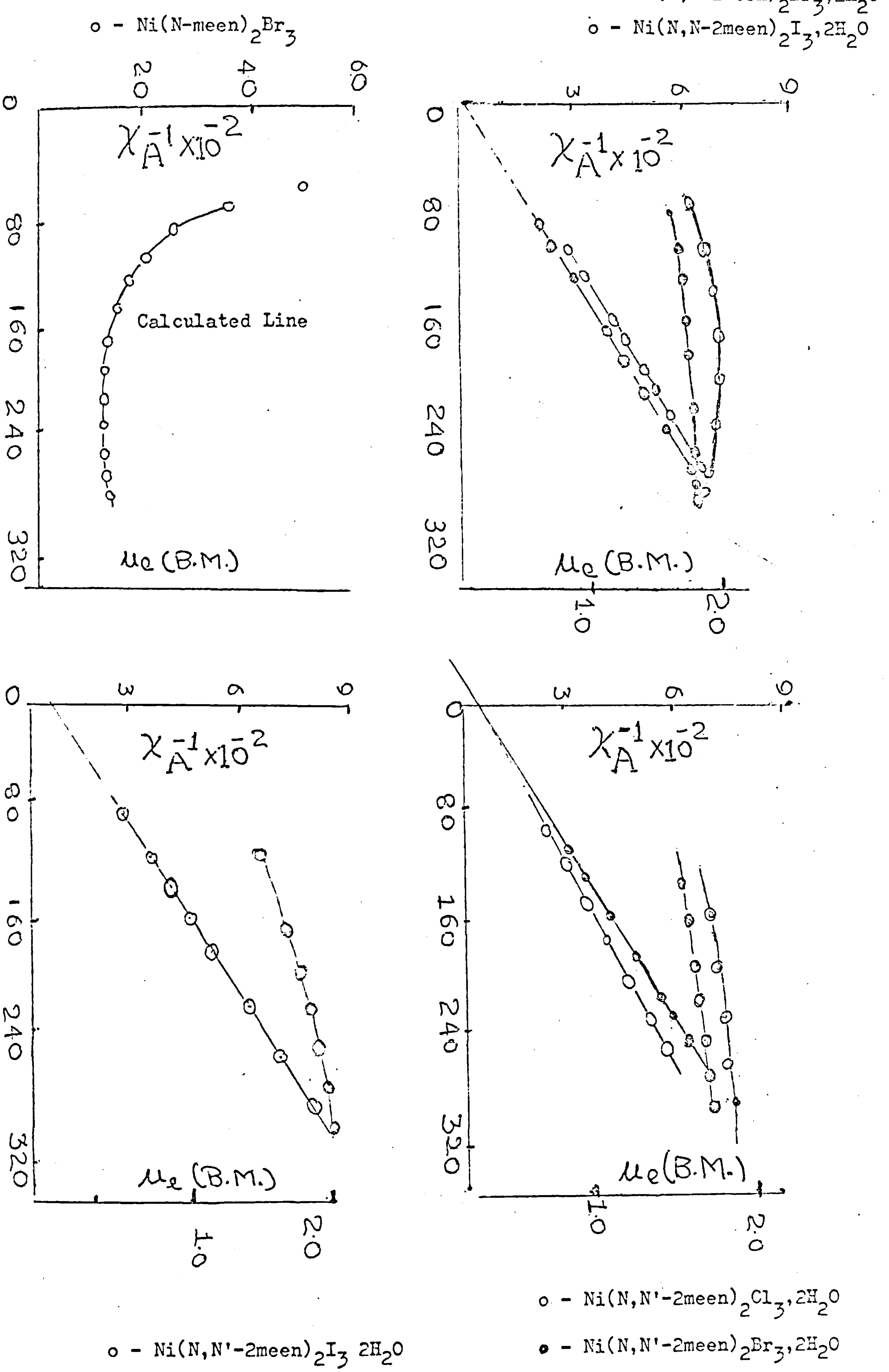
Compound $(NN'\text{-}2Meen)_2Br_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/X'_A x10^{-2}$	μeff B.M.
296.0	1229	1497.5	6.68	1.91
284.4	1311	1579.5	6.335	1.902
276.0	1355	1623.5	6.161	1.901
244.0	1533	1801.5	5.553	1.882
223.0	1692	1960.5	5.102	1.878
196.3	1928	2196.5	4.555	1.865
150.1	2583	2851.5	3.508	1.858
112.4	3281	3549.5	2.818	1.794
90.2	3920	4188.5	2.388	1.744

Dia. Corrn. x 10^{-6} = -268.48

θ = -25°

FIG. 48(a)



Reciprocal magnetic susceptibility against temperature and magnetic moments against temperature for:-

TABLE 36

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*
Compound $(N,N'\text{-}2Meen)_2I_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/X'_A x10^{-2}$	μeff B.M.
296.0	1179	1495	6.688	1.889
283.0	1247	1563	6.401	1.888
273.1	1298	1614	6.198	1.887
244.0	1470	1786	61 5.599	1.875
222.8	1620	1936	5.16	1.865
196.1	1859	2175	4.599	1.827
148.8	2462	2778	3.600	1.827
128.5	2818	3134	3.180	1.802
112.3	3211	3527	2.836	1.787
90.1	3851	4167	2.40	1.740

$\theta = -30^\circ$ Dia. Corrn. x 10^{-6} = -316.4

* These are nickel complexes

TABLE 37

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound $(NN\text{-}2eten)_2I_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.R.
296.3	1178	1543	6.51	1.915
284.2	1248	1613	6.301	1.907
273.1	1302	1667	6.056	1.907
244.1	1483	1848	5.49	1.92
223	1635	2000	5.088	1.882
196.1	1857	2222	4.466	1.882
1489	2492	2857	3.50	1.852
128.5	2861	3226	3.05	1.843
112.5	3240	3605	2.750	1.816
90.0	3904	4269	2.322	1.769

$\theta = -26^{\circ}$ Dia. Corrn. x $10^{-6} = -707.63$

*

Compound $(NN'\text{-}2eten)_2Cl_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.R.
296	1243	1527	6.55	1.908
282.1	1303	1587	6.30	1.900
272.0	1355	1639	6.10	1.896
244.0	1527	1811	5.523	1.888
223.2	1673	1957	5.11	1.876
196.0	1924	2208	4.53	1.868
148.2	2533	2817	3.53	1.835
130	2841	3125	3.20	1.810
112.1	3262	3546	2.82	1.790
88.6	3916	4200	2.381	1.730

$\theta = -26^{\circ}$ Dia. Corrn. x $10^{-6} = -284.34$

TABLE 38

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

Compound $Ni(N,N\text{-}2eten)_2Cl_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$1/X'_A x10^{-2}$	μeff B.M.
296.0	1259	1543	6.48	1.919
283	1329	1613	6.20	1.919
273	1383	1667	6.00	1.916
244.1	1564	1848	5.41	1.907
223	1716	2000	5.000	1.896
196.1	1938	2222	4.499	1.894
148.8	2573	2857	3.499	1.850
128.8	2941	3226	3.10	1.831
112.5	3321	3605	2.775	1.808
90.2	3985	4269	2.343	1.760

$\theta = -22^\circ$ Dia. Corrn x 10^{-6} 284.34

Compound $Ni\ (N,N\text{-}2eten)_2Br_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$1/X'_A x10^{-2}$	μeff B.M.
296.4	1246	1563	6.40	1.933
283.0	1297	1614	6.198	1.919
276.0	1330	1647	6.00	1.914
244.3	1530	1847	5.412	1.907
223.2	1683	2000	5.000	1.898
196.0	1910	2227	4.489	1.876
150.0	2498	2815	3.552	1.845
128.8	2909	3226	3.100	1.803
112.5	3252	3569	2.802	1.803
90.0	3871	4188	2.388	1.744

$\theta = -23^\circ$ Dia. Corrn. x 10^{-6} 317.22

TABLE 39

VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

*

Compound $(NN'\text{-}2eten)_2Br_3,2H_2O$ Field 5 amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.4	1350	1667.2	6.00	1.995
283.0	1417	1734.2	5.768	1.990
272.6	1483	1800.2	5.555	1.990
244.1	1683	2000.2	5.000	1.985
223.2	1862	2179.2	4.588	1.981
196.0	2134	2451.2	4.08	1.968
150.0	2820	3137.2	3.188	1.948
128.8	3256	3573.2	2.798	1.927
113.3	3689	4006.2	2.499	1.912
90.0	4491	4808.2	2.08	1.868

$\theta = -26^\circ$ Dia. Corrn. x 10^{-6} = -317.22

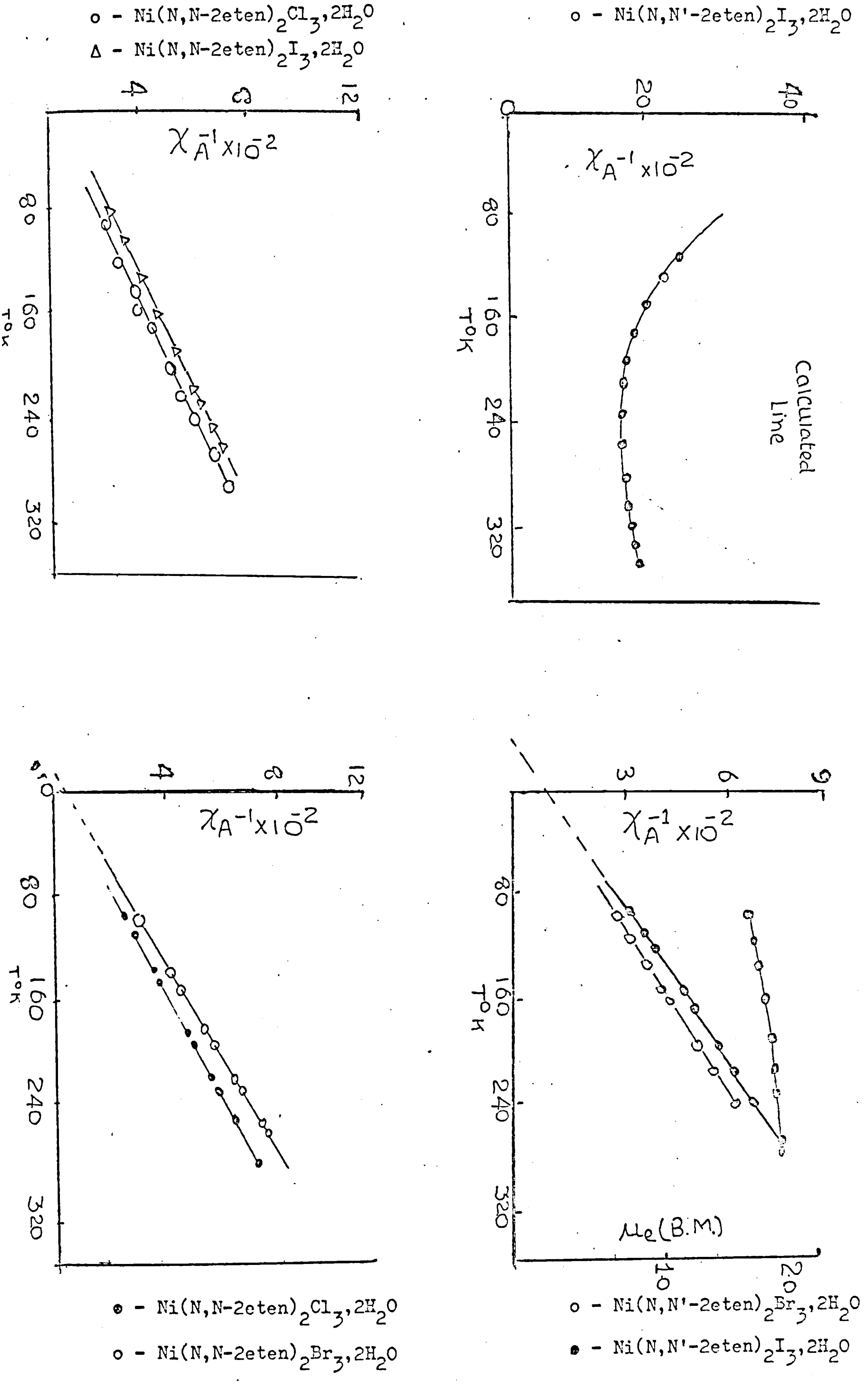
*

Compound $(NN'\text{-}2eten)_2I_3,2H_2O$ Field 5amps

Temp °K	$X'_M x10^6$	$X'_A x10^6$	$^1/_{X'_A} x10^{-2}$	μeff B.M.
296.4	1196	1561.8	6.407	1.933
283.1	1274	1639.8	6.10	1.932
272.6	1319	1684.8	5.94	1.924
244.0	1502	1867.8	5.355	1.920
210.0	1857	2222.8	4.50	-
196.2	1903	2268.8	4.41	1.893
150.1	2559	2924.8	3.42	1.881
112.4	3360	3725.8	2.684	1.838
86.0	3138	4503.8	2.222	1.767

$\theta = -30^\circ$ Dia. Corrn. x 10^{-6} = -365.84

FIG. 49



Reciprocal magnetic susceptibility against temperature and magnetic moments against temperature for:-

Antiferromagnetic Interactions in Complexes with reference to Ni(III)

Magnetically normal low-spin nickel(III) complexes should have spin only magnetic moment 1.7 - 1.8 B.M., for one unpaired electron. In the first approximation no orbital contribution to the magnetic moment should arise in spin-paired nickel(III) octahedral complexes so that temperature independent moment 1.73 B.M. is expected. However, a spin-orbit coupling should affect the magnetic moment according to the equation $\mu eff = \mu S.O.(1 - \frac{2\lambda}{\Delta})$. where $\mu S.O.$ = spin-only value (magnetic moment)

Δ = separation between the ground level and level being "mixed in".

λ = spin-orbit-coupling constant.

For compounds in which intramolecular antiferromagnetic interactions occur, the magnetic susceptibility (or χ_A) can be calculated on the basis of spin-spin coupling theory. Figgis and Martin[93] developed a formula for a calculation of the magnetic susceptibility of the M-M system with the spin system $(\frac{1}{2}, \frac{1}{2})$. Earnshaw and Lewis[94,95] have made similar calculations for the spin system $(\frac{1}{2}, \frac{1}{2})$, $(\frac{3}{2}, \frac{3}{2})$, $(\frac{5}{2}, \frac{5}{2})$. Wojciechowski[96-98] has derived the magnetic susceptibility equation for the following spin systems:

$(1, 1), (2, 2)$ $(1, \frac{1}{2})$ $(\frac{3}{2}, \frac{1}{2})$ $(2, \frac{1}{2})$ $(\frac{5}{2}, \frac{1}{2})$ $(\frac{3}{2}, 1)$ $(2, 1)$
$(\frac{5}{2}, 1)$ $(2, \frac{3}{2})$ $(\frac{5}{2}, \frac{3}{2})$ $(\frac{5}{2}, 2)$,

and determined the temperature dependence of magnetic susceptibility for the negative and positive values of the exchange integral assuming the values from 0 to $\pm$ 500 cm^{-1}. Wojciechowski made these calculations also for the spin systems $(\frac{1}{2}, \frac{1}{2})$ $(\frac{3}{2}, \frac{3}{2})$ $(\frac{5}{2}, \frac{5}{2})$. The calculations made by Wojciechowski for the $d^n d^n$ electron structure of the M-M system at the negative values of the exchange integral enable us to draw the following conclusions.

(1) The Curie-Weiss law is obeyed over the paramagnetic range and the magnetic moment per metal atom calculated from it is equal to the theoretical value calculated from the equation

$$\mu = 2\sqrt{S\ (S + 1)\ \mu\beta}$$

The magnetic moment calculated from the Curie equation

$$\mu = 2.84\sqrt{\chi_M\ T\ \mu\beta}$$

decreases with temperature.

(2) The Neel[118] temperature for a given electron structure of the M-M system depends linearly on the exchange integral J. In the case of the interaction of two metal ions with different electron structures, that is, if the $d^n d^n$ electron configuration and the negative values of the exchange integral J are taken into account, the magnetic moment calculated from the Curie-Weiss law over its range of application, are the same as those calculated from the Curie equation for magnetic susceptibilities with J = 0. The magnetic moment calculated for one metal ion is close to the magnetic moment calculated as an arithemtic mean of the moment for each metal ion of the M-M system. This means that

$$\mu \approx \sqrt{S1\ (S1 + 1)} + \sqrt{S2\ (S2 + 1)}\ \mu\beta$$

For high value of -J determined by the equation

$$\mu = 2\sqrt{(\lvert S_1 - S_2\rvert)\ (\lvert S_1 - S_2\rvert + 1)}\ \mu\beta$$

For high value of -J it obeys the Curie law.

The magnetic moment μeff calculated from the Curie law for the magnetic susceptibilities calculated at different values of J is changed with temperature from

$$\mu = 2\sqrt{(\lvert S_1 - S_2\rvert)\ (\lvert S_1 - S_2\rvert + 1)}\ \mu\beta$$

to

$$\mu = \sqrt{2}\left\{\sqrt{S_1\ (S_1 + 1)} + \sqrt{S_2\ (S_2 + 1)}\right\}\mu\beta$$

These equations show that the two straight lines which represent the relationship reciprocals of magnetic susceptibilities ⟶ temperature for J = 0 and -J assuming very high values are limiting the range of the antiferromagnetic properties of complexes with the M-M system of $d^n d^m$ electron structure. If J is +ve for all electron configurations of the M-M system, that is for the $d^n d^n$ and $d^n d^m$ electron configurations the magnetic moment increases. For high values of the exchange integral J the curve reciprocal magnetic susceptibility ⟶ temperature is a straight line with the Weiss constant Θ equal to zero. For intermediate values of the exchange integral the magnetic susceptibility obeys the Curie-Weiss law over a small temperature range with positive values of Θ.

The application range of this law decreases with the increase of the exchange integral value J. At low temperatures the curves $\chi_M^{-1} = f\,(T,J)$ are convergent to a straight line representing the relationship $\chi_M^{-1} = f(T,J = \infty)$. It may be the assumed that the two straight lines representing the relationship

$$\chi_M^{-1} = f\,(T,J = 0) \text{ and } \chi_M^{-1} = X\,(T,J = \infty)$$

are limiting the ferromagnetic properties of the compounds in which an M-M interaction occurs. The magnetic moment of the M-M systems is being changed with temperature if the exchange integral J is +ve from

$$\mu = \sqrt{2}\left\{\sqrt{S_1\,(S + 1)} + \sqrt{S_2\,(S_2 + 1)}\right\}\mu\beta$$

to

$$\mu = 2\sqrt{S(S + 1)}\,\mu\beta \qquad \text{where} \qquad S = S_1 + S_2$$

According to Kanamori[46,99,119] whether the exchange integral in a complex like M - X - M bonding is +ve or -ve depends on the angle of this bonding. If the angle is close or equal to 90°, the exchange would be +ve. As mentioned above no complex/compound with the +ve value of J has been known until now.

Morichita et. al.[100] suggest on the basis of the magnetic studies of chromium(III) complexes that exchange integral depends also on the radii of ions appearing in the outer sphere of the complex. This interaction decreases as the radius of the complex ion increases. It has been shown by Kambe[101] that the atomic susceptibility χ_A of the metal atom can be calculated by using equation

$$\chi_A = \frac{\frac{g^2N\beta^2}{6kT} \sum S^+ (S^+ + 1) (2S^+ + 1) \exp\frac{J}{kT} \ (S^+(S^+ + 1) - 2S(S + 1)}{\sum (2S^+ + 1) \exp \frac{J}{kT} [S^+ (S^+ + 1) - 2S (S + 1)]} + N\alpha$$

where

S^+ can have values $S_1 + S_2$, $S_1 + S_2 - 1$, ... $S_1 - S_2$

g = spectroscopic splitting factor

β = Bohr magneton = 0.9174×10^{-20} erg/gauss^{-1}

N = Avogadro number = 6.023×10^{23} mole^{-1}

$N\alpha$ = temperature independent paramagnetism

J = exchange integral.

T = Absolute temperature

k = Boltzmann's constant

= 1.380×10^{-16} erg degree

= 0.6950 cm^{-1}

For Ni^{3+} for one unpaired electron $S_1 = S_2 = \frac{1}{2}$ and therefore

$$\chi_A = \frac{g^2N\beta^2}{3kT} \left[\frac{1}{3 + \exp (x)} \right] + N\alpha$$

$$= \frac{k}{T} \left[\frac{3}{3 + \exp (x)} \right] + N\alpha \text{ where}$$

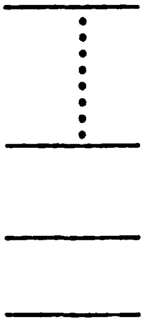
$$k = \frac{g^2N\beta^2}{3k} \quad \text{and} \quad x = -J/_{kT}$$

Mathematical Treatment of Binuclear Complexes

First, the simplifying assumptions are made that interacting ions are identical and that their ground terms are effectively S terms (i.e. they are A or E and have no first order orbital contribution). If each ion has a spin angular momentum specified by the quantum number S then the molecule has a total angular momentum specified by the quantum number S'. This can have the values 0 to 25 in integral steps: a total of $(3S + 1)$ values. Each of these values corresponds to a particular energy level. A given level has a multiplicity of $(2S' + 1)$ and its energy is $J[S'(S' + 1)]$ above ground level, where J is the exchange coupling constant, Not infrequently the value of J is defined in such a way as to be twice that used here and the energy of a level is then $J[S'(S' + 1)]$.

The minus sign necessarily associated with J if the interaction is antiferromagnetic, is taken into account in the order of the levels $S' = 0$ defines the ground level and $S' = 2S$ defines the highest. If the interaction were ferromagnetic, the ground level would be that with parallel spins i.e. $S' = 2S$. Fig.$_{50}$ given below illustrates the separation of the levels.

FIG. 50



S'	Multiplicity = $2S' + 1$	Energy = $J[S'(S' + 1)]$
$2S$	$4S + 1$	$J[2S(2S + 1)$
2	S	$6J$
1	3	$2J$
0	1	0

(The multiplicities and energies produced by exchange interaction in a binuclear complex).

The problem now is exactly the same as with multiplet widths comparable to kT, and the susceptibility of the molecules is obtained by applying Van Vleck's[42, 43] equation.

$$\chi_M = \frac{N\Sigma\left(\frac{E_i^2(1)}{kT} - 2Ei(2)\right)\exp\left(-\frac{Ei(0)}{kT}\right)}{\Sigma \exp -\frac{Ei\ (0)}{kT}} \qquad (1)$$

where

Ei (0) is the energy of level i in the absence of H

Ei (1) is the coefficient of the first order Zeeman effect

Ei (2) is the coefficient of the second order.

Zeeman effect. (In cases where there is no magnetic moment, associated with the level i then, of course, the first and second order coefficients will be zero).

The first order Zeeman effect is to split each level into its 2S' + 1 component level ranging in energy from $-g\beta HS'$ to $+g\beta HS'$

$$\therefore \quad \frac{Ei^2\ (1)}{kT} \text{ becomes } \frac{g^2\beta^2}{kT}\ [S')^2 + (S' + 1)^2 + \ldots\ 0\ \ldots(-S')^2$$

$$= \frac{g^2\beta^2}{kT} \quad \frac{S'(S' + 1)\ (2S' + 1)}{3}$$

The denominator of the equation (1) must include the factor (2S' + 1) since each component of a degenerate set of levels must be counted separately. If the second order Zeeman term is incorporated into the Nα term, equation (1) reduced to

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \quad \frac{\Sigma S'(S' + 1)\ (2S' + 1)\ \exp\left(-\frac{Ei\ (0)}{kT}\right)}{\Sigma\,(2S' + 1)\ \exp\left(-\frac{Ei\ (0)}{kT}\right)} + N\alpha \qquad (2)$$

The way in which equation (2) is applied can be seen by taking a specific example, say that of binuclear molecule with identical paramagnetic ions with $S = {}^{3}/_{2}$. Four levels occur corresponding to $S' = 0, 1, 2$ and 3 with energies of 0, $2J$, $6J$ and $12J$.

$\therefore \quad \chi_M =$

$$Ng^2\beta^2 \; \frac{[0 + 1.2.3 \exp\left(-\frac{2J}{kT}\right) 2.3.5 \exp\left(-\frac{6J}{kT}\right) + 3.4.7 \exp\left(-\frac{12J}{kT}\right)]}{[\exp(0) + 3\exp\left(-\frac{2J}{kT}\right) + \exp\left(-\frac{6J}{kT}\right) + 7\exp\left(-\frac{12J}{kT}\right)]} + M$$

Multiplying through x^{12} where $x = \exp{}^{(J/kT)}$ and substituting $\chi_A = {}^{1}/_{2}\, \chi_M$

$$\therefore \quad \chi_A = \frac{Ng^2\beta^2}{3kT} \; \frac{[42 + 15x^6 + 3x^{10}]}{[7 + 5x^6 + 3x^{10} + x^{12}]} + N\alpha$$

The equation for other values of S are derived in the same manner and are collected below:

For $S = {}^{1}/_{2} \quad \chi_A = \frac{3k}{T} \left[\frac{1}{3 + x^2}\right] + N\alpha$

$$S = 1 \quad \chi_A = \frac{3k}{T} \left[\frac{5 + x^4}{5 + 3x^4 + x^6}\right] + N\alpha$$

$$S = {}^{3}/_{2} \quad \chi_A = \frac{3k}{T} \left[\frac{14 + 5x^6 + x^{10}}{7 + 5x^6 + 3x^{10} + x^{12}}\right] + Na$$

$$S = 2 \quad \chi_A = \frac{6k}{T} \left[\frac{30 + 14x^8 + 5x^{14} + x^{18}}{9 + 7x^8 + 5x^{14} + 3x^{18} + x^{20}}\right] + N\alpha$$

$$S = {}^{5}/_{2} \quad \chi_A = \frac{3k}{T} \left[\frac{55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28}}{11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}}\right] + N\alpha$$

Where $x = \exp(J/kT)$ and $K = \frac{Ng^2\beta^2}{3k} = 0.1251\, g^2$

If Na is neglected then substitution of $J = 0$ ($\therefore x = 1$) and $g = 2$, followed by insertion of the values of χ_A in Langevin's[46] formula leads to spin-only moments of $\sqrt{3}$ $\sqrt{8}$ $\sqrt{15}$ $\sqrt{24}$ and $\sqrt{35}$ B.M.

The unit of J should be noted. As energy term is conventionally, if rather loosely, measured in cm^{-1} when

$$\frac{J}{kT} = \frac{J\ (\text{in cm}^{-1})}{0.69503 \times T\ (\text{in degrees})}$$

J also frequently measured in degrees by incoproating k, when

$$\frac{J}{kT} = \frac{J\ (\text{in degrees})}{T\ (\text{in degrees})}$$

The conversion factor for 1 degree = 0.69503 cm^{-1}.

Derivation of theoretical curve from the experimental data

This can be illustrated by taking an example of Nien_2Cl_3:

A graph of $\frac{1}{\chi_A} \longrightarrow T$ was plotted. From the graph two convenient temperatures were taken and inserted into the equation.

$$\chi_{Ni} = \frac{K}{T}\left[\frac{1}{1 + \frac{1}{3}\exp(x)}\right] + N\alpha$$

Thus at

$$280^{\circ}K = 5.931 \times 10^{-2} = \frac{K}{280}\left[\frac{1}{1 + \frac{1}{3}\exp\left({}^{-J}/_{280\,k}\right)}\right] + N\alpha \text{ and}$$

$$120^{\circ}K = 265.0 \times 10^{-6} = \frac{K}{120}\left[\frac{1}{1 + \frac{1}{3}\exp\left({}^{-J}/_{120\,k}\right)}\right] + N\alpha$$

Now solving the simultaneous equation we get

$$\frac{593.1 \times 10^{-6}}{265.0 \times 10^{-6}} = \frac{\frac{K}{280}\ \frac{1}{1 + \frac{1}{3}\exp\left({}^{-J}/_{280\,k}\right)} + N\alpha}{\frac{K}{120}\ \frac{1}{1 + \frac{1}{3}\exp\left({}^{-J}/_{120\,k}\right)} + N\alpha}$$

$$2.238 = \frac{3 + \exp\left({}^{-J}/_{120\,k}\right)}{7 + 2.333\exp\left({}^{-J}/_{280\,k}\right)}$$

$$\therefore\ 15.666 + 5.221\exp\left({}^{-J}/_{280\,k}\right) = 3 + \exp\left({}^{-J}/_{120\,k}\right)$$

$$\therefore\ 12.666 + 5.221\exp\left({}^{-J}/_{280\,k}\right) = \exp\left({}^{-J}/_{120\,k}\right)$$

Substituting the different value of J, the value giving the best fit was found, e.g.

If we take J = 360 k

$\therefore$ L.H.S. = 5.983 and

R.H.S. = 3.0

It can be seen that these are not equal.

If, however, J = 400 k

then L.H.S. = 5.25 and

R.H.S. = 3.33

If J = 460 k

L.H.S. = 4.20 and

R.H.S. = 3.83

If J = 500 k

L.H.S. = 3.37

R.H.S. = 4.16

The best fit value of J was found as -470 k as

$$12.666 + 5.221 \exp\left(\frac{-470}{280}\right) = \exp\left(\frac{-470}{120}\right)$$

$$3.94 = 3.91$$

$\therefore$ L.H.S. = R.H.S.

Having found the value of J the values of k and g were found

$$265.1 \times 10^{-6} = \frac{\mathbf{k}}{120} \left[\frac{1}{1 + \frac{1}{3} \exp(3.9\,k)}\right.$$

$$265.1 \times 10^{-6} = \frac{\mathbf{k}}{120} \left[\frac{1}{1 + \frac{1}{3} \times (3.9 \times 0.6949)}\right] \quad (\because\ k = 0.6949^{\mathrm{cm}^{-1}})$$

$$\therefore \quad \mathbf{k} = 0.6040$$

$$\because \quad \mathbf{k} = \frac{g^2 N\beta^2}{3k} = \frac{g^2 \times (6.023 \times 10^{23}) \times (.9174 \times 10^{20})^2}{3 \times 1380 \times 10^{-16}}$$

$$\therefore \quad g = \sqrt{\mathbf{k}/.1250} = \sqrt{\frac{0.6040}{0.1250}} = 2.19$$

For

$Nien_2Cl_3$

$g = 2.19$

$k = 0.6040$

$J = -470\ k$ which corresponds to

$= -327\ cm^{-1}\ (326.60\ cm^{-1})$

The g value derived from e.s.r. would give 2.185 which was in reasonable agreement with this value.

The theoretical values of susceptibilities at various temperatures were then calculated and theoretical curve ox χ_M^{-1} versus T plotted. Fig.45 page 171 illustrates the type of cruves resulting from the theoretical equation using J = 327 cms and g = 2.19 values.

The minimum is the Neel point below which the susceptibility reduced sharply. Above the Neel points the curve corresponds to Curie-Weiss law behaviour.

If the binuclear molecule is composed of different paramagnetic ions (i and k) the appropriate equations, though more complicated can be derived in the same way using the values of S' from Si - Sk to Si + Sk. If the moment in the absence of interaction is exactly µ S.O. then g = 2 but g will depart from this value depending on the orbital contribution. If this is achieved by the mixing of higher terms into ground terms (A or E term) then g should be independent of temperature and the formulae still hold with $g \neq 2$. The further tacit assumption has been made that metal-metal interactions are confined within the molecule and do not take place throughout the lattice. Ideally this should be checked by solutions measurements,, but because of their limited solubility in organic solvents and instability, these are not possible. The precise mechanism of the interaction was not known with certainty, but it would appear that direct exchange may be possible by sideways overlap of either the $dx^2 - y^2$ orbitals or dx^2 dy^2 and dz^2 orbitals. Forster and Ballhansen[102] on the other hand used the molecular orbital approach and concluded that σ bonding between singly occupied $3d2^2$ orbital of each M was more likely.

Stereochemistry and Conclusion

(A) Bisdiamine complexes (ethylenediamine and propylene diamine).

(i) Spectral evidence:

Ethylenediamine is able to form cis bridged structures as in nickel(II) halide complexes. When the bis diamine complexes of nickel(II) are oxidised to nickel(III) complexes they would be expected to have similar structures, since the oxidation is heterogeneous i.e., the solid complex is oxidised. This type of cis structure agrees well with the infrared spectral evidence, when it appears that the diamine ligands are cis.

(ii) Magnetic and e.s.r. evidence:

Temperature dependent magnetic moments and the e.s.r. parameters of nickel(III) complexes could be explained by assuming magnetic coupling between the two nickel ions in the cis dimeric complex, see Fig.5\ page .

(B) Bis complexes with alkyl substituent

(i) Spectral evidence:

In N-substituted diamine complexes steric interaction between the substituent alkyl groups prevent the close approach of the donor atoms to the nickel. This results in a weaker ligand field effect which causes the visible spectrum to shift towards the red. This may also indicate an increase in distortion and in the tetragonal nature of the complex.

(ii) Magnetic evidence:

The Curie-Weiss constant and the magnetic moments are higher (2.0 - 2.2 B.M.) than those of the unsubstituted ethylenediamine complexes, and indicate increased distortion. The complexes are again therefore most likely to be binulcear (or polynuclear).

(C) Tris diamine complexes (ethylenediamine and propylenediamine)

(i) The visible spectra of the tris complexes have fewer bands and less splitting indicating that distortion from octahedral are considerably less than in the case of bis diamine complexes.

(ii) Magnetic evidence indicates that the complexes are almost always magnetically dilute. The most likely structure for tris ethylenediamine and propylenediamine complexes is octahedral. The fact that tris complexes with N-substituted diamines could not be prepared is good evidence for the steric interactions of the types discussed.

FIG.51

CIS CONFIGURATION

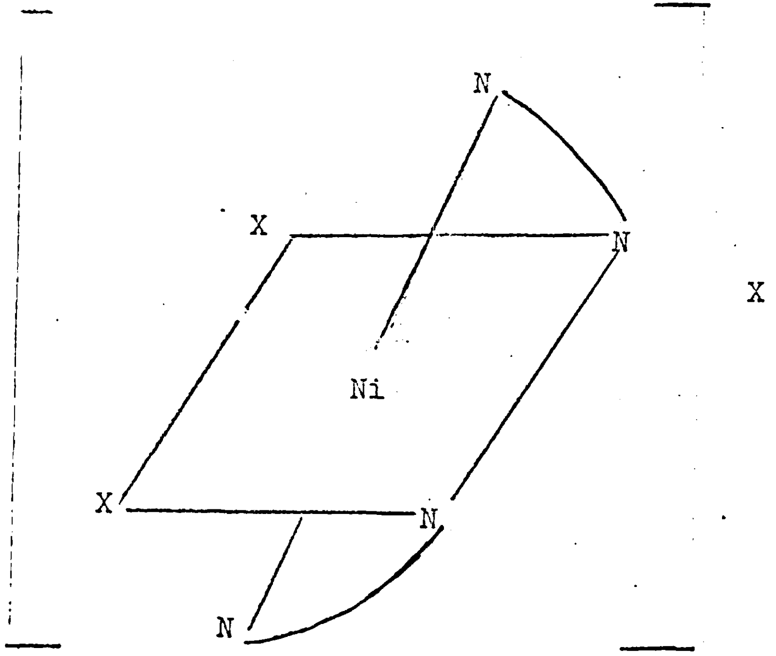
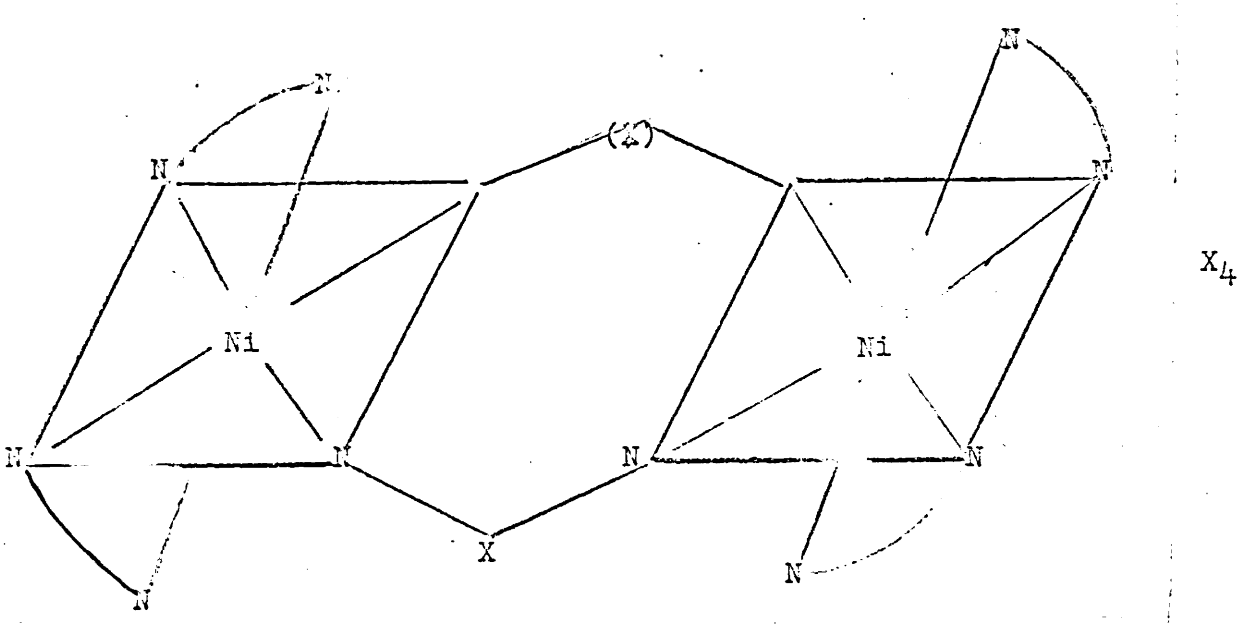
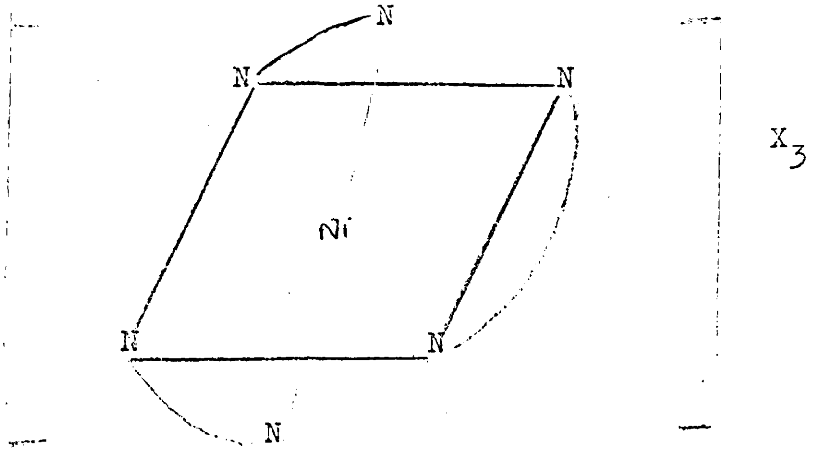


FIG.)

DIMER CIS CONFIGURATION



TRIS -- CONFIGURATION



Appendix - E.S.R. Spectroscopy

Introduction

Complexes containing large organic chelating ligands were difficult to assign the true valency state of the metal ion.[103] Therefore there had been (and has been) a controversy over the identification of Ni(III) and Ni(IV) species in solution.[104-108] The critics[107, 109] of the Ni(III) assignment base their arguments on the expected difference between a free radical type and a $3d^7$ type epr signal. Magnetic susceptibility is not sensitive enough to distinguish between the two. More recently additional claims of Ni(III) species in solution were[110, 111] made, however, attempts to observe the epr signal either failed[110] or were not reported.[111] During studies of some physical properties in solution of the iron through zinc tetra phenyl porphyrins Wolberg et. al.[112] have found evidence for Ni(III) tetraphenyl porphyrin cation.

Their e.s.r. spectra at liquid nitrogen temperature displayed axial symmetry. The intensity of the original signal constantly decreased. The room temperature and liquid temperature spectra were satisfied a spin Hamiltonian of effective spin ½. The g factor for the asymmetric signals were calculated by comparing the experimental curves with simulated[114] ones the g factor for the symmetric signal was measured directly from the experimental spectrum .

Species	Temp.	g aver.	$g_{\parallel}$	$g_{\perp}$
Ni(III)TPP$^+$	77	2.235	2.116	2.295

These two epr signals were interpreted for a square planar d^7 configuration.

Preparation of epr study of solution of oxidized nickel dithiocarbonato complexes were made by Solozenkin, P.M. Kopitsya.[29] Here epr spectrum was measured at 20° with singlet $g_s = 2.100 \pm 0.001$ and $\Delta H = 63 \pm 4$. At 77°K the spectrum was anisotropic with $g_1 = 2.032$, $g_2 = 2.127$ and $g_3 = 2.137$ and can be described by spin corresponding to orthoxombic symmetry which points low spin - $S = \frac{1}{2}$ Ni(III) with a recangular pyramid structure. The temperature dependent spectra is reminisent of the behaviour predicted by Liher and Ballhausen[51] for an octahedral complex with tetragonal Jahn-Teller[63] distortion. The effect of the magnetic properties of a 2E level, the static and dynamic Jahn-Teller effect in a 2E state, including strong Jahn-Teller coupling effects and also perturbations effect were well established by Ham, (review article by Ham 1969) and also in Abragam and Bleaney.[120]

Electron spin resonance and bulk paramagnetism studies of some diaryl bis (diethyl phenyl phosphine) Co(II) complexes were also well studied by Gerloch and Lewis and Bentley et.[121] al. Relationship between e.s.r. g-values and covalent bonding in tetragonal copper (II) compounds were studied by Smith.[122]

For d^7 in a strong octahedral field we have just one electron in eg orbital outside the closed sub shell ($t2g^6$). The configuration is therefore $(t2)^6(e)$, $S = \frac{1}{2}$. With one electron more than can be accommodated in the (t2) shell the extra electron must enter the (e) shell giving net spin = $\frac{1}{2}$. Since matrix elements of the spin orbit coupling vanish within the e mainfold the configurations $(t2)^6\ (e)^1$ with one electron in the e-shell and $(t2)^6\ (e)^3$ with one hole in the e shell have similar ground states are experimentally difficult to distinguish. The g values are close to the free spin value lying above it only through spin orbit coupling to the excited $(t2)^5\ (e)^2$ states. A Jahn-Teller effect is to be expected in cubic or trigonal symmetry giving a change from an isotropic to anisotropic spectrum as the temperature is lowered. Some experimental results for $d^7\ (t2)^6\ (e)^1$ in strong octahedral coordination is shown below . In two cases all three g values are unequal and an average is given for g1. Values of g are isotropic in the spectrum observed at higher temperatures in cubic or trigonal symmetry. The resonance values given here for Ni^{3+} in MgO, CaO were attributed to Ni^+ ($3d^9$) in the references quoted but are ascribed to Ni^{3+} by Hochi, Muller and Wysling.

Table 40

Ion	Host lattice	$g_{\parallel}$	$g_{\perp}$	$\bar{g}$
$3d^7$,Ni^{3+}	MgO			2.1693
	CaO			2.282
	Al_2O_3	2.045 powder		2.146
$4d^7$-Rh^{2+}	$ZnWO_4$	2.375	2.12 (average)	
$5d^7$ Pt^{3+}	Al_2O_3	2.011	2.328	2.220
	$BaTiO_3$	1.950	2.459	

Spin orbit coupling mixes some of the ($4T_1$) T_5 states into the ground state making the g values depart from the free spin value and introducing some anisotropy. The d^7 ion in an octahedral field with small or no distortion is of particular interest because the two ground orbital levels of the doublet are not split by the ligand field. In addition the spin orbit coupling has no matrix elements within the doublet even when the two-fold spin degeneracy is included, and the magnetic field has no matrix elements between the two orbital states. The ground state of an ion in a trigonal field has a four-fold degeneracy of an unusual kind.

A distortion of tetragonal or rhombic (lower) symmetry will split the orbital doublet and the system will be peculiarly susceptible to strain. It is likely that a spectrum appropriate to an effective spin of $\frac{1}{2}$ with anisotropic g values and hyperfine structure corresponding to some symmetry lower than trigonal will be observed. If there is little or no strain, we may expect a static or dynamic Jahn-Teller effect, the theory of this is rather complex.

Calculation of g and Δ (ligand field splitting parameter)

$$h\upsilon = g\beta H$$

$$\therefore \quad \upsilon = gH\frac{\beta}{H}$$

$$\upsilon = gH \times \text{constant}$$

We know that at 3 cm radiation, reseonance frequency = 9500 Mc/sec

h = Planck's constant = 6.624×10^{-27}

β = Bohr magneton = 0.917×10^{-20} ergs

g = spin only value = 2.0023

The resonance in this case

$$H = \frac{h\upsilon}{g\beta} = \frac{6.624 \times 10^{-27} \times 9.5 \times 10^{7}}{2.0023 \times 0.917 \times 10^{-20}}$$

$$\therefore \quad H = 3.427 \text{ gauss}$$

$$\therefore \quad g = \frac{3.427}{3.140} \times \frac{2.0023}{1} = 2.185$$

Using this g value we may be able to calculate ligand field splitting parameter Δ, neglecting other effects from the following equation.

$$g = {}^{2}[\,1 - \frac{(\pm 2\lambda)}{\Delta}\,] \quad \text{where } \lambda = \text{spin-orbit coupling constant}$$

The free ion value (cm^{-1}) of spin-orbit coupling constant for d^7 in strong field 2E state = -715

$$g = {}^{2}[1 - \frac{(2 \times -715)}{\Delta}]$$

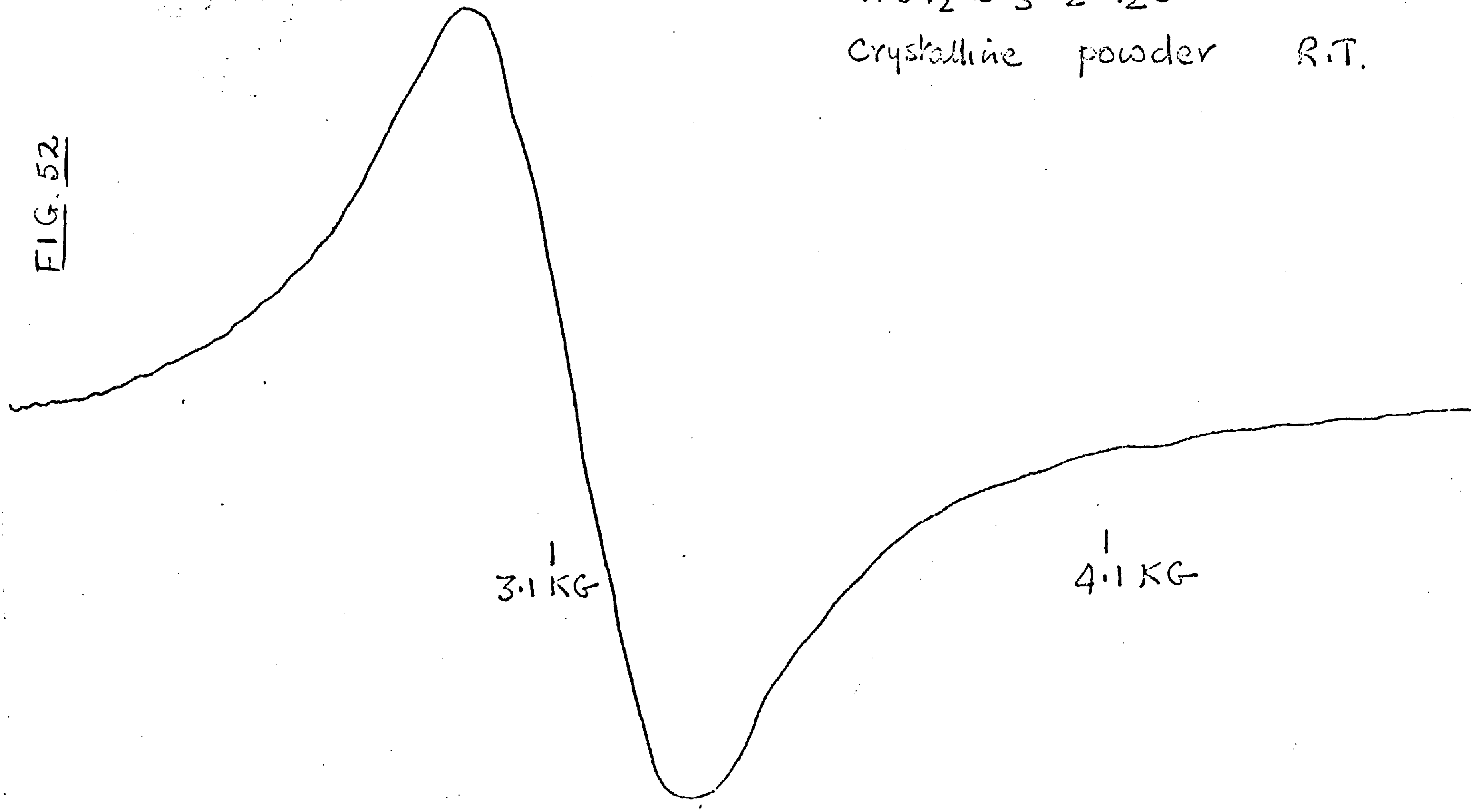
$$2.185 = 2 + [1 + \frac{1430}{\Delta}]$$

$$2.185 = 2 + \frac{2860}{\Delta}$$

$$\therefore \quad \Delta = 15490 \text{ cm}^{-1}$$

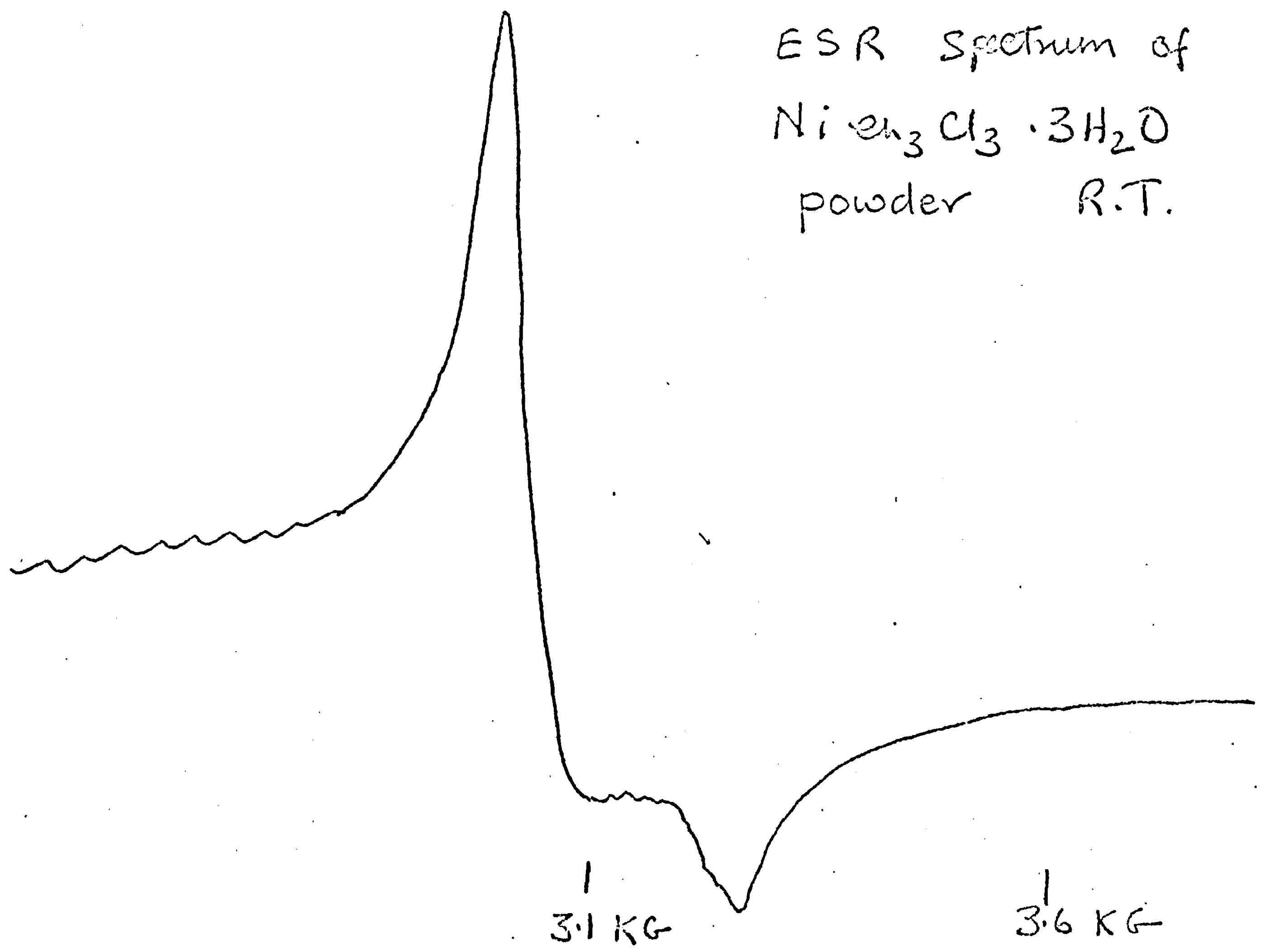
The g value for $Nien_3Cl_3$ from magnetic moments is also near this value (see page)

FIG. 52



E.S.R. Spectrum of
Ni en_2 Br_3 $\frac{1}{2}$ H_2O
Crystalline powder R.T.

FIG. 53



ESR Spectrum of
Ni $en_3Cl_3 \cdot 3H_2O$
powder R.T.

REFERENCES

1. Figgis, B. N. and Lewis, J., Prog. Inorg. Chem., 1964, 6, 197.
2. Curtis, N.F., Coord. Chem. Rev., 1968, 3, 3.
3. Jensen, K. A., Nygaard, B., and Pedeygen ibid, 1963, 17, 1126.
4. Jensen, K. A., Nygaard, B., Acta. Chem. Scand., 1949, 3, 474.
5. Wymore, C.E., and Bailar, J.C., J. Inorg. Nuclear Chem., 1960, 14, 42.
6. Barclay, G. A. and Nyholm, R. S., Chem. and Ind. 1953, 378.
7. Nyholm, R. S., J. Chem. Soc., 1952, 2096.
8. Klemm, W., Brandt, W., and Hoppe, R., Z. Anorg. Chem., 1961, 308, 179.
9. Addision, C.C., and Ward, B. G., Chem. Comm., 1966, 819.
10. Babaeva, A.V., Barranovski, I. B., and Afanaseva, G. G., Russ. J. Inorg. Chem., 1965, 10, 686.
11. Jensen, K. A., Reid, E. E. and Jelineck, A., J. Org. Chem., 1950, 15,448.
12. Riebsomer, J. L., J. Org. Chem., 1950, 15, 237.
13. Daudel, A., and Bucher P., J. Chim. Phys., 1945, 6, 42.
14. Feigl. F., Ber., 1928, 57B, 758.
15. Polster. M., and Okac. A., Zechoslav. Chem. Communs., 1958, 13, 568.
16. Dubsky, J. V., and Kuvas. M., Chem. Abstracts, 1931, 25, 2708.
17. Jensen, K. A., and Wilkins, R. G., Nature, 1951, 167, 434.
18. Jensen, K. A. and Orgel, L. E. Conference report of Coordination Chemistry.
19. Nyholm, R. S., J. Chem. Soc., 1950, 2061, also 1950, 843.
20. Bhattacharyya, S., Bose, S., and Basu, S., J. Inorg Nucl. Chem., 1970, 32, 1033.
21. Allen, G. C., and Warren, K. D., J. Inorg. Chem., 1969, 8, 1895.
22. Kreisman, P., Marsh, R., Preer, J. R. and Gray, H. B., J. Amer. Chem. Soc., 1968, 90; 4, 1067.
23. Lalor, F., Hawthorne, M. F., Maki, A. H., Darlington, K., Davidson, A., Gray, H. B., Dori, Z., and Steifel, E. I., J. Amer. Chem. Soc., 1967, 89, 2278.

24. Maki, A. H., Edelstein, N., Davidson, A., and Holm R. H., *ibid.*, 1964, *86*, 4850.

25. Olson, D. C., and Vasilèvskis, *Inorg. Chem*, 1969, *8*, 1611.

26. Vleck, A. A., *Prog. Inorg. Chem.*, 1963, *5*, 358.

27. McCleverty, *ibid.*, 1968, *10*, 49.

28. Olson, D. C., Mayweg, V. P. and Schvanzer, G. N., *ibid.*, 1966, *88*, 4876.

29. Solozenikin, P. Y., and Kopitsya, N. I.,(*Inst. Khim. Dushanabe*) USSR, *Dokl. Akad. Nauk. Tudzh, USSR,* 1969, *92(S)*, 3622.

30. Hergoz, S., and Hein F., *Z. Anorg. U. Allegem. Chem.*, 1952, *267,* 337.

31. Curtis, N. F., *J. Chem. Soc.*, 1964. 2644.

32. Curtis, N. F., and Cook, D. F., *J. Chem. Soc.*, (*C*), 1967, 962.

33. Goldenberg, N., *Trans. Farraday*. Soc., *36*, 847, 1940.

34. Blach, A. L. and Holm, R. H. *J. Amer. Chem. Soc.*, 1966, *88*, 5201.

35. Bolton, R., Miller, J. and Parker, A. J., *Chem. and Ind.* 1962, 426.

36. Curtis, N. F. *ibid*., 1961, 3147.

37. Figgis, B. N. and Nyholm, R. S. *J. Chem. Soc*., 1958, 4190.

38. Lewis, J. and Wilkins, R., Ed. Modern Coordination Chemistry, Int. Sc. Publication Inc., New York, 1960, p. *403*.

39. Latimer, L. Oxidation Potentials, Prentice Hall, N. Y. 1938, p.*190*

40. Chatt, J. *J. Chem. Soc.*, 1950, 471, also 1950, 2301.

41. James, J. M., Ph.D. thesis, Univ. of London, 1965.

42. Van Vleck, J. H. *J. Chem. Phys.*, 1935, *3*, 803.

43. Van Vleck, J. H. and Shereman, A. *Rev. Mod. Phys*., 1935, *7*, 167.

p.137

44. Techniques of Inorg. Chem., Vol. IV./(Jonassen, H., and Weissberger, A).,

45. Introduction to Magneto Chemistry,1968, (Earnshaw, A.).

46. Magnetochemistry, 1962, (Selwood. P.).

47. Haas and Gorter, *Proc. Roy. Acad., Sci., Amsterdam,* 1930, *33*, 1101.

48. Reekie, *Proc. Roy. Soc.*, *A*., 1939, *173,* 367.

49. Abragam, A., and Pryce, M. H. L. *Proc. Roy. Soc., (London),* 1951, *A*, *206*, 173

50. Tanabe, Y. and Sugano S., *J. Phys. Soc. Japan,* 1954, *9*, 766.

51. Liehr, A. D. and Ballhausen, C. J., *Ann Phys. (N.Y.),* 1958, 3, 304.

52. Orgel, L. E. *J. Chem. Phys.* 1955, 23, 1004.

53. Perumareddi, J. R. *J. Phys. Chem.*, 1967, 71, 3144.

54. Perumareddi, J. R., *J. Phys. Chem.*, 1967, 71, 3155.

55. Holah, D. G. and Fackler (Jr.) J. P., *Inorg. Chem.*, 1965, 4, 954.

56. Holah, D. G., and Fackler (Jr.) J. P. *Inorg. Chem.*, 1965, 4, 1112.

57. Earnshaw, A., Larkworthy L. F. and Patel, K. S., *J. Chem. Soc.,* 1965, 3267.

58. Bersuker, I. B. *Zh. Strukt. khim.*, 1961, 2, 350.

59. Tracy, J. W., Gregory, N. W., Stewart, J. M. and Lingafelter, *ibid.*, 1962, 15, 460.

60. Klemm, W., Brandt., W and Hoppe, R. Z., *Anorg. Allegem. Chem.,* 1961, 308, 179.

61. McClure, D. S., *J. Chem. Phys.*, 1962, 36, 2757.

62. McClure, D. S., *J. Chem. Phys.*, 1962, 37, 1571.

63. Jahn, H. A. and Teller, E. *Proc. Roy. Soc., London*, 1937, (A), 161, 220.

64. Barraclough, C. G., *Trans. Faraday Soc.*, 1966, 62, 1033.

65. Otsuka, J., *J. Phys. Soc. Japan,* 1966, 21, 596.

66. Ballhausen, C. J., Introduction to Ligand Field Theory. McGraw Hill Book Co., N.Y. (1962).

67. Figgis, B. N. Introduction to Ligand Field Theory (1964).

68. Baldwin, M. E., *J. Chem. Soc.*, 1960, 4369.

69. Baldwin, M. E.,*J. Chem. Soc.,* 1961, 471.

70. Powell, D. B. and Sheppard, N., *Spectrochim, Acta*, 1961, 17, 68.

71. Powell, D. B. and Sheppard, N., *J. Chem. Soc.*, 1961, 1112.

72. Powell, D. B. and Sheppard, N., *J. Chem. Soc.*, 1959, 791.

73. Fujita, J. Nakamato, K., and Kobayashi, M., *J. Amer. Chem. Soc.*, 1956, 78, 3295.

74. Mizushima, S., Schischima, I., Nakagawa, I., and Quagliano, J.W., *J. Phys. Chem.*, 1955, 59, 293.

75. Mizushima. S., and Quagliano, J.W., *J. Amer. Chem. Soc.*, 1953, 75, 6084.

76. Nakahara, Saito and Kuroya, Bull, Chem. Soc. Japan, 1959, 29, 428.

77. Nakahara, Saito and Kuroya, Acta. Cryst. 1955, 25, 731.

78. Merritt, P. F. and Wiberley, S. E. J. Phys. Chem., 1955, 59, 55.

79. Richard, P.F. and Thompson, H.W., J. Chem. Soc., 1947, 12, 48.

80. Morris, M. L. and Busch, D. H. J. Amer. Chem. Soc., 1960, 82, 1521.

81. Chamberlain, M. M. and Bailer, J. C., ibid., 1959, 81, 6412.

82. Hughes and McWhinnie, W. R., J. Inorg. Nucl. Chem., 1966, 28, 1659.

83. McWhinnie, W. R., J. Inorg. Nucl. Chem., 1964, 26, 21.

84. Cotton, F. A., Goodgame, D. M. Z., and Soderberg, R. M., Inorg. Chem., 1963, 1162.

85. Baldwin, M. E., Spectrochimica Acta., 1963, 19, 315.

86. Bailer, J.C. and Corey, E.J., J. Amer. Chem. Soc., 1959, 81, 2623.

87. Basolo, F., and Pearson, R. G., Mechanisms of Inorganic Reactions, Willey, N.Y. (1958).

88. Harris C.M., and MacKenzie E.D., J. Inorg. Nuc. Chem., 1962, 19, 372

89. Kohlazansch, K.W.F., 'Ramanspektren', Inostr. Lit. Moscow, 1952, p.346.

90. Nakamota, K., Fujita, J. Tanaka, S., and Kobayashi, J. Amer. Chem. Soc., 1957, 79, 4904.

91. Hathaway, B.J., and Underhill, A.E., J. Chem. Soc., 1961, 3091.

92. Gatehouse, B.M., Livingstone, S.E., and Nyholm, R.S., J. Chem. Soc., 1957, 613.

93. Figgis, B.N., and Martin, J. Chem. Soc., 1956, 3837.

94. Earnshaw, A., and Lewis, J., Nature, 1958, 181, 1262.

95. Earnshaw, A., Figgis, B.N, and Lewis, J. J. Chem. Soc., 1966, 1656

96. Wojciechowski, W., Inorg. Chim., Acta, 1967, 1, 319.

97. Wojciechowski, W., Inorg. Chim. Acta., 1967, 1, 324.

98. Wojciechowski, W., Inorg. Chim. Acta., 1967, 1, 329.

99. Kanamori, J., J. Phys. Chem. Solids, 1959, 10, 87.

100. Morichita, Hori, T. K., Bull. Chem. Soc. Japan, 1965, 38, 1276.

101. Kambe, J., J. Phys. Soc. Japan, 1950, 5, 48.

102. Foster, L. S. and Ballhausen, C.J., Acta. Chem. Scand. 1962, 16, 1385.

103. Schrauzer, G. N., Accounts Chem. Res., 1969, 2, 72.

104. Davidson, A., Edelstein, N., Holm, R.H., and Maki, A.H., J. Amer. Chem. Soc., 1963, 85, 2029.

105. Goan, J. C., Berg., E., and Podall, M.E., J. Org. Chem., 1964, 29, 975.

106. Maki, A.H., Edelstein, N., Davidson, A., and Holm, R.H., J. Amer. Chem. Soc., 1964, 86, 4580.

107. Stiefel, E.I., Waters, J.H. Billing, E., and Gray, H.B. ibid., 1965, 87, 3016

108. Maki, A.H., Berry, T.E., Davidson, A., Holm, R.H. and Balch, A.L., ibid., 1966, 88, 1080.

109. Kreisman, P. Marsh, R. Preer, J.R., and Gray, H.B., ibid., 90, 1067.

110. Meek, D. W., Alyea, E.C., Stalick, J.K. and Ibers, J. Ibid., 1969 91, 4920.

111. Wilson, R.J., Warren, L.F. (Jr), and Hawthorn, M. F. ibid., 1969 91, 758.

112. Wolberg, A., and Manassen, J., J. Amer. Chem. Soc., 1970, 92, 2982.

113. Moreczy, J.T., Hill, B.N., Walters, A.E., Schutze, H.G. and Bonner, W.H., Anal. Chem. 1955, 27, 1899.

114. Larden, M., and Gunthard, H.S.H., J. Chem. Phys., 1966, 44, 2010

115. Finhoit J.E., Anderson, R.W., Fife, J.A., and Caulton, K.G., Inorg. Chem., 1965, 4, 43.

116. Trew, V.C.G., and James J.M., J. Chem. Soc.(A), 1967, 728

117.(i) Antsyshkina, A.S., and Porai-Koshits, M.A., Doklady Akad Nauk., U.S.R.R., 1962, 143, 105

(ii) Antsyshkina, A.S., Porai-Koshits, M.A., Shvelashvilt, A.E., and Minacheva, L.H. Proc. 9 ICCCC - 1966, 413.

118. Neel, L., Ann~~u~~al Phys., 1932, 18, 64

119. Kanamori, J., Magnetism, Vol. 1., (Redo G., Shul. H. Eds). Academic Press, N.Y., 1963). (From Ref. 96).

120. Abragram A., and Bleaney, B., Electron Paramagnetic Resonance of Transition Ions. (Clarendon Press, Oxford, 1970).

121. Gerloch M., Lewis J., Bentley, R.B., Mabb~~i~~s, F.E., and Smail, W.R., J. Chem. Soc., (A), 1970, 3003.

122. Smith, D.W., J. Chem. Soc., (A), 1970, 3108.

123 Nakamoto K. And McCarthy P. J. Spectroscopy And Structure of Metal Chelate Compounds (Page 89, C.R. Hare).