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

by

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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.

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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 electrons, if Hund's rules are obeyed, or one unpaired electron if electron pairing takes place.
### Electronic configuration of nickel complexes

<table>
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<tr>
<th>Complex and valence state</th>
<th>Electronic Arrangements</th>
<th>Electrons unpaired</th>
<th>Magnetic moments (B.M.)</th>
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*Bonding orbital shows ←→*
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<td>dep³ or 3d^4s^4p^2</td>
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<td>5</td>
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<tr>
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<td>1.73</td>
<td>3</td>
<td>3d^2 4s^4p^3</td>
<td>Octahedral</td>
<td>6</td>
</tr>
<tr>
<td>Ni III(3)</td>
<td></td>
<td>1</td>
<td>1.73</td>
<td>3</td>
<td>d^2 4s^4p^3</td>
<td></td>
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Until recently the number of well established complexes of nickel(III) was relatively small. Nickel(III) complexes of oximes, phosphines, diphosphines, di and tri arsine, fluoride, nitrate and various diacido-bis (diamino ethane) derivatives have been reported.

The first clearly defined nickel(III) compound was described by Jensen when the red planar compound $[\text{NiBr}_2 \left( \text{C}_2\text{H}_5\right)_2\text{P}_2]_2$, bis (triethyl phosphine) dibromo nickel(II), was treated with bromine, a violet substance having the formula $\text{NiBr}_2 \left( \text{C}_2\text{H}_5\right)_2\text{P}_2$ was obtained which was monomeric in freezing benzene. The results were explained by assuming that nickel atom is five covalent. Riebsomer showed that the compound is paramagnetic, containing one unpaired electron.

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

Feigl 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 thought that the oxime and not the metal atom was oxidised.

Dubsky and Kuras 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, and
which was believed by Jensen to be a mixture of nickel(II) and nickel (IV) in equal amounts.

Nyholm 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)$_2$Cl$_2$.

Oximes and diarsine which form rings with the central atom give stable nickel(III) complexes, while the phosphine compounds prepared by Jensen and Nygaard 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.

In the five coordinate square pyramidal complex, one of the axial positions is free and the solvent can coordinate with the metal to convert the five coordinate complex to six coordinate, 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.

Allen et. al. 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 D$s$/D$t = 3.00$ for $[\text{NiF}_6]^{3-}$, and D$t = 388$ cm$^{-1}$ for the sodium compound. The spectra of hexafluoro nickelate (III) anion are analysed in terms of $2\Sigma (t_2g^6)g^1$ (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 102).
The molecular and electronic structure of dichlorobis(diarsine) nickel chloride is postulated by Kreisman et al. as distorted octahedral. The monocation Ni(diars)₂Cl₂⁺ is monomeric and has the structure shown in the figure given below.

The four arsenic atoms of two diarsine 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 has a rhombic g tensor with Ag = 2.16 found by Kaki et al.

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

The nickel(III) dithiocarbonate complex have been prepared and e.p.r. of the solution have been studied by Kopitsya et al. which points low spin \( S = \frac{3}{2} \) Ni(III) with a rectangular pyramidal structure.
Hawthorne et al. have studied X-ray diffraction, magnetic, spectral and electrochemical properties of bis[\(\pi-(3)-1,2\)-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 \(d^7\) (\(\text{Ni}^{III}\)) anions possess a symmetrical "non-slipped" sandwich structure (Fig. 2), while the \(d^8\) (\(\text{Ni}^{II}\)) metal complexes suffer a slip distortion from a symmetrical \(\pi\) sandwich, and the electrically neutral \(d^6\) (\(\text{Ni}^{IV}\)) 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 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.

Babaeva 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 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:

<table>
<thead>
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<th>Description</th>
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<tr>
<td>en</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>N-eten</td>
<td>N-ethylethylene diamine</td>
</tr>
<tr>
<td>N-Meen</td>
<td>N-Methylethylene diamine</td>
</tr>
<tr>
<td>NN-2eten</td>
<td>N,N-Diethylethylene diamine</td>
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<tr>
<td>NN'-2eten</td>
<td>N,N'-Diethylethylene diamine</td>
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<tr>
<td>NN-2meen</td>
<td>N,N-Dimethylethylene diamine</td>
</tr>
<tr>
<td>NN'-2meen</td>
<td>N,N'-Dimethylethylene diamine</td>
</tr>
<tr>
<td>Pn</td>
<td>1,10 Phenanthroline</td>
</tr>
<tr>
<td>E.D.T.A.</td>
<td>Ethylenediamine tetraacetic acid</td>
</tr>
<tr>
<td>2mePn</td>
<td>2-Methyl 1,2-diamino propane</td>
</tr>
<tr>
<td>Pic-γ</td>
<td>γ-Picoline</td>
</tr>
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</table>

(1) The C-alkyl substituted diamines were used as Propylenediamine.

We also used the following ligands, but not mentioned in this work:
Aliphatic amines as ligands

The redox chemistry of the nickel-cyclic amine complexes has already received attention. In the reduction process, a one electron reversible electrode reaction was observed by Olson et. al. 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, and therefore Olson 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 and o-phenylenediamine 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.
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 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. 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[34] and \(\text{Hg[Co(SCN)_4]}\).[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).
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. Weller and Strauss at Oxford, England and also by Dr. Bernhardt of Kulheim, 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 absorption 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, phosphines, oximes and ethylenediamines 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 tetradeionate macrocyclic amine ligands have been extensively studied by Curtis. 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 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. 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 in the preparation of platinic trin-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 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 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 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 \((\text{Nien}_2^X_3)\) and \((\text{Nien}_2^X_2Y)\)

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

(1) \(\text{Ni(en}_2^2\text{Cl}_3\)\):

Dichloro bis(ethylenediamine)nickel(III)chloride\([\text{NiCl}_2^{\text{en}_2}\text{]}\)Cl.

Blue bis ethylenediamine nickel(II) chloride was made by the method of James et al. 5.0g of finely powdered \((\text{Nien}_2^2\text{Cl}_2\) 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 \(\text{Nien}_2^2\text{Cl}_2\text{Cl},\text{HCl 2H}_2\text{O}\). A sample of the product was taken and analysed. The chloride and nickel percentage agreed with the above formula.

<table>
<thead>
<tr>
<th>nickel chloride (percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.40</td>
</tr>
<tr>
<td>16.48</td>
</tr>
<tr>
<td>39.41 calculated</td>
</tr>
<tr>
<td>39.30 found</td>
</tr>
</tbody>
</table>
In the tris series of complexes this type of hydro chloride was confirmed by complete analysis (see Table 2a 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$_2$SO$_4$, HCl and HClO$_4$ to give further Ni(III) complexes. (See pages 32, 33)

The complex when heated above ~ 30°C decomposed and its deep green colour changed to blue. The analytical data is given in Table 2a page 35.

(2) $[\text{Nien}_2\text{Br}_3\ 0.5\text{H}_2\text{O}]$: Dibromo bis(ethylenediamine)nickel(III)bromide, hemi-hydrate.

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

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 \( \text{Ni}n\text{Br}_3^\text{HBr}_2\text{H}_2\text{O} \). The rest of the remaining product was washed with aqueous ethanol, and finally with absolute ethanol, to remove \( \text{HBr} \). The filtrate was found to be yellow-brown. The complex was dried in vacuum.

The complex now contained 0.5 mole \( \text{H}_2\text{O} \) which was difficult to remove even when left for 3 days in a vacuum desiccator over \( \text{P}_2\text{O}_5 \). 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:

<table>
<thead>
<tr>
<th>Complex</th>
<th>(Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}n\text{Br}_3^\text{HBr}_2\text{H}_2\text{O} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>11.22</td>
<td>4.08</td>
</tr>
<tr>
<td>11.20</td>
<td>3.94</td>
</tr>
<tr>
<td>11.33</td>
<td>4.08</td>
</tr>
</tbody>
</table>

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 H₂O) 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) Ni₉I₃

Di iodo bis(ethylenediamine)nickel(III) iodide

\[ [\text{NiI}_2(\text{en}_2)]\text{I} \]

A molar alcoholic solution of iodine (cold) was added drop by drop to a cold benzene suspension of Ni₉I₂ 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 Ni₉I₃HI \(2\text{H}_2\text{O}\). As was shown by the Nickel analysis: calcd: 8.12%, found 8.00%.

(ethylenediamine)

In the tris 'en' series of complexes this type of hydrogen halide was verified by complete analysis (see page SS Table 146). 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 $\text{Nien}_2 X_3$:

A. Reaction of $[\text{Nien}_2 \text{Cl}_2] \text{Cl}$ with $\text{NCl}_2[\text{PtCl}_6]$:

Preparation of $[\text{Nien}_2 \text{Cl}_2]_2 \text{PtCl}_6$:

A solution of sodium hexachloroplatinate(IV) acidified with hydrochloric acid was added to $[\text{Nien}_2 \text{Cl}_2] \text{Cl}$. 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:

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Percentage)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>calculated</td>
<td>12.95</td>
<td>21.48</td>
</tr>
<tr>
<td>found</td>
<td>12.89</td>
<td>21.32</td>
</tr>
<tr>
<td>found</td>
<td>12.90</td>
<td>21.40</td>
</tr>
</tbody>
</table>

The reaction showed that nickel(III) remained six coordinate and it was further found that one anion could easily be replaced by $\text{ClO}_4^-$, $\text{HSO}_4^-$, $\text{NO}_3^-$ and halides. This result was also confirmed by potentiometric titration.

B. Reaction of $[\text{Nien}_2 \text{Cl}_2] \text{Cl}$ with HBr:

Preparation of the complex of the formula $\text{Nien}_2 \text{Cl}_2 \text{Br}$:

When a solution of hydrobromic acid was allowed to react with a deep-green complex of $\text{Nien}_2 \text{Cl}_2 \text{Cl}$, a brick-red product was formed. It was filtered off, washed with alcohol (absolute ethanol) and dried. The complex was analysed for metal.

<table>
<thead>
<tr>
<th></th>
<th>Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
<td>17.78</td>
</tr>
<tr>
<td>found</td>
<td>17.80, 17.82</td>
</tr>
</tbody>
</table>
C. Reaction of \([\text{Nien}_2\text{Cl}_2]\text{Cl}\) with bromine:

Preparation of the compound of the formula \(\text{Nien}_2\text{Br}_2\text{Cl},\text{H}_2\text{O}\):

(i) 5 ml Liquid bromine diluted with 5 ml of benzene was allowed to react with \([\text{Nien}_2\text{Cl}_2]\text{Cl}\), 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\(\mathcal{A}\) page 35).

(ii) Alternatively, 2N HCl was allowed to react with a violet complex of \([\text{Nien}_2\text{Br}_2]\text{Br},\text{H}_2\text{O}\). 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 \(\text{Nien}_2\text{Br}_2\text{Cl},\text{H}_2\text{O}\).

<table>
<thead>
<tr>
<th>Calculated for ([\text{Nien}_2\text{Br}_2]\text{Cl},\text{H}_2\text{O})</th>
<th>Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
<td>15.28</td>
</tr>
<tr>
<td>found</td>
<td>15.16</td>
</tr>
</tbody>
</table>

(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 \(\text{Ni(II)}\text{en}_2\text{Cl}_2\) 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 \(\text{Nien}_2\text{Br}_2\text{Cl},\text{H}_2\text{O}\)

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.28</td>
</tr>
<tr>
<td>found</td>
<td>15.20</td>
</tr>
</tbody>
</table>
D. Reaction of $[\text{Nien}_2\text{Cl}_2]\text{Cl}$ with potassium iodide:

Preparation of the compound of the formula $\text{Nien}_2\text{Cl}_2\text{I}$:

10% KI solution was added to a green complex of $[\text{Nien}_2\text{Cl}_2]\text{Cl}$, 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 $\text{Nien}_2\text{Cl}_2\text{I}$ Ni (Percentage)
calculated 15.59
found 15.46

E. Reaction of $[\text{Nien}_2\text{Cl}_2]\text{Cl}$ with iodine:

Preparation of the compound of the formula $\text{Nien}_2\text{I}_2\text{Cl}$:

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

Calculated for $\text{Nien}_2\text{I}_2\text{Cl}$ Ni (Percentage)
calculated 12.88
found 12.78

(ii) Alternatively, 2N HCl solution was allowed to react with violet-red $[\text{Nien}_2\text{I}_2]\text{I}$ 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$_2$Cl$_2$ with constant stirring; the deep red product was filtered off and treated as before. The product was [Nien$_2$I$_2$Cl] and was analysed for nickel, found 12.82%.

F. Reaction of [Nien$_2$I$_2$]I with HBr:

Preparation of the compound of the formula Nien$_2$Br:

When hydrobromic acid solution was allowed to react with the deep violet complex [Nien$_2$I$_2$]I, a deep red product was formed. It was filtered off, dried and analysed for metal only.

<table>
<thead>
<tr>
<th>Calculated for Nien$_2$I$_2$Br</th>
<th>Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
<td>11.50</td>
</tr>
<tr>
<td>found</td>
<td>11.46</td>
</tr>
</tbody>
</table>

G. Reaction of [Nien$_2$I$_2$]I with bromine:

Preparation of the compound of the formula Nien$_2$Br$_2$I

5 ml of Liquid bromine diluted with 5 ml of benzene was treated with [Nien$_2$I$_2$]I and a red complex was formed. It was filtered off, washed with absolute ethanol and dried by vacuum. This red-violet complex Nien$_2$Br$_2$I was completely analysed as shown in Table 2a page 35.

Reactions with acid

(1) Halogen acids. - The complex of the formula Nien$_2$X$_3$ 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$_2$X$_2$,HX,2H$_2$O found in the original preparation; e.g. Nien$_2$Cl$_2$I 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 Nien₂Cl₂Cl, HCl, 2H₂O found in the original preparation.

1. Reaction of [Nien₂Cl₂]Cl with 20% HClO₄:
   Preparation of the compound of the formula Nien₂Cl₂(ClO₄)₂:
   A cold 20% HClO₄ solution was added to Nien₂Cl₂Cl. 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 3.
   Infra-red spectroscopy indicates that the compound contains ionic perchlorate (see page 7b).

2. Reaction of [Nien₂Cl₂]Cl with 60% HClO₄:
   Preparation of the complex of the type Nien₂(ClO₄)₂Cl:
   [Nien₂Cl₂]Cl was added to 60% HClO₄ 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 3 for analytical data). The compound was not explosive.

3. Reaction of [Nien₂Cl₂]Cl with 20% HNO₃:
   Preparation of the compound of the formula Nien₂Cl₂(NO₃)₂:
   20% HNO₃ was added to a green-black [Nien₂Cl₂]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 3.
4. Reaction of Nien₂Cl₂Cl on 50% nitric acid:

Preparation of the compound of the formula Nien₂(NO₃)₂Cl:

50% HNO₃ was added to [Nien₂Cl₂]Cl to make a paste which was transferred to a 50 ml (Quickfit) flask containing 20 ml of 50% HNO₃ + 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 [Nien₂Cl₂]Cl with 20 H₂SO₄:

Preparation of the compound of the formula Nien₂Cl₂(HSO₄)₂:

20% sulphuric acid was allowed to react with [Nien₂Cl₂]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 Nien₂Cl₂(HSO₄)₂.

6. Reaction of [Nien₂Cl₂]Cl with 60% H₂SO₄:

Preparation of the compound of the formula Nien₂(HSO₄)₂Cl:

[Nien₂Cl₂]Cl was added to cold 60% H₂SO₄ and made into a paste. The paste was transferred to a 50 ml flask containing 20 ml of 60% H₂SO₄ 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 Nien₂(HSO₄)₂Cl.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Microanalysis) (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>(1) Nien₂Cl₃</td>
<td>deep-green</td>
<td>Calcd: 16.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 17.39</td>
</tr>
<tr>
<td>(2) Nien₂Br₂½H₂O</td>
<td>violet</td>
<td>Calcd: 11.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 11.33</td>
</tr>
<tr>
<td>(3) Nien₂I₃</td>
<td>violet-red</td>
<td>Calcd: 8.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 8.72</td>
</tr>
<tr>
<td>(4) Nien₂Br₂Cl½H₂O</td>
<td>brick-red</td>
<td>Calcd: 12.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 12.29</td>
</tr>
<tr>
<td>(5) Nien₂Br₂I</td>
<td>violet-red</td>
<td>Calcd: 10.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 11.28</td>
</tr>
<tr>
<td>(6) Nien₂I₃</td>
<td>violet-red</td>
<td>Calcd: 8.58</td>
</tr>
<tr>
<td>(repeated)</td>
<td></td>
<td>Found: 8.98</td>
</tr>
</tbody>
</table>
### Compounds of the type (Nien₂X₃)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>(Percentage)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>metal</td>
<td>chloride</td>
<td>ClO₄⁻/SO₄⁻</td>
</tr>
<tr>
<td>(7) Nien₂Cl₂(NO₃)</td>
<td>brown</td>
<td>Calcd: 18.76</td>
<td>22.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 18.71</td>
<td>22.54</td>
<td></td>
</tr>
<tr>
<td>(8) Nien₂Cl(NO₃)₂</td>
<td>deep brown</td>
<td>Calcd: 17.24</td>
<td>10.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 17.09</td>
<td>10.12</td>
<td></td>
</tr>
<tr>
<td>(9) Nien₂Cl₂(HSO₄)</td>
<td>deep green</td>
<td>Calcd: 16.92</td>
<td>20.44</td>
<td>27.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 16.87</td>
<td>20.03</td>
<td>27.16</td>
</tr>
<tr>
<td>(10) Nien₂Cl(HSO₄)₂</td>
<td>green-black</td>
<td>Calcd: 14.35</td>
<td>8.68</td>
<td>47.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 14.29</td>
<td>8.55</td>
<td>46.87</td>
</tr>
<tr>
<td>(11) Nien₂Cl₂(ClO₄)</td>
<td>deep-green</td>
<td>Calcd: 16.86</td>
<td>20.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 16.89</td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td>(12) Nien₂Cl(ClO₄)₂</td>
<td>green-black</td>
<td>Calcd: 14.20</td>
<td>8.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 14.26</td>
<td>8.16</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 2 (b)**

**Other Analyses**
Compounds of the type NiPn^X^ and NiPn^X^Y
(See Table 3(a) and Table 3(b), pages 45, 46)

1. Dichloro bis(1:2-propylenediamine)nickel(III) chloride dihydrate, 
[NiCl₂Pn²Cl₂]Cl₂H₂O

8.0 g of blue Ni(II)Pn₂Cl₂,2H₂O 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 NiPn₂Cl₂Cl₁HCl₁₂H₂O. To confirm the formula sample was analysed.

Calculated for NiPn₂Cl₂HCl₁₂H₂O 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 \([\text{NiPn}_2\text{Cl}_2]\text{Cl}\).

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

\([\text{NiPn}_2\text{Cl}_2]\text{Cl}\)

3.49130 g of \(\text{NiPn}_2\text{Cl}_2\text{Cl}_2\text{H}_2\text{O}\) was left in a vacuum desiccator containing \(\text{P}_2\text{O}_5\) 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 \(\text{NiPn}_2\text{X}_3\) with \(\text{HNO}_3\), \(\text{H}_2\text{SO}_4\), \(\text{HClO}_4\), \(\text{HCl}\) and other halides to give further \(\text{Ni}(\text{III})\) complexes (discussed later in pp. 43 and 44).

When heated above 30°C the complexes decomposed and changed to blue, indicating the presence of \(\text{Ni}(\text{II})\). The complete analytical data for both the complexes are given in Table 2.

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

\([\text{NiPn}_2\text{Br}_2]\text{Br}\)

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 \(\text{NiPn}_2\text{Br}_2\text{H}_2\text{O}\) (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 impure and contained propylenediaminumm dibydrobromide. 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 \([\text{NiPN}_2\text{Br}_2\text{Br},\text{HBr},2\text{H}_2\text{O}]\). 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.

\[
\begin{array}{c|cc}
\text{Ni} & \text{Br} & \text{(Percentage)} \\
\text{Expected} & 12.16 & 49.67 \\
\text{Found} & 12.20 & 49.88 \\
\end{array}
\]

A known weight of \([\text{NiPN}_2\text{Br}_2\text{Br},2\text{H}_2\text{O}]\) was left in a vacuum dessicator, containing \(\text{P}_2\text{O}_5\) 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 \([\text{NiPN}_2\text{Br}_2\text{Br}]\).

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 \( \sim 30^\circ C \) turned blue.

Reactions of compounds of the type NiPn\(_2\)X\(_3\).

(A) Preparation of \([\text{NiPn}\(_2\)Cl\(_2\)]\text{PtCl}_6\).

An acidified solution of sodium hexachloroplatinate(IV) was added to \([\text{NiPn}\(_2\)Cl\(_2\)]\text{Cl}\). This sparingly soluble green-black product was filtered off and dried in vacuum. The nickel metal analysis agreed with the above formula.

<table>
<thead>
<tr>
<th>Compound ([\text{NiPn}(_2)Cl(_2)]\text{PtCl}_6)</th>
<th>Ni</th>
<th>Pt  (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>expected</td>
<td>12.18</td>
<td>20.25</td>
</tr>
<tr>
<td>found</td>
<td>12.22</td>
<td>20.19</td>
</tr>
</tbody>
</table>

It was also found that one acid residue could easily be replaced by ClO\(_4^\text{-}\), HNO\(_3^\text{-}\), HSO\(_4^\text{-}\) and other halides. This result was also confirmed by potentiometric titration.

(B) Reaction of \([\text{NiPn}\(_2\)Cl\(_2\)]\text{Cl}\) with hydrobromic acid

Preparation of the compound of the formula NiPn\(_2\)Cl\(_2\)Br.

(i) Black \([\text{NiPn}\(_2\)Cl\(_2\)]\text{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\(_2\)Cl\(_2\)Br was as follows. A cold paste of Ni(II)Pn\(_2\)Cl 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_{2}Cl_{2}Br] Ni (Percentage)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
<td>16.40</td>
</tr>
<tr>
<td>found</td>
<td>16.28</td>
</tr>
</tbody>
</table>

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

(C) Reaction of [NiPn_{2}Cl_{2}]Cl with iodine solution.

Preparation of the compound of the formula NiPn_{2}I_{2}Cl.

(i) A saturated solution of iodine in benzene was mixed with [NiPn_{2}Cl_{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.

<table>
<thead>
<tr>
<th>Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
</tr>
<tr>
<td>found</td>
</tr>
</tbody>
</table>

(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_{2}Cl_{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_{2}O) and finally the product was washed with absolute alcohol and dried in vacuum. The nickel analysis confirmed the formula NiPn_{2}I_{2}Cl

<table>
<thead>
<tr>
<th>Compound NiPn_{2}ClI_{2} Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
</tr>
<tr>
<td>found</td>
</tr>
</tbody>
</table>
(D) Reaction of $\text{[NiPn}_2\text{Cl}_2\text{]}\text{Cl}$ with potassium iodide.

Preparation of the compound of the formula $\text{NiPn}_2\text{Cl}_2\text{I} \times \text{H}_2\text{O}$

(i) When 10% KI solution was added to a black-green complex of $\text{NiPn}_2\text{Cl}_2\text{Cl}$, 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.

<table>
<thead>
<tr>
<th>Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated 14.51</td>
</tr>
<tr>
<td>found 14.62</td>
</tr>
</tbody>
</table>

(ii) An alternative method for preparing the hydrated salt $\text{NiPn}_2\text{Cl}_2\text{I} \times \text{H}_2\text{O}$ was as follows. A cold paste of Ni(II) Pn$_2$I$_2$ 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$_2$O : C$_2$H$_5$OH). The product was filtered off, washed with absolute ethanol and dried in vacuum. The product was analysed only for metal.

<table>
<thead>
<tr>
<th>Calculated for $\text{NiPn}_2\text{Cl}_2\text{I} \times \text{H}_2\text{O}$ Ni (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated 13.32</td>
</tr>
<tr>
<td>found 13.26</td>
</tr>
</tbody>
</table>

(E) Reaction of $\text{[NiPn}_2\text{Br}_2\text{]}\text{Br}$ with HI.

Preparation of the compound of the formula $\text{NiPn}_2\text{Br}_2\text{I}$.

When hydroiodic acid solution was allowed to react with a black-green $\text{[NiPn}_2\text{Br}_2\text{]}\text{Br}$ 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$_2$O$_5$ and
paraffin for 24 hours to give the anhydrous complex NiPn$_2$Br$_2$I which was completely analysed (see Table 3(a) page 45).

(F) Reaction of complexes of the type NiPn$_X_3$

(i) The complex of the formula Ni(III)Pn$_X_2$Y 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$_2$HX$_2$H$_2$O found in the original preparation, e.g. NiPn$_2$Br$_2$I.

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$_2$Br$_2$BrHBr$_2$H$_2$O which was identical to NiPn$_2$Br$_2$BrHBr$_2$H$_2$O found in the original preparation (see page 39).

<table>
<thead>
<tr>
<th>Complex NiPn$_2$Br$_2$BrHBr$_2$H$_2$O</th>
<th>Ni</th>
<th>Br (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
<td>10.41</td>
<td>56.76</td>
</tr>
<tr>
<td>found</td>
<td>10.23</td>
<td>57.00</td>
</tr>
</tbody>
</table>

(G) Reaction of [NiPn$_2$Cl$_2$]Cl with HClO$_4$

(a) Action of 20% perchloric acid. Preparation of NiPn$_2$Cl$_2$(ClO$_4$).

A cold solution of perchloric acid (20%) was added to the black-green complex, [NiPn$_2$Cl$_2$]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$_2$Cl$_2$(ClO$_4$).
(b) Action of 60% HClO₄. Preparation of NiPn₂Cl(ClO₄)₂

A cold solution of 60% HClO₄ was added to [NiPn₂Cl₂]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% HNO₃ and action of 20% H₂SO₄

These solutions were added to [NiPn₂Cl₂]Cl and gave respectively:

(i) a brown product for HNO₃, and (ii) a green-black product for H₂SO₄. 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

\[ [\text{NiPn}_2\text{Cl}_2\text{NO}_3] \]

Dichloro bis(propylenediamine) nickel(III) hydrogen sulphate

\[ [\text{NiPn}_2\text{Cl}_2\text{HSO}_4] \]

(I) Action of 60% HNO₃. Preparation of NiPn₂Cl(NO₃)₂

60% HNO₃ acid was added to [NiPn₂Cl₂]Cl to make a paste which was added to 15 ml of 60% HNO₃ and 0.5% propylenediamine. The mixture was refluxed for 48 hours under nitrogen cautiously. The product was
Compounds of the type (NiPn₂X₃)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Microanalysis) (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPn₂Cl₃ 2H₂O</td>
<td>black-green</td>
<td>Calcd: 20.62 6.90 16.05 17.0 30.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 20.75 6.74 16.09 16.89 30.67</td>
</tr>
<tr>
<td>NiPn₂Cl₃</td>
<td>black-green</td>
<td>Calcd: 22.96 6.30 17.8 18.40 33.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 22.80 6.49 16.74 18.28 34.18</td>
</tr>
<tr>
<td>NiPn₂Br₂HBr 2H₂O</td>
<td>black-green</td>
<td>Calcd: 12.70 4.0 9.56 10.41 56.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found - 3.91 9.95 10.05 55.79</td>
</tr>
<tr>
<td>NiPn₂Br₃</td>
<td>black-green</td>
<td>Calcd: 16.13 4.48 12.54 13.14 53.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 15.66 4.24 12.13 13.12 53.04</td>
</tr>
<tr>
<td>NiPn₂Br₂I</td>
<td>brown-red</td>
<td>Calcd: 14.60 4.08 11.35 11.91 58.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 14.60 3.68 11.49 11.69 59.09</td>
</tr>
<tr>
<td>NiPn₂Cl₂I 2H₂O</td>
<td>brown-red</td>
<td>Calcd: 16.30 5.60 12.71 13.32 45.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 15.89 - 12.35 13.09 44.98</td>
</tr>
<tr>
<td>NiPn₂Cl₂Br</td>
<td>black-green</td>
<td>Calcd: 21.03 5.62 16.29 16.40 42.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 21.22 - 16.50 16.38 42.06</td>
</tr>
</tbody>
</table>
Compounds of the type \( \text{NiPn}_2X_3 \)

**TABLE 3(b)**

Other Analyses

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Metal %</th>
<th>Chloride%</th>
<th>( \text{SO}_4^{2-} ) or ( \text{ClO}_4^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NiPn}_2\text{Cl}_2(\text{NO}_3)_2 )</td>
<td>brown</td>
<td>Calcd: 17.23</td>
<td>20.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 17.20</td>
<td>20.05</td>
<td></td>
</tr>
<tr>
<td>( \text{NiPn}_2\text{Cl}(\text{NO}_3)_2 )</td>
<td>deep brown</td>
<td>Calcd: 16.69</td>
<td>9.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 16.62</td>
<td>9.68</td>
<td></td>
</tr>
<tr>
<td>( \text{NiPn}_2\text{Cl}_2(\text{HSO}_4)_2 )</td>
<td>deep green</td>
<td>Calcd: 15.66</td>
<td>18.92</td>
<td>25.64 (( \text{SO}_4^- ))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 15.61</td>
<td>18.88</td>
<td>25.60</td>
</tr>
<tr>
<td>( \text{NiPn}_2\text{Cl}(\text{HSO}_4)_2 )</td>
<td>black-green</td>
<td>Calcd: 12.44</td>
<td>7.503</td>
<td>40.70 (( \text{SO}_4^- ))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 12.48</td>
<td>17.000</td>
<td>40.63</td>
</tr>
<tr>
<td>( \text{NiPn}_2\text{Cl}_2(\text{ClO}_4)_2 )</td>
<td>deep green</td>
<td>Calcd: 15.57</td>
<td>18.80</td>
<td>25.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 15.29</td>
<td>18.66</td>
<td>25.09 (without ( \text{ClO}_4^- ))</td>
</tr>
<tr>
<td>( \text{NiPn}_2\text{Cl}(\text{ClO}_4)_2 )</td>
<td>black-green</td>
<td>Calcd: 13.30</td>
<td>8.04</td>
<td>45.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 13.00</td>
<td>7.99</td>
<td>44.06</td>
</tr>
</tbody>
</table>
a deep brown-red. The analytical results are shown in Table 3(b) page 46.

(J) Action of 60% $\text{H}_2\text{SO}_4$. Preparation of NiPn$_2$Cl(HSO$_4$)$_2$.

[NiPn$_2$Cl$_2$]Cl was made into a paste with cold 60% sulphuric acid. This was transferred to a flask containing 15 ml of $\text{H}_2\text{SO}_4$ (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$_3$X$_3$) and (NiPn$_3$X$_3$).

(A)  (i) Tris(ethylenediamine)nickel(III) chloride, hydrogen chloride, dihydrate. Nien$_3$Cl$_3$,HCl,2H$_2$O.

(ii) Tris(ethylenediamine)nickel(III) chloride, trihydrate. Nien$_3$Cl$_3$,3H$_2$O.

(iii) Tris(ethylenediamine)nickel(III) chloride. Nien$_3$Cl$_3$.

Finely powdered pink Nien$_3$Cl$_2$,2H$_2$O 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 Ni₃Cl₃•HCl•2H₂O. The complete analytical report is given in Table μ(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 Ni₃Cl₃•3H₂O and the complete analytical results are recorded in Table μ(a) page 55.

This trihydrated tris(ethylenediamine)nickel(III) chloride complex was left in a desiccator containing P₂O₅ 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 Ni₃Cl₃.

Complex Ni₃Cl₃ Ni Cl (Percentage)
calculated 17.07 30.44
found 17.10 30.52

This complex (Ni₃Cl₃) absorbed 3 mol of H₂O 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 H₂O) 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% ethylenediamine. When Ni(ethylenediamine)Cl₃·3H₂O or Ni(ethylenediamine)Cl₃ was ground with hydrochloric acid the product was Ni(ethylenediamine)Cl·HCl·2H₂O which was identical to Ni(ethylenediamine)Cl·HCl·2H₂O found in the original preparation.

(B)

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

Ni(en)Cl·HBr·2H₂O

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

Ni(en)Cl·2H₂O

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

Ni(en)Cl

8.0 g of finely powdered (pink) Ni(ethylenediamine)Cl·2H₂O 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:

<table>
<thead>
<tr>
<th>Liquid bromine</th>
<th>4 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4 ml</td>
</tr>
<tr>
<td>Water</td>
<td>1 ml</td>
</tr>
</tbody>
</table>
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 \( \text{Nien}_3\text{Br}_3\cdot\text{HBr}_2\cdot\text{H}_2\cdot\text{O} \). The brown-red complex was washed with absolute ethanol containing 1.0% ethylenediamine and dried in vacuum, and analysed for \( \text{Nien}_3\text{Br}_3\cdot\text{H}_2\cdot\text{O} \). The complete analytical results are shown in Table 4(a).

This dihydrate complex when left in a desiccator containing \( \text{P}_2\text{O}_5 \) 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 \( \text{Nien}_3\text{Br}_3 \).

**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.

\( \text{Nien}_3\text{Br}_3\cdot\text{H}_2\cdot\text{O} \) and \( \text{Nien}_3\text{Br}_3 \) were ground with hydrobromic acid in a pestle and mortar, filtered off and dried in vacuum. The product
in both cases was \( \text{Nien}_3\text{Br}_3,\text{HBr},2\text{H}_2\text{O} \), which was identical to \( \text{Nien}_3\text{Br}_3,\text{HBr},2\text{H}_2\text{O} \), found in the original preparation.

(C)

(i) Tris(ethylenediamine)nickel(III) iodide, hydrogen iodide dihydrate.
\[ \text{Nien}_3\text{I}_3,\text{HI},2\text{H}_2\text{O} \]

(ii) Tris(ethylenediamine)nickel(III) iodide, dihydrate.
\[ \text{Nien}_3\text{I}_3,2\text{H}_2\text{O} \]

(iii) Tris(ethylenediamine)nickel(III) iodide.
\[ \text{Nien}_3\text{I}_3 \]

6.0 g of finely powdered pink \( \text{Nien}_3\text{I}_2,2\text{H}_2\text{O} \) 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: hydriodic 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) on 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 \( \text{Ni}_3\text{I}_3\cdot 2\text{H}_2\text{O} \).

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
<td>8.96</td>
<td>58.13</td>
</tr>
<tr>
<td>found</td>
<td>9.00</td>
<td>57.69</td>
</tr>
</tbody>
</table>

\( \text{Ni}_3\text{I}_3\cdot 2\text{H}_2\text{O} \) was left in a desiccator containing \( \text{P}_2\text{O}_5 \) for 48 hours and lost two water molecules to give anhydrous \( \text{Ni}_3\text{I}_3 \).

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.

\( \text{NiPn}_3\text{Cl}_3\cdot \text{HCl}\cdot 2\text{H}_2\text{O} \)

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

\( \text{NiPn}_3\text{Cl}_3\cdot 2\text{H}_2\text{O} \)

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

\( \text{NiPn}_3\text{Cl}_3 \)

The paste of \( \text{NiPn}_3\text{Cl}_3\cdot 2\text{H}_2\text{O} \) 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 blad-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.

\[
\text{NiPn}_3\text{Cl}_3,\text{HCl},2\text{H}_2\text{O} \quad \text{Ni (Percentage)}
\]

<table>
<thead>
<tr>
<th></th>
<th>calculated</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>15.14</td>
<td>15.00</td>
</tr>
</tbody>
</table>

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\(_3\)Cl\(_3\),2H\(_2\)O was analysed for metal and halogen as shown in Table 4(b) page 56.

NiPn\(_3\)Cl\(_3\),2H\(_2\)O was left in a desiccator over P\(_2\)O\(_5\) and lost two water molecules. Metal and halide analyses shown below confirmed the formula NiPn\(_3\)Cl\(_3\).

\[
\text{NiPn}_3\text{Cl}_3 \quad \text{Ni} \quad \text{Cl} \quad \text{(Percentage)}
\]

<table>
<thead>
<tr>
<th></th>
<th>calculated</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
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<td>19.86</td>
</tr>
<tr>
<td>Cl</td>
<td>35.15</td>
<td>35.60</td>
</tr>
</tbody>
</table>

(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\(_3\)Br\(_3\),2H\(_2\)O

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

NiPn\(_3\)Br\(_3\)

The complete analyses were carried out for both complexes in Table (iii) Tris(propylenediamine)nickel(III) iodide

NiPn\(_3\)I\(_3\)

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)$_3$X$_3$] and [Ni(Pn)$_3$X$_3$]

**TABLE II (a)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Microanalysis) (Percentage)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>(1) Ni$_3$Cl$_3$ 3H$_2$O</td>
<td>deep green-black</td>
<td>Calcd:</td>
<td>18.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>18.05</td>
</tr>
<tr>
<td>(2) Ni$_3$Cl$_3$HCl 2H$_2$O</td>
<td>deep green-black</td>
<td>Calcd:</td>
<td>17.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>17.85</td>
</tr>
<tr>
<td>(3) Ni$_3$Br$_3$ 2H$_2$O</td>
<td>brown-red violet</td>
<td>Calcd:</td>
<td>13.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>14.00</td>
</tr>
<tr>
<td>(4) Ni$_3$Br$_3$HBr 2H$_2$O</td>
<td>brown-red violet</td>
<td>Calcd:</td>
<td>12.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>12.17</td>
</tr>
<tr>
<td>(5) Ni$_3$I$_3$HI 2H$_2$O</td>
<td>violet</td>
<td>Calcd:</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Compounds analysed for metal and halides only.*
**Compounds of the type \([\text{Ni}(en)_3X_3]\) and \(\text{Ni(Fu)}_3X_3\)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Microanalysis) (Percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>(6) Ni(en)$_3$I$_3$</td>
<td>violet-red</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found:</td>
</tr>
<tr>
<td>(7) Ni(en)$_3$Cl$_3$ 2H$_2$O</td>
<td>green-black</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found:</td>
</tr>
<tr>
<td>(8) Ni(en)$_3$Br$_3$ 2H$_2$O</td>
<td>green-black</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found:</td>
</tr>
<tr>
<td>(9) Ni(en)$_3$Br$_3$</td>
<td>green-black</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found:</td>
</tr>
<tr>
<td>(10) Ni(Fu)$_3$I$_3$</td>
<td>violet</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found:</td>
</tr>
</tbody>
</table>

*Compounds analysed for metal and halides only.*
Compounds of the type $\text{Ni(AA)}_2X_3$ where $\text{AA} = \text{N-meen, N,N'-meen,}$

$\text{N,N'-meen}$ (see Tables 6(a) and 6(b), pages 63, 64)

$\text{N-eten, N,N'-eten, N,N'-2eten}$

(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. $\text{Ni(N-eten)}_2\text{Br}_3$

5.0 g of finely powdered Bis N-ethylethylenediamine nickel(II) bromide, dihydrate $\text{Ni(N-eten)}_2\text{Br}_2\cdot2\text{H}_2\text{O}$ made by the method of James 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 3 ml 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 \( \text{Ni}(\text{N-eten})_2\text{Br}_3\cdot\text{HBr}\cdot2\text{H}_2\text{O} \). (To confirm the presence of hydrogen halides in alkyl and dialkyl substituted ethylenediamine series, bis and mono complexes, two samples (i) \( \text{Ni}(\text{N,N-2eten})_2\text{I}_3\cdot\text{HI}\cdot2\text{H}_2\text{O} \) and (ii) dibromo mono \( (\text{N,N'-2eten}) \) nickel bromide, hydrogen dihydrate: \( \text{Ni}(\text{N,N'-2eten})\text{Br}_3\cdot\text{HBr}\cdot2\text{H}_2\text{O} \) 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 \( \text{P}_2\text{O}_5 \). The resulting anhydrous \( \text{Ni}(\text{N-eten})_2\text{Br}_3 \) was completely analysed as shown in Table 5(a) page 61.

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

(i) Dichloro bis(\text{N-eten}) nickel chloride
\[
\text{Ni}(\text{N-eten})_2\text{Cl}_2 
\]

(ii) Di-iodo bis(\text{N-eten}) nickel iodide
\[
\text{Ni}(\text{N-eten})_2\text{I}_3
\]

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 was completely analysed (see Table 5(a) page 61).

C.

(i) Di-iodo bis(\text{N,N-2eten}) nickel iodide, hydrogen iodide, dihydrate
\[
\text{Ni}(\text{N,N-2eten})_2\text{I}_3\cdot\text{HI}\cdot2\text{H}_2\text{O}
\]

(ii) Di-iodo bis(\text{N,N-eten}) nickel iodide
\[
\text{Ni}(\text{N,N-2eten})_2\text{I}_3
\]

6.0 g of blue \( \text{Ni}(\text{N,N-2eten})_2\text{I}_2\cdot2\text{H}_2\text{O} \) 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 | page U/ |). The analysis confirmed the formula Ni(N,N'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-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

\[ \text{Ni}(N,N\text{-2eten})_2\text{Cl}_2,2\text{H}_2\text{O} \]

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

\[ \text{Ni}(N,N'\text{-2eten})_2\text{Cl}_2,2\text{H}_2\text{O} \]
(iii) Dibromo bis(N,N-2eten)nickel(III) bromide dihydrate
   \[ \text{Ni(N,N-2eten)}_2\text{Br}_3\cdot2\text{H}_2\text{O} \]

(iv) Dibromo bis(N,N'-2eten)nickel(III) bromide dihydrate
   \[ \text{Ni(N,N'-2eten)}_2\text{Br}_3\cdot2\text{H}_2\text{O} \]

(v) Di-iodo bis(N,N'-2eten)nickel(III) iodide dihydrate
   \[ \text{Ni(N,N'-2eten)}_2\text{I}_3\cdot2\text{H}_2\text{O} \quad (5\text{a} \text{p} 61) \]

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
   \[ \text{Ni(N,N'-2eten)Br}_3\cdot\text{HBr}\cdot2\text{H}_2\text{O} \]

(ii) Dibromo mono(N,N-2eten)nickel(III) bromide hemiethyl alcohol
   \[ \text{Ni(N,N-2eten)Br}_3\cdot\text{C}_2\text{H}_5\cdot\text{OH} \]

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)$_2$X$_3$, 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 $[\text{Ni(AA)}_2X_3]$ 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**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Microanalysis) (Percentage)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N</td>
<td>H</td>
</tr>
<tr>
<td>(1) Ni(N-eten)$_2$Br$_3$</td>
<td>violet-brown</td>
<td>Calcd:</td>
<td>20.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>-</td>
</tr>
<tr>
<td>(2) Ni(N-eten)$_2$I$_3$</td>
<td>violet-red</td>
<td>Calcd:</td>
<td>15.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>15.68</td>
</tr>
<tr>
<td>(3) Ni(NN-2eten)$_2$I$_3$</td>
<td>violet-red</td>
<td>Calcd:</td>
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</tr>
<tr>
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<td></td>
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<td>21.54</td>
</tr>
<tr>
<td>(4) Ni(NN-2eten)$_2$I$_3$HI 2H$_2$O</td>
<td>violet-red</td>
<td>Calcd:</td>
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</tr>
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<td></td>
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<td>Found</td>
<td>18.75</td>
</tr>
<tr>
<td>(5) Ni(NN'-2eten)$_2$I$_3$ 2H$_2$O</td>
<td>violet-red</td>
<td>Calcd:</td>
<td>20.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>20.51</td>
</tr>
<tr>
<td>(6) Ni(NN'-2eten)Br$_3$HBr 2H$_2$O</td>
<td>violet</td>
<td>Calcd:</td>
<td>13.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>13.33</td>
</tr>
<tr>
<td>(7) Ni(NN-2eten)Br$_2$C$_2$H$_5$OH</td>
<td>violet</td>
<td>Calcd:</td>
<td>17.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>17.56</td>
</tr>
</tbody>
</table>
Compounds of the type \([\text{Ni}(AA)_2X_3]\) where \(AA = N\text{-}eten, \text{N},N\text{-}2eten\) and \(NN'\text{-}2eten\) and \(X = \text{Cl, Br or I}\) (for abbreviations see p. 15)

**TABLE 5 (b) Other Analyses**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Percentage)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>metal</td>
</tr>
<tr>
<td>((8)) (\text{Ni(N-eten)}_2\text{Cl}_3)</td>
<td>green-deep (black)</td>
<td>Calcd: 17.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 16.99</td>
</tr>
<tr>
<td>((9)) (\text{Ni(NN-2eten)}_2\text{Cl}_3\text{2H}_2\text{O})</td>
<td>green-black</td>
<td>Calcd: 13.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 13.50</td>
</tr>
<tr>
<td>((10)) (\text{Ni(NN'-2eten)}_2\text{Cl}_3\text{2H}_2\text{O})</td>
<td>green-black</td>
<td>Calcd: 13.52</td>
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<tr>
<td></td>
<td></td>
<td>Found: 13.90</td>
</tr>
<tr>
<td>((11)) (\text{Ni(NN-2eten)}_2\text{Br}_3\text{2H}_2\text{O})</td>
<td>violet</td>
<td>Calcd: 10.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 10.33</td>
</tr>
<tr>
<td>((12)) (\text{Ni(NN'-2eten)}_2\text{Br}_3\text{2H}_2\text{O})</td>
<td>violet</td>
<td>Calcd: 10.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found: 10.38</td>
</tr>
</tbody>
</table>
Compounds of the type \([\text{Ni(AA)}_2X_3]\) where AA = N-μeen, and NN-2μeen and NN'-2μeen and \(X = \text{Cl, Br and I}\)
(for abbreviations see p.15)

\[\text{TABLE I(a)}\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Microanalysis) (Percentage)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Ni</th>
<th>halides</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) (\text{Ni(N-μeen)}_2\text{Cl}_3 \cdot 2\text{H}_2\text{O})</td>
<td>green-black</td>
<td>Calcd: 20.62 6.90 16.0 17.0 30.49</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>21.01 6.85 0 17.08 30.55</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) (\text{Ni(N-Neen)}_2\text{Br}_3)</td>
<td>black-green</td>
<td>Calcd: 16.13 4.49 12.55 13.14 53.67</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(3) (\text{Ni(N-Neen)}_2\text{I}_3)</td>
<td>violet</td>
<td>Calcd: 12.26 3.44 9.53 9.99 64.76</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>Found</td>
<td>0 4.13 9.63 10.12 63.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) (\text{Ni(NN-2μeen)}_2\text{Cl}_2\text{HCl} \cdot 2\text{H}_2\text{O})</td>
<td>green deep black</td>
<td>Calcd: 22.0 7.63 8.13 14.19 34.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>21.61 7.20 7.82 14.23 34.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) (\text{Ni(NN-2μeen)}_2\text{Cl}_3 \cdot 2\text{H}_2\text{O})</td>
<td>deep green</td>
<td>Calcd: 25.40 7.5 12.5 15.56 28.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>24.57 7.00 0 15.46 27.96</td>
<td></td>
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</tr>
</tbody>
</table>

*Analysis carried out only for metal and halides

0 Not done
Compounds of the type \([\text{Ni(AA)}_2 X_3]\) where AA = N-meen, and NN-2meen and NN'-2meen and \(X = \text{Cl}, \text{Br} \text{ and I}\)

(for abbreviations see p. 15)

**TABLE 6 (b)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis (Microanalysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Percentage)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Ni(NN-2meen)(_2) Cl(_3)</td>
<td>green-black</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>Ni(NN-2meen)(_2) Br(_3) 2H(_2)O</td>
<td>violet</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>Ni(NN-2meen)(_2) I(_3) 2H(_2)O</td>
<td>violet-red</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>Ni(NN'-2meen)(_2) Cl(_3) 2H(_2)O</td>
<td>green-black</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>Ni(NN'-2meen)(_2) Br(_3) 2H(_2)O</td>
<td>violet</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
</tr>
<tr>
<td>Ni(NN'-2meen)(_2) I(_3) 3H(_2)O</td>
<td>Violet-red</td>
<td>Calcd:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
</tr>
</tbody>
</table>
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^70,72 Powell and others. The assignments of the NH₂ modes given by Powell^70 also agree with those for Co(III) ethylenediamine complexes studied by Baldwin 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 Cowey 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 have indicated that cobalt ethylenediamine ring is in the gauche conformation, which also supports later from X-ray crystallographic data on the compounds [Coen₂Cl₂]Cl,HCl, 2H₂O and [Coen₂Cl₂]. The trans form is not suitable for coordination because the two nitrogen atoms are far apart (see Fig. 3 p. 47). 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 NH₂ groups are: symmetrical stretching, asymmetrical stretching, bending, wagging, twisting and rocking; in the regions ~3350 cm⁻¹, ~1560 - 1610 cm⁻¹,
Conformations of the ethylenediamine molecule

Cis $C_{2v}$

Trans $C_{2v}$

Gauche 1.

Gauche 2.

Relation of two coordinated bisulfate ethylenediamine molecules in the gauche form.
NH\textsubscript{2} stretching region occurs between 3300 and 3073 cm\textsuperscript{-1}. The band finds at about \(~1600\) cm\textsuperscript{-1} may be assigned to NH\textsubscript{2} banding vibration. The N-H stretching vibration occurs in the range 3390 - 3160 cm\textsuperscript{-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, Baldwin and also by Powell and Sheppard.

N-substituted diamines show somewhat different characteristics. Basole et al. 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\textsuperscript{-1}, \(~1380\) cm\textsuperscript{-1}, \(~1286\) cm\textsuperscript{-1}, and \(~890\) cm\textsuperscript{-1} may be assigned to the vibrations of CH\textsubscript{2} groups, CH\textsubscript{2} band, CH\textsubscript{2} wag and CH\textsubscript{2} rock, respectively. The band near 1080 cm\textsuperscript{-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 suggested that the region 1120 - 1150 cm\textsuperscript{-1} can be used to distinguish cis and trans 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\textsuperscript{-1}. Baldwin reported that in
a trans bis (ethylene diamine) 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 in agreement with the previous
assignment of Richard and Thompson. Morris and Bush also found a
splitting of this band in the trans complexes. Thus it was suggested
by Baldwin that CH₂ rocking region between 870 - 900 cm⁻¹ provides a
means for the differentiation of cis and trans isomers of bis(ethylene diamine)
type, cis complexes show two bands while complexes with trans
configuration show one band. Hughes and McWhinnie investigated the i.r.
spectra of thirteen cis and eight trans bis ethylene diamine 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.

Baldwin's empirical rules are generally applicable to the
Ni(III) diamine complexes, but not to the nickel(II) complexes made by
James.

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 \( v_3 (T_2) \) antisymmetrical stretch (ca. 1100 cm⁻¹) and
\( v_4 (T_2) \) antisymmetric band (ca. 625 cm⁻¹) are infrared active. The
non-degenerate symmetrical stretch \( v_1 (A_1) \) which is Raman active is
usually observed as a weak band at about 930 cm⁻¹. Harris and McKenzie
showed that on coordination Td symmetry is lowered to $C_3^v$, or $C_2^u$, depending on whether the perchlorate group is acting as uni- or bidentate. If the coordination is through a single oxygen the $v_3$ bands at 1100 cm$^{-1}$ in the free ion splits into two bands. If the coordination is through two oxygens the $v_3$ band is split into three.

(b) Nitrate

The free nitrate has $D_{4h}$ symmetry which is lowering to $C_2^u$ on coordination through one or two oxygens. On coordination the $v_3$ and $v_4$ modes of the free ion are split. Cotton et. al. 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, the four vibrational frequencies of the sulphate ion are:

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ (A) 981</td>
<td>stretching vibrations</td>
</tr>
<tr>
<td>$v_2$ (E) 451</td>
<td>bending vibrations</td>
</tr>
<tr>
<td>$v_3$ ($T_2$) 1104</td>
<td>stretching vibrations</td>
</tr>
<tr>
<td>$v_4$ ($T_2$) 613</td>
<td>bending vibrations</td>
</tr>
</tbody>
</table>

In the solid state i.r. spectra of sulphates (or HSO$_4^-$) $v_1$ is invariably present while the triply degenerate frequencies $v_3$ and $v_4$ sometimes split into two or three bands corresponding to lowering of the symmetry of the ion to $C_3^v$ and $C_2^v$ respectively. There are mainly three reasons of lowering of the symmetry in the solid.
(i) Distortion of the $\text{SO}_4^{2-}$ in the crystal lattice.

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

(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.

<table>
<thead>
<tr>
<th>Species</th>
<th>Symmetry</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free $\text{SO}_4$</td>
<td>Td</td>
<td>-</td>
<td>-</td>
<td>$T_2$</td>
<td>$T_2$</td>
</tr>
<tr>
<td>Monodentate</td>
<td>$C_{3v}$</td>
<td>$A_1$</td>
<td>$E$</td>
<td>$A_1+E$</td>
<td>$A_1+E$</td>
</tr>
<tr>
<td>Bidentate</td>
<td>$C_{2v}$</td>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_1+B_1+B_2$</td>
<td>$A_1+B_1+B_2$</td>
</tr>
</tbody>
</table>

The frequencies corresponding to $v_1$ ($A_1$) for the $\text{SO}_4^{2-}$ 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. 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 $\text{HSO}_4^{-2}$ or $\text{SO}_4^{2-}$) 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.

<table>
<thead>
<tr>
<th>Stretching</th>
<th>Regions in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ ($A_1$)</td>
<td>977</td>
</tr>
<tr>
<td>$v_3$ ($T_2$)</td>
<td>1050 - 1170</td>
</tr>
<tr>
<td>$v_4$ ($T_2$)</td>
<td>580 - 670</td>
</tr>
</tbody>
</table>

It is also difficult to distinguish between bridging sulphate and bidentate sulphate groups as both have symmetry $C_{2v}$. 
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. Complexes like [Ni(en₂Br₂)Br] or Ni(en₂IBr₂) which may be [Ni(en₂IBr)Br] or [Ni(en₂Br₂)I] 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, nitrato and sulphato 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 HSO₄⁻ 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 NO₃⁻, HSO₄⁻ or ClO₄⁻.

Abbreviations in the following tables are as follows:

m = moderate  sh = shoulder
s = strong     w = wide
vs = very strong
TABLE 7(a)

I.R. Spectra in the region 4000 - 600 cm⁻¹

Compounds of the type (1) - Nien₂X₃

<table>
<thead>
<tr>
<th>Compound:</th>
<th>Nien₂Cl₃</th>
<th>Nien₂Br₃·5H₂O</th>
<th>Nien₂I₃</th>
<th>Nien₂BrCl₂·5H₂O</th>
<th>Nien₂Br₂I·5H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCH and NH₂ stretching</td>
<td>3330 m</td>
<td>3318 m</td>
<td>3330 m</td>
<td>3320 m</td>
<td>3318 m</td>
</tr>
<tr>
<td></td>
<td>3208 s</td>
<td>3123 s</td>
<td>3220 s</td>
<td>3275 s</td>
<td>3196 s</td>
</tr>
<tr>
<td></td>
<td>3104 s</td>
<td>3098 s</td>
<td>3130 s</td>
<td>3200 s</td>
<td>3136 s</td>
</tr>
<tr>
<td>CH₂ stretching</td>
<td>2928 m</td>
<td>2953 m</td>
<td>2953 m</td>
<td>2950 m</td>
<td>2950 m</td>
</tr>
<tr>
<td></td>
<td>2887 m</td>
<td>2889 m</td>
<td>2889 m</td>
<td>2889 m</td>
<td>2945 m</td>
</tr>
<tr>
<td>NH₂ scissors</td>
<td>1600 s</td>
<td>1598 s</td>
<td>1583 s</td>
<td>1597 s</td>
<td>1590 s</td>
</tr>
<tr>
<td></td>
<td>1587 m</td>
<td>1578 m</td>
<td>1562 m</td>
<td>1570 m</td>
<td>1578</td>
</tr>
<tr>
<td>CH₂ scissors</td>
<td>1468 m</td>
<td>1465 m</td>
<td>1475 w</td>
<td>1468 m</td>
<td>1468 m</td>
</tr>
<tr>
<td>CH₂ wag</td>
<td>1386 s</td>
<td>1380 s</td>
<td>1385 s</td>
<td>1380 s</td>
<td>1384 w</td>
</tr>
<tr>
<td></td>
<td>1376 m</td>
<td>1370 m</td>
<td>1375</td>
<td>1373 m</td>
<td>1373 m</td>
</tr>
<tr>
<td>NH₂ wag</td>
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<td>1328 m</td>
<td>1330 m</td>
<td>1325 m</td>
<td>1326 m</td>
</tr>
<tr>
<td></td>
<td>1310 m</td>
<td>1308 m</td>
<td>1318 m</td>
<td>1308 m</td>
<td>1313 w</td>
</tr>
<tr>
<td>CH₂ twist</td>
<td>1296 m</td>
<td>1289 m</td>
<td>1278 m</td>
<td>1290 m</td>
<td>1286 m</td>
</tr>
<tr>
<td></td>
<td>1278 w</td>
<td>1272 w</td>
<td>1268 w</td>
<td>1278 w</td>
<td>1270 w</td>
</tr>
<tr>
<td>NH₂ twist</td>
<td>1148 m</td>
<td>1165 m</td>
<td>1133 w</td>
<td>1150 m</td>
<td>1140 w</td>
</tr>
<tr>
<td>Ring skelatal</td>
<td>1116 vs</td>
<td>1110 vs</td>
<td>1108 vs</td>
<td>1110 vs</td>
<td>1109 vs</td>
</tr>
<tr>
<td></td>
<td>1110 vs</td>
<td>1088 vs</td>
<td>1088 vs</td>
<td>1080 vs</td>
<td>1088 vs</td>
</tr>
<tr>
<td></td>
<td>1070 vs</td>
<td>1068 vs</td>
<td>1068 vs</td>
<td>1060 vs</td>
<td>1066 vs</td>
</tr>
<tr>
<td>Compound:</td>
<td>I.R. Spectra in the region 4000-600 cm⁻¹</td>
<td>Compounds of the type (1) - Nien₂X₂ (continued)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------</td>
<td>--------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nien₂Cl₂</td>
<td>1105 m</td>
<td>Nien₂Br₂</td>
<td>1096 m</td>
<td>Nien₂Br₂I₂H₂O</td>
<td>1095 m</td>
</tr>
<tr>
<td>Nien₂Cl₂</td>
<td>960 m</td>
<td>Nien₂</td>
<td>980 m</td>
<td>Nien₂</td>
<td>980 m</td>
</tr>
<tr>
<td>NH₂ twist</td>
<td>900 m</td>
<td>NH₂</td>
<td>890 m</td>
<td>NH₂</td>
<td>890 m</td>
</tr>
<tr>
<td>CH₂ ring or</td>
<td>8978 m</td>
<td>CH₂ ring or</td>
<td>8978 m</td>
<td>CH₂ ring or</td>
<td>8978 m</td>
</tr>
<tr>
<td>NH₂ skeletal</td>
<td>865 s</td>
<td>NH₂ skeletal</td>
<td>865 s</td>
<td>NH₂ skeletal</td>
<td>865 s</td>
</tr>
<tr>
<td>NH₂ Rock</td>
<td>720 m</td>
<td>NH₂ Rock</td>
<td>720 m</td>
<td>NH₂ Rock</td>
<td>720 m</td>
</tr>
<tr>
<td>699 s</td>
<td>699 s</td>
<td>707 s</td>
<td>707 s</td>
<td>718 s</td>
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</tr>
<tr>
<td>718 m</td>
<td>718 m</td>
<td>718 s</td>
<td>718 s</td>
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</tr>
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<td>708 s</td>
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<td>715 m</td>
<td>695 s</td>
<td>695 s</td>
</tr>
<tr>
<td>690 s</td>
<td>690 s</td>
<td>695 s</td>
<td>695 s</td>
<td>699 s</td>
<td>699 s</td>
</tr>
<tr>
<td>Compound:</td>
<td>N$\text{N}_2\text{Cl}_2$(NO$_3^-$)</td>
<td>N$\text{N}_2\text{Cl}$(NO$_3^-$)$_2$</td>
<td>N$\text{N}_2\text{Cl}_2$(HSO$_4^-$)</td>
<td>N$\text{N}_2\text{Cl}$(HSO$_4^-$)$_2$</td>
<td>N$\text{N}_2\text{Cl}_2$(ClO$_4^-$)</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>HOH and NH stretching$^2$</td>
<td>3300 m</td>
<td>3286 m</td>
<td>3320 sh</td>
<td>3320 sh</td>
<td>3316 m</td>
</tr>
<tr>
<td></td>
<td>3283 s</td>
<td>3175 s</td>
<td>3290 sh</td>
<td>3290 sh</td>
<td>3226 s</td>
</tr>
<tr>
<td></td>
<td>3173 s</td>
<td></td>
<td>3257 m</td>
<td>3253 m</td>
<td>3190 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3134 s</td>
<td>3210 s</td>
<td>3118 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3184 s</td>
<td></td>
</tr>
<tr>
<td>CH$_2$ stretching</td>
<td>2969 m</td>
<td>2978 m</td>
<td>2965 m</td>
<td>2969 m</td>
<td>2979 m</td>
</tr>
<tr>
<td></td>
<td>2900 m</td>
<td>2900 m</td>
<td>2902 m</td>
<td>2902 m</td>
<td>2899 m</td>
</tr>
<tr>
<td>NH$_2$ scissors</td>
<td>1600 s</td>
<td>1602 s</td>
<td>1608 s</td>
<td>1606 s</td>
<td>1602 vs</td>
</tr>
<tr>
<td></td>
<td>1592 m</td>
<td>1596 m</td>
<td>1592 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$ scissors</td>
<td>1468 w</td>
<td>1467 w</td>
<td>1468 w</td>
<td>1466 w</td>
<td>1468 w</td>
</tr>
<tr>
<td>CH$_2$ wag</td>
<td>1386 m</td>
<td>1390 w</td>
<td>1397 w</td>
<td>1395 m</td>
<td>1398 w</td>
</tr>
<tr>
<td></td>
<td>1378 m</td>
<td>1376 m</td>
<td></td>
<td>1380 m</td>
<td>-</td>
</tr>
<tr>
<td>NH$_2$ wag</td>
<td>1328 w</td>
<td>1327 m</td>
<td>-</td>
<td>1330 w</td>
<td>1330 w</td>
</tr>
<tr>
<td></td>
<td>1308 m</td>
<td>1306 w</td>
<td>-</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>CH$_2$ twist</td>
<td>1298 m</td>
<td>1296 m</td>
<td>1298 m</td>
<td>1298 m</td>
<td>-</td>
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<tr>
<td></td>
<td>1276</td>
<td>1280 w</td>
<td>1278</td>
<td>1280 w</td>
<td></td>
</tr>
<tr>
<td>NH$_2$ twist</td>
<td>1152 m</td>
<td>1150 m</td>
<td>1152 m</td>
<td>1150 m</td>
<td>1138 m</td>
</tr>
</tbody>
</table>
### TABLE 7(d)

**I.R. Spectra in the region 4000 - 600 cm\(^{-1}\)**

**Type (1) [Oxyanions (ClO\(_4\), NO\(_3\), and HSO\(_4\)_]**

<table>
<thead>
<tr>
<th>Compounds of the type (^{\text{Nien}})(<em>{\text{x}})(</em>{\text{z}}) (Continued)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound:</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Ring skeletal</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(^{\text{NH}})(_{\text{2}}) twist</td>
</tr>
<tr>
<td>unassigned</td>
</tr>
<tr>
<td><strong>N = Very broad band</strong></td>
</tr>
<tr>
<td>(^{\text{NH}})(_{\text{2}}) twist</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>CH(_{\text{2}}) rock or</td>
</tr>
<tr>
<td>ring skeletal</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(^{\text{NH}})(_{\text{2}}) rock</td>
</tr>
<tr>
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### Table 8(a)

I.R. Spectra in the region 4000 - 600 cm⁻¹

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TABLE 8(c)

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

Compounds of the type \( \text{NiPn}_2X_3 \)

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<th>Compound:</th>
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<th>( \text{NiPn}_2\text{I}_2 )</th>
<th>( \text{Pn}_2\text{Cl}_2(\text{ClO}_4) )</th>
<th>( \text{Pn}_2\text{Cl}_2(\text{NO}_3) )</th>
<th>( \text{Pn}_2\text{Cl}(\text{HSO}_4)_2 )</th>
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<td>3246 m</td>
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<td>2889 s 2760 m</td>
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<td>1566 m 1518 m</td>
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<td>1468 s</td>
<td>1468 s</td>
<td>1468 s</td>
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\[\text{Note: m = medium, w = weak, vs = very strong, s = strong, sh = shoulder, w = weak}\]
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TABLE 9(c)

I.R. Spectra in the region 4000 - 600 cm⁻¹

Compounds of the type Ni₃X₃ and NiPn₃X₃

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Note:  
\(b\) = unassigned broad absorption in this region.
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<td>3368 w</td>
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<td>1583 vs</td>
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<td>1470 vs</td>
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<td>1080 vs</td>
<td>1090 vs</td>
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<td>( \text{Ni(N-eten)}_2^3\text{I}_3 )</td>
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<td>----------------------------------</td>
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<td>846 s</td>
<td>860 s</td>
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<td>Cl$_3$, 2H$_2$O</td>
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**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$_2$N-2meen and N$_2$N'-2meen
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)

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<td>1090 vs</td>
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<td>1068 vs</td>
<td>1066 vs</td>
<td>1068 vs</td>
<td>1066 vs</td>
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<td>1065 vs</td>
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Note: b = unassigned broad absorption in this region.
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 valence 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 optical and magnetic properties of transition metals. A more advanced approach has been developed by van Vleck, Mulliken, Orgel, Liher 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. 4-9 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 $d_0$ orbitals.
FIG. 4
Ligand field splitting of the d orbitals. (a) Tetrahedral, (b) Octahedral, (c) Octahedron with tetragonal distortion, (d) Square Planar.

Real forms of d orbitals

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ALAN CARRINGTON & ANDREW D. McLACHLAN
(b) Orbitals dxy, dxz and dyz with their lobes directed between the axes, the t\textsubscript{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\textsubscript{2g}" whose lobes point between the coordinates. An electron occupying an \textit{e}g orbital will suffer greater repulsion than an electron occupying \textit{t}\textsubscript{2g} 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.47. However, environments of other symmetries are often found in complexes such as Td (Tetrahedral); D\textsubscript{4h} (tetragonal); D\textsubscript{5h} (dodecahedral); D\textsubscript{2h} (trigonal bipyramidal); C\textsubscript{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 \( \Delta \) will be discussed.

Two important and opposite factors determine the population distribution of d electrons under the influence of purely an electrostatic 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 \( \Delta \) 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 $\Delta_0$, and the mean pairing energy of the electrons $P$. The energy required to pair two electrons is of the order of $20 \text{ kk (20,000 cm}^{-1})$, 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.

<table>
<thead>
<tr>
<th>CFSE(DQ) in $d^{4-7}$ System</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_g$ [ \uparrow \downarrow ]</td>
</tr>
<tr>
<td>[ Weak field ]</td>
</tr>
</tbody>
</table>

$\Delta_0 > P$ spin-free or high spin complexes are found and where $\Delta_0 < P$ spin-paired or low spin complexes are found.

In order for spin-pairing to occur that is low-spin state to prevail the value of $(\Delta_0 - P)$ should be greater than zero. Values of $B$ may be calculated from the interelectron repulsion parameters determined for gaseous ions. In each case $P > \Delta_0$ spin-free or high spin complexes are found and where $\Delta_0 > P$ spin-paired or low spin complexes are found.
On the basis of experimental data $\Delta_o$ 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 spectrochemical series such as that $\Delta_o$ 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 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.

\[
\begin{align*}
\text{d}^4 & - t_2g \quad \text{high spin} \\
\text{d}^7 & - t_2g \quad \text{low spin} \\
\text{d}^9 & - t_2g \quad \text{Cu}^{2+}, \text{Ag}^{2+}
\end{align*}
\]

The distortion may result in a compressed or elongated octahedron. Structural evidence shows that almost invariably there are four short and two long bonds.
ENERGY LEVELS OF THE $d^7$ CONFIGURATION AS A FUNCTION OF $D_q$ FOR OCTAHEDRAL FIELDS.

The crossover point for the high spin, $^4T_{1g}(F)\, (t_{2g}^3e_g^2)$, and low spin, $^2E_g(H)\, (t_{2g}^2e_g^2)$, ground states occurs at approximately $10\, D_q + 4B + 4C = 0$. For high spin the spin-allowed transitions to $^4T_{2g}(F),\, ^4T_{1g}(F)$, and $^4A_{2g}(F)$ will be observed. Three high energy spin-allowed transitions from $^2E_g$ to $^2T_{1g},\, ^2T_{2g}$, and $^2T_{1g}$ will be observed for low spin. One spin forbidden transition $^4T_{1g}$ will be observed.

This diagram is reproduced from Reference 123.
In the octahedral complex the ground state of a d⁷ ion can be either \( ^4T_1 (t_{2g})^5 (e_g)^2 \) or \( ^2E_g (t_{2g})^6 (e_g)^1 \), depending upon the strength of the crystal field. The gaseous Ni³⁺ 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. Located just a bit higher than \( ^4F \) 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, the \( 2E_g \) crosses all the quartet levels on its way down (see Fig. 7). The features connected with the crossing are however more complicated because of the effects of spin-orbit coupling and many authors have neglected this effect in their calculations. The crystal field theory predicts distortions from octahedral symmetry for the d⁷ low spin configuration (see page 95). Hence this ground state could not be degenerate and leads to future splitting of \( t_{2g} \) and \( e_g \) 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. In aqueous d⁴ complexes, Holah attributed the broad highly asymmetric band, in the visible region to a tetragonal distortion of the octahedron because of the Jahn-Teller effect. This has been also confirmed by crystallographic studies in chromium(II) compounds.

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

\[
\begin{align*}
B_1g & \rightarrow B_2g \\
B_1g & \rightarrow E_g \\
B_1g & \rightarrow A_1g
\end{align*}
\]
The analysis of the spectrum of the hexafluoro nickelate(III) ion $\text{NiF}_6^{3-}$ 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. suggest $t_2^6e_g^1$ low spin ground state, although the very large temperature dependence of the magnetic moment is surprising for a non-magnetic $E_g$ level. But their measurements based on four parameters indicate $2_{E_g}$ ground state, in agreement with observations on the behaviour of Ni$^{3+}$ Al$_2$O$_3$ hosts. For an $E_g$ 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 $90^\circ K$ 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 $^4T_1 - 2_{E_g}$ cross over point. Allen 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 matrices for $d^7 O_h$ systems. The bands assigned for the fluoride complexes ($\sim 6\sim 7$ kk, $\sim 12\sim 13$ kk, $\sim 15\sim 16$ kk and $-19\sim 20$ kk) are all of moderate intensity and at 67 kk the band is not possible to assign to the spin forbidden $2_{E} - 4_{T_2}$ 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 and others. The results of Barraclough 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 $^2E_g$ ground state there is a single electron in the doubly degenerate level which would give substantial Jahn-Teller distortion. The inclusion of spin orbit coupling does not affect this conclusion as $^2E_g$ 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 $D_{4h}$ symmetry without calculated interelectron repulsion parameters. The spectra require both the assumption of a low spin ground state with $D_q/B$ slightly above the $^2E_g - ^4T_{1g}$ 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 repulsion for $d^3$ and hence $d^7$ were obtained by Otsuka, the one electron contributions to the diagonal matrix elements are incorrectly given in his papers. The correct method for counting the $D_s$ and the $D_t$ splittings is reported by Ballhansen, who encountered +ve values of $D_t$ represent elongation along four fold axis and negative values correspond to compression.

Matrices for several $d^4$ system in $D_4$ symmetry have also been given by Berzulenu and Ivanov, but this is also not satisfactory. A most valid approach has been given by Perumareddi, 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. q) shows that the tetragonal distortion as represented by $D_t/B$ has by far the greatest influence on the ground state (see Fig. q page 102).
FIG. 8

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

FREE ION WEAK INTERMEDIATE STRONG FIELD TERMS CRYSTAL FIELD C.F. TERMS CONFIGURATIONS

26
36 (-13 $Dq$)

36 (25$a$)

36 (-60$a$)

STRONG FIELD TERMS CONFIGURATIONS

THIS DIAGRAM IS NOT TO SCALE EXCEPT ON THE FAR RIGHT HAND SIDE. THE 3 SUBSCRIPT IS DELETED FOR Td SYMMETRY. THE NUMBERS UNDER A TERM ARE THE TOTAL DEGENERACY.

THIS DIAGRAM IS REPRODUCED FROM REFERENCE 67
ENERGY LEVEL DIAGRAM FOR d^7 CONFIGURATION IN TETRAGONAL (D4) FIELD

\[ \gamma = 0, \quad c'/b = 4.90, \quad Dq/b = 2.30, \quad \text{AND} \quad Ds/dt = 3.0 \]

This diagram is reproduced from Reference 21.
The energy level diagram for d\textsuperscript{7} ions in the strong field case is given in Figs. 7 and 9.

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

Because of strong field and Jahn-Teller effect a regular octahedral would be changed into tetragonally distorted octahedral.
<table>
<thead>
<tr>
<th>Nien₂Cl₃</th>
<th>Nien₂Br₃</th>
<th>Nien₂I₃</th>
<th>Nien₂Cl²I</th>
<th>Nien₂Cl₂</th>
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**TABLE 12**

**Reflectance Spectra (room temperature) - Band Positions in cm⁻¹**

**Compounds of the type Nien₂X₃**
<table>
<thead>
<tr>
<th>NiPn₂Cl₃₂H₂O</th>
<th>NiPn₂Br₃₂H₂O</th>
<th>NiPn₂Br₃</th>
<th>NiPn₁Br₃</th>
<th>NiPn₂Cl₂Br</th>
<th>NiPn₂Cl₂</th>
<th>NiPn₂I₂</th>
<th>NiPn₂ClBr₂</th>
<th>NiPn₂Cl(Clo₄)₂</th>
<th>NiPn₂Cl₂(Clo₄)₂</th>
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TABLE 13(b)

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

Compounds of the type NiPn\(_2\)X\(_3\) (continued)

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<tr>
<th>NiPn(_2)Cl(_2)</th>
<th>NiPn(_2)Cl(_2)</th>
<th>NiPn(_2)Cl</th>
<th>NiPn(_2)Cl(_2)</th>
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<td>Table 14. Reflectance Spectra (from temperature) - Band Positions in cm⁻¹</td>
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<td>Compounds of the type Ni(AA)X₃, where AA = (en) and (Pn)</td>
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- Ni₄Cl₃Cl₃, HCl₂H₂O
- Ni₄Br₃Cl₃, HBr₂H₂O
- Ni₄Br₂Br₃, 3H₂O
- Ni₄Br₁Br₂Cl₂, 2H₂O
- Ni₄Br₁Br₂Cl₂, 2H₂O
- Ni₄Cl₃Cl₃, 3H₂O
- Ni₄Cl₂Cl₄, 3H₂O
- Ni₄Cl₁Cl₃Br₂, 3H₂O
- Ni₄Cl₁Cl₂Br₂Cl₂, 3H₂O
- Ni₄Cl₁Cl₂Br₂Cl₃, 3H₂O
- Ni₄Cl₁Cl₂Br₃Cl₂, 3H₂O
- Ni₄Cl₁Cl₂Br₄Cl₂, 3H₂O
- Ni₄Cl₁Cl₃Br₃Cl₂, 3H₂O
- Ni₄Cl₁Cl₃Br₄Cl₂, 3H₂O
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<th>Ni(N-eten)$_2$I$_3$</th>
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<th>Ni(N,N-2eten)$_2$Br$_3$</th>
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<th>Ni(N,N-2eten)$_3$HBr</th>
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<tr>
<td>14,000</td>
<td>14,600</td>
<td>14,800</td>
<td>14,800</td>
<td>14,800</td>
<td>14,800</td>
<td>14,800</td>
<td></td>
</tr>
<tr>
<td>16,800</td>
<td>16,800</td>
<td>16,800</td>
<td>16,800</td>
<td>16,800</td>
<td>16,100</td>
<td>16,100</td>
<td></td>
</tr>
<tr>
<td>18,600</td>
<td>18,600</td>
<td>19,400</td>
<td>19,500</td>
<td>19,500</td>
<td>19,500</td>
<td>19,500</td>
<td></td>
</tr>
<tr>
<td>26,000</td>
<td>26,500</td>
<td>26,500</td>
<td>26,500</td>
<td>26,500</td>
<td>26,500</td>
<td>26,500</td>
<td></td>
</tr>
<tr>
<td>32,000</td>
<td></td>
<td>31,500</td>
<td></td>
<td></td>
<td></td>
<td>31,500</td>
<td></td>
</tr>
<tr>
<td>37,300</td>
<td>37,800</td>
<td>37,800</td>
<td>38,000</td>
<td>37,800</td>
<td>37,800</td>
<td>37,600</td>
<td></td>
</tr>
<tr>
<td>44,500</td>
<td>45,000</td>
<td>43,800</td>
<td>44,800</td>
<td>45,000</td>
<td>44,500</td>
<td>44,500</td>
<td></td>
</tr>
<tr>
<td>46,200</td>
<td>47,000</td>
<td>46,800</td>
<td></td>
<td></td>
<td></td>
<td>46,800</td>
<td></td>
</tr>
</tbody>
</table>
**TABLE 15(b)**

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

Compounds of the type Ni(AA)\(_2\)X\(_3\) where AA = (N-eten), N,N'-2eten), (N,N-2eten) (continued)

<table>
<thead>
<tr>
<th>Ni(N,N-2eten)(_2)Cl(_3), 2H(_2)O</th>
<th>Ni(N,N-2eten)(_2)Br(_3), 2H(_2)O</th>
<th>Ni(N,N'-2eten)(_2)I(_3), 2H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,600</td>
<td>7,600</td>
<td>8,000</td>
</tr>
<tr>
<td>11,800</td>
<td>11,800</td>
<td>12,000</td>
</tr>
<tr>
<td>14,800</td>
<td>14,800</td>
<td>14,800</td>
</tr>
<tr>
<td>16,800</td>
<td>16,500</td>
<td>16,100</td>
</tr>
<tr>
<td>19,500</td>
<td></td>
<td>17,000</td>
</tr>
<tr>
<td>26,100</td>
<td>26,000</td>
<td>26,500</td>
</tr>
<tr>
<td>38,200</td>
<td>37,900</td>
<td>37,800</td>
</tr>
<tr>
<td>45,200</td>
<td>45,200</td>
<td>45,000</td>
</tr>
<tr>
<td>Ni(N,meen)$_2$Cl$_3$, $\text{H}_2\text{O}$</td>
<td>Ni(N-meen)$_2$Br$_3$</td>
<td>Ni(N-meen)$_2$I$_3$</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>8,000</td>
<td>7,800</td>
<td>8,000</td>
</tr>
<tr>
<td>11,700</td>
<td>12,000</td>
<td>11,800</td>
</tr>
<tr>
<td>16,000</td>
<td>16,800</td>
<td>16,800</td>
</tr>
<tr>
<td>16,800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26,000</td>
<td>26,200</td>
<td>26,500</td>
</tr>
<tr>
<td>33,000</td>
<td>33,200</td>
<td>33,800</td>
</tr>
<tr>
<td>37,800</td>
<td>38,000</td>
<td>36,500</td>
</tr>
<tr>
<td>44,000</td>
<td>45,200</td>
<td>46,000</td>
</tr>
<tr>
<td>Ni((N,N-2meen)_2Br)_2H_2O</td>
<td>Ni(N,N-2meen)_2I</td>
<td>Ni((N,N'-2meen)_2Cl)_2H_2O</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>7,800</td>
<td>8,000</td>
<td>8,000</td>
</tr>
<tr>
<td>11,800</td>
<td>11,800</td>
<td>11,800</td>
</tr>
<tr>
<td>14,800</td>
<td>14,800</td>
<td>14,800</td>
</tr>
<tr>
<td>16,800</td>
<td>16,800</td>
<td>16,100</td>
</tr>
<tr>
<td>19,400</td>
<td>19,800</td>
<td>19,800</td>
</tr>
<tr>
<td>26,800</td>
<td>26,800</td>
<td>26,500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34,000</td>
</tr>
<tr>
<td>38,000</td>
<td>38,800</td>
<td>36,800</td>
</tr>
<tr>
<td>44,800</td>
<td>46,000</td>
<td>43,200</td>
</tr>
</tbody>
</table>
Diffuse Reflectance Spectra (Room Temperature)

FIGURE: 10

(1) $\text{N$en}_2\text{Cl}_3$

(2) $\text{N$en}_2\text{Br}_3, \text{H}_2\text{O}$

(3) $\text{N$en}_2\text{I}_3$
FIGURE:11 Visible Absorption Spectra of Solids (Room Temperature)

Nien₂Cl₂(ClO₄)

Nien₂Cl(ClO₄)₂

FIGURE:12

Nien₂Br₂Cl₂•H₂O
Visible Absorption Spectra of Solids (Room Temperature)

**FIGURE 13**

- Ni$_2$Cl$_2$(CIO$_4$)$_2$
- Ni$_2$Cl(CIO$_4$)$_2$
- Ni$_2$Cl(HSO$_4$)$_2$
- Ni$_2$Cl$_2$(NO$_3$)

Intensity (arbitrary units)

$k$ $K$
FIGURE: 14

Visible Absorption Spectra of Solids (Room Temperature)

Figure: 15

Intensity

0 10 20 30 40 50

NiPn₂Cl₃·2H₂O

NiPn₂Cl₃

NiPn₂Br₂·2H₂O

NiPn₂Br₂
Figure 16: Visible Absorption Spectra of Solids (Room Temperature)

Figure 17:
Visible Absorption Spectra of Solids (Room Temperature)

(A) \( \text{NiPn}_2\text{Cl}_2(\text{ClO}_4) \)

(B) \( \text{NiPn}_2\text{Cl}_6(\text{NO}_3) \)

(C) \( \text{NiPn}_2\text{Cl}_2(\text{HSO}_4) \)

(D) \( \text{NiPn}_2\text{Cl}(\text{ClO}_4)_2 \)
FIGURE: 3  Visible Absorption Spectra of Solids (Room Temperature)

Nien₃I₃, 2H₂O

Nien₃Cl₃, 3H₂O

Nien₂Br₃, 2H₂O

FIGURE: 20

Nien₃Cl₃, HCl₃H₂O

Nien₂Br₃, HBr₂H₂O

Nien₃I₃, HI₂H₂O

INTENSITY (arbitrary units)
Visible Absorption Spectra of Solids (Room Temperature)

FIGURE: 21

Ni\textsubscript{en}\textsubscript{2}Br\textsubscript{3};HBr \textsubscript{2}H\textsubscript{2}O

Ni\textsubscript{en}\textsubscript{2}Br\textsubscript{3}

FIGURE: 22

NiPn\textsubscript{3}Cl\textsubscript{3};2H\textsubscript{2}O

NiPn\textsubscript{3}Br\textsubscript{3};2H\textsubscript{2}O

- kk -
Visible Absorption Spectra of Solids (Room Temperature)

FIGURE: 23

Intensity (arbitrary units)

Nien$_2$Br$_3$$\cdot$H$_2$O
Nien$_2$I$_3$
Nien$_3$I$_3$
Nien$_3$Br$_3$

0 20 40 50
Visible Absorption Spectra of Solids (Room Temperature)

Figure 24

[Graph showing absorption spectra for NiPn Cl₃ and NiPn₂Cl₃]
Visible Absorption Spectra of Solids (Room Temperature)

\[ \text{Intensity (arbitrary units)} \]

\[ \text{Ni(N,N' 2etlen)}_2 \text{I}_3 \]

\[ \text{Ni(N,N' 2etlen)}_2 \text{Cl}_3 \]
FIGURE 25(a)
Visible Absorption Spectra of Solids (Room Temperature)

- Ni(N,N2eten)2Br3
- Ni(N,N2eten)2I3
- Ni(N,N2eten)2Cl3, 2H2O
Visible Absorption Spectra of Solids (Room Temperature)

FIGURE: 26

- Ni(N-eten)$_2$Br$_3$ --- (a)
- Ni(N,N'2eten)$_2$Br$_3$ --- (b)
- Ni(N,N'2eten)$_2$Br$_3$H$_2$O --- (c)

INTENSITY

0  20  40  60
Visible Absorption Spectra of Solids (Room Temperature)

- $\text{Ni(N-eten)}_2\text{I}_3$
- $\text{Ni(N-eten)}_2\text{Br}_3$
- $\text{Ni(N-eten)}_2\text{Cl}_3$
Visible Absorption Spectra of Solids
(Room Temperature)

**FIGURE: 28**

- **Ni(N-meen)$_2$Cl$_3$** (c)
- **Ni(N-meen)$_2$Br$_3$** (b)
- **Ni(N-meen)$_2$I$_3$** (a)

**FIGURE: 29**

- **Ni(N,N'-2meen)$_2$I$_3$**
- **Ni(N,N'-2meen)$_2$I$_3$**

INTENSITY (arbitrary units)
Visible Absorption Spectra of Solids (Room Temperature)

Intensity (arbitrary units)
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 low spin ground state in which appreciable tetragonal Jahn-Teller 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 $2^2A_1^g$ ground terms and a splitting of the observed bands. The effect of reducing the symmetry on the several states is shown below:

<table>
<thead>
<tr>
<th>Oh</th>
<th>$D_4h$</th>
<th>$D_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $E_g$</td>
<td>$A_1^g + B_1^g$</td>
<td>$E$</td>
</tr>
<tr>
<td>(2) $T_2g$</td>
<td>$A_2^g + E_g$</td>
<td>$A_2 + E$</td>
</tr>
<tr>
<td>(3) $T_1g$ (G)</td>
<td>$B_2^g + E_g$</td>
<td>$A_1 + E$</td>
</tr>
<tr>
<td>(4) $T_1g$ (H)</td>
<td>$A_2^g + E_g$</td>
<td>$A_2 + E$</td>
</tr>
</tbody>
</table>

$^2T_1^g$ (G) and $^2T_2^g$ are likely to be very close (see diagram Fig 5.74). In pure Oh symmetry it seems possible that only two bands may occur. It is difficult to determine therefore which transition $^2E \rightarrow ^2T_1^g(G)$ or $^2E \rightarrow ^2T_2$ be lower. Allen and Warren indicate that the $^2T_1^g$ state is slightly lower and assignments will be given on this basis. The energy level diagram (pages 97, 98) for a $D_4h$ field indicates that the quartet/doublet cross-over point the $^2A_2$ and $^2E$ terms are very close although at higher ligand fields these diverge and $^2E$ moves towards the $^2A$ term.

Allen and Warren calculate that the bands for the various transitions in the NiF$_6^{-3}$ ion would be at the following wave numbers.
<table>
<thead>
<tr>
<th>Band Position, KK</th>
<th>Observed</th>
<th>Calculated</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6.8</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>12.3</td>
<td>11.7</td>
<td>2A1 → 2B1</td>
</tr>
<tr>
<td></td>
<td>15.7</td>
<td>14.0</td>
<td>2A1 → 2E</td>
</tr>
<tr>
<td></td>
<td>19.2</td>
<td>16.1</td>
<td>2A1 → 2E</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.8</td>
<td>2A1 → 2B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.6</td>
<td>2A1 → 2A2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.4</td>
<td>2A1 → 2E</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.1</td>
<td>2A1 → 2E</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.2</td>
<td>2A1 → 2B2</td>
</tr>
<tr>
<td></td>
<td>32.0</td>
<td>--</td>
<td>π - eg</td>
</tr>
<tr>
<td></td>
<td>37.0</td>
<td>--</td>
<td>π - eg</td>
</tr>
</tbody>
</table>

\[ D_q = 1620 \text{ cm}^{-1}, \quad B = 703 \text{ cm}^{-1}, \quad DS/Dt = 3.0 \quad \text{and} \quad Dt = 423 \text{ cm}^{-1}. \]

The symmetry tables for the ligand field bands relate to \( D_4 \) symmetry and the charge transfer bands to \( O_h \) 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 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, 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).

\[ \begin{align*}
2E_g & \rightarrow 2T_{2g} \\
2E_g & \rightarrow 2T_{1g} (G) \\
2E_g & \rightarrow 2T_{1g} (H)
\end{align*} \]

and on the whole for the compounds of the type \([Ni(AA)_2]X_3\) where \(AA\) = ethylenediamine and propylenediamine (see Table 11 page 107) three bands are observed.

On Oh symmetry these may be assigned

Band 1 \[ 2E_g \rightarrow 2T_{2g} \text{ near } 13,000 \text{ cm}^{-1} \]

Band 2 \[ 2E_g \rightarrow 2T_{1g} (G) \text{ near } 17,000 \text{ cm}^{-1} \]

Band 3 \[ 2E_g \rightarrow 2T_{1g} (H) \text{ near } 27,000 \text{ cm}^{-1} \]

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

\[ D_3 \]

\[ \begin{align*}
E_E & \rightarrow A_2 \\
E & \rightarrow E \\
E & \rightarrow A_1 \\
E & \rightarrow A_1 \\
E & \rightarrow E \\
E & \rightarrow E \\
2E_g & \rightarrow ^4T_{1g} \\
\end{align*} \]

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 | 9,000 cm⁻¹ |
| Band 2 | 12,000 cm⁻¹ |
| Band 3 | 16,000 cm⁻¹ |
| Band 4 | 19,000 cm⁻¹ |
| Band 5 | 26,000 cm⁻¹ |
| Band 6 | 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 ultraviolet 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 $\rightarrow$ Metal or $L \rightarrow M$; 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 $\rightarrow$ ligand or $M \rightarrow L$.

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

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Frequencies cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\text{A}_1\text{g} \rightarrow 2\text{B}_1\text{g})</td>
<td>7,000 - 8,000</td>
</tr>
<tr>
<td>(2\text{A}<em>1\text{g} \rightarrow 2\text{E}</em>\text{g}(\text{G})(\text{T}_1))</td>
<td>11,000 - 13,000</td>
</tr>
<tr>
<td>(2\text{A}_1\text{g} \rightarrow 2\text{A}_2\text{g}(\text{G}))</td>
<td>12,000 - 15,000</td>
</tr>
<tr>
<td>(2\text{A}<em>1\text{g} \rightarrow 2\text{E}</em>\text{g}(\text{G})\text{T}_2)</td>
<td>16,000 - 17,000</td>
</tr>
<tr>
<td>(2\text{A}<em>1\text{g} \rightarrow 2\text{E}</em>\text{g}(\text{G})\text{T}_3)</td>
<td>17,000 - 17,500</td>
</tr>
<tr>
<td>(2\text{A}_1\text{g} \rightarrow 2\text{A}_2\text{g}(\text{H}))</td>
<td>18,000 - 19,000</td>
</tr>
<tr>
<td>(2\text{A}<em>1\text{g} \rightarrow 2\text{E}</em>\text{g}(\text{H})) (or) (2\text{B}_2\text{g})</td>
<td>26,000 - 27,000</td>
</tr>
<tr>
<td>Charge-transfer bands to (\Sigma)h symmetry</td>
<td></td>
</tr>
<tr>
<td>(\pi - \text{eg})</td>
<td>36,000 - 45,000</td>
</tr>
<tr>
<td>(\pi - \text{eg}) (\text{(two to three bands)})</td>
<td></td>
</tr>
</tbody>
</table>
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.

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

i.e., \( \mu = 1 + 4\pi K \)

where \( \mu \) is the magnetic permeability of the material (not to be confused with \( \mu \) for magnetic moment) and \( K \) is the volume susceptibility of the material. A more convenient quantity than \( K \) is \( \chi \), which is the susceptibility per gram, which is given by \( \chi = \frac{K}{d} \) 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

For diamagnetic substances \( I \), \( K \) and \( \chi \) are negative, \( \mu < 1 \), and they experience a force in the opposite direction to the magnetic field gradient. The value of \( \chi \) 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). Classical mechanics gave as the expression for the susceptibility

\[ \chi_A = \frac{-\hbar e^2}{6\mu_0 c^2} \sum \gamma^2 \]

where \( \gamma^2 \) 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 diamagnetism 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 \( \chi_M \) is the molecular susceptibility

\( n_A \) is the number of atoms of susceptibility

\( \chi_A \) is the molecule, and

\( \lambda \) is the constitution correction, dependent on the nature of the bond in the molecule. From the published values of \( \chi_A \) and \( \lambda \) 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 \( \chi \) are positive \( \mu > 1 \) and they experience a force in the same direction as the magnetic field gradient. The value of \( \chi \) is of the order of \( 10^{-4} \) 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):

\[
\chi = \frac{C}{T} \quad (1)
\]

only a few substances obey this Curie Law very rigidly and very large deviations frequently occur. Weiss improved the Curie Law by introducing a correction \( \Theta \):

\[
\chi = \frac{C}{T} + \Theta \quad (2)
\]

This is so called the Curie-Weiss Law and has a wide applicability. Weiss interpreted \( \Theta \) 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 counteracted 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 $\mu$ Langevin deduced an expression for the susceptibility, which accords with Curie's Law.

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

van Vleck used a quantum mechanical treatment and deduced a similar equation:

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

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

Nowadays magnetic moments are expressed in $\beta$, Bohr magnetons (B.M.). $\beta$ 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 $0.927 \times 10^{-20}$ ergs gauss$^{-1}$. Substituting the value of $\beta$ in the equation (4), the Langevin-Debye equation is obtained.

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

where $\mu$ 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 $\chi_A$ is the quantity measured in order
to derive $\mu$ so that, rearranging (5) and neglecting $N\alpha$, we get

$$\mu e = \sqrt{\frac{3k\chi_A T}{Np^2}}$$

where

- $\mu e = \text{the effective magnetic moment}$
- $k = \text{Boltzmann constant}$
- $N = \text{Avogadro number}$
- $T = \text{absolute temperature}$
- $\chi_A = \text{is the susceptibility per atom or ion; (including diamagnetic}
  \text{correction).}$

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 distinguished three
separate cases according to the relative sizes of the spin multiplet
widths, $\hbar\nu$ of the atoms ground state and the thermally available
energy $kT$.

(i) Multiplet intervals small compared to $kT$; $\hbar\nu \ll kT$
(ii) Multiplet intervals large compared to $kT$; $\hbar\nu \gg kT$
(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 in 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

\[ \Rightarrow \mu = \sqrt{n(n+2)} \]

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

<table>
<thead>
<tr>
<th>No. of d electrons</th>
<th>Ion</th>
<th>$\mu = \frac{[4S(S+1)]}{L(L+1)}$</th>
<th>$\mu = \frac{[4S(S+1)]}{2}$</th>
<th>$\mu$, E.M. observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1$</td>
<td>$T_{1}^3$, $V^{4+}$</td>
<td>3.00</td>
<td>1.73</td>
<td>1.73 to 1.8</td>
</tr>
<tr>
<td>$d^2$</td>
<td>$V^3$</td>
<td>4.47</td>
<td>2.83</td>
<td>2.8 to 3.1</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$Cr^{3+}$, $Mn^{4+}$</td>
<td>5.20</td>
<td>3.87</td>
<td>3.7 to 4.0</td>
</tr>
<tr>
<td>$d^4$</td>
<td>$Mn^{3+}$, $Cr^{2+}$</td>
<td>5.48</td>
<td>4.90</td>
<td>4.8 to 5.1</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$Fe^{3+}$</td>
<td>5.92</td>
<td>5.92</td>
<td>5.7 to 6.1</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$Co^{3+}$</td>
<td>5.43</td>
<td>4.90</td>
<td>5.1 to 5.7</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$Co^{2+}$, (Ni(III))</td>
<td>5.20</td>
<td>3.87</td>
<td>4.3 to 5.2</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$Ni^{2+}$</td>
<td>4.47</td>
<td>2.83</td>
<td>2.6 to 3.5</td>
</tr>
<tr>
<td>$d^9$</td>
<td>$Cu^{2+}$</td>
<td>3.00</td>
<td>1.73</td>
<td>1.7 to 2.2</td>
</tr>
<tr>
<td>$d^{10}$</td>
<td>$Zn^{2+}$</td>
<td>0.00</td>
<td>0.00</td>
<td>diamagnetic</td>
</tr>
</tbody>
</table>
The "quenching" of the orbital contribution is caused by the crystal field in a manner which will be discussed later. Providing the system is magnetically dilute the Curie Law should hold in this case.

Multiplet widths large compared to $kT$; $h\nu \gg kT$

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; $h\nu$ 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

For ferromagnetic substance $\chi$ 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 $\Delta E = Js_i s_j$ (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 $\chi$ 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 $\chi$ is independent of field and follows the Curie-Weiss Law (see below).

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 $\chi$ 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 $45^\circ$ axis through $45^\circ$ converts the $d_{x^2-y^2}$ orbital into the $d_{xy}$ orbital, while $t_{2g}$ orbitals are interconvertible by $90^\circ$ rotations. In an octahedral complex the $d$ orbitals are split into $t_{2g}$ and $e_g$ levels, thus removing the degeneracy of the $d_{x^2-y^2}$ and $d_{xy}$ orbitals and eliminating their contribution to the orbital angular momentum. However, $d_{xy}$ and $d_{yz}$ 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 - d⁶(t₂g⁶) and d⁷(t₂g⁶eg¹)
Spin-free - d³(t₂g³), d⁴(t₂g³eg¹), d⁹(t₂g⁶eg³)

Configurations which will give some orbital contribution are:
Spin-free d¹, d², d⁶ and d⁷
Spin spaired d⁴ and d⁸

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 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

\( \mu_e = \) the observed magnetic moment
\( \mu_o = \) the spin only moment
\( \Delta = \) the energy separation to the nearest level of the same multiplicity.
\( \alpha = \) constant. Its value 4 for F terms.
\( \xi \) = spin-orbital coupling constant.
<table>
<thead>
<tr>
<th>ground term weak</th>
<th>( \lambda )</th>
<th>ground term strong</th>
<th>( \lambda )</th>
<th>ion</th>
<th>( \xi )</th>
<th>No. of d electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4_{t_1g} )</td>
<td>-238</td>
<td>( 2_{eg} )</td>
<td>-715</td>
<td>( \text{Ni}^{3+} )</td>
<td>715</td>
<td>7</td>
</tr>
<tr>
<td>( 5_{t_2g} )</td>
<td>-145</td>
<td>( 1_{A_{1g}} )</td>
<td>-</td>
<td>( \text{Co}^{3+} )</td>
<td>580</td>
<td>6</td>
</tr>
<tr>
<td>( 5_{eg} )</td>
<td>+89</td>
<td>( 3_{t_1g} )</td>
<td>-178</td>
<td>( \text{Mn}^{3+} )</td>
<td>355</td>
<td>4</td>
</tr>
</tbody>
</table>
Determination of Susceptibility

Methods for the measurement of magnetic 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 was used for magnetic susceptibility determinations for solids and liquids. It consists essentially of the suspension of a cylindrical sample of the substance in question in a non-homogeneous 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

\[ A = \text{area of the cross-section of a material between the magnetic poles at that point in the field} \]

and \( I \) is the intensity of magnetisation, i.e. Force/unit area.

\[ \beta = \mu H = H + 4 \pi I \]

\[ = \mu H - H = 4 \pi I \]

\[ \therefore I = H \left( \mu - 1 \right) \frac{1}{4\pi} \]  \( \quad (1) \)
This gives the intensity of magnetisation $I$ at any point in terms of the field strength $H$ and the permeability of the medium $\mu$. 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

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

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

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

$\mu_1 = $ the permeability of the material

$\mu_2 = $ the permeability of the medium (usually air or nitrogen)

$\therefore $ the equation (2) can be

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

$$\therefore F_s = \frac{1}{2}(K_1 - K_2)A(H_1^2 - H_2^2) \quad (\therefore \mu = 1 + 4\pi K \quad \text{general expression for a volume susceptibility})$$

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

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

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

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 = \( \ell \), i.e. \( H_2 \) is arranged to be zero which can be readily provided by a sufficient length of the material is used.

\[
\therefore K_1 = \frac{2F_s}{A(H_1^2)} + K_2 \tag{4}
\]

The mass susceptibility \( \chi = K/P \) where \( P \) = density.

\[
\therefore \chi \times M = K \times V \quad (P = \frac{M}{V} = \frac{W_s}{\ell A} \text{ where } M = \text{mass} \quad V = \text{volume} \quad W_s = \text{wt. of a sample})
\]

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

\[
\therefore \chi = \frac{2F_s}{W_s} \times \frac{1}{\ell A \cdot \frac{H_1}{P}^2} + K_2 \tag{5}
\]

Since \( 2\ell /H_1^2 \) is constant for a given length of material and constant field, it is customary to write equation (5) as

\[
\chi = \frac{\alpha F_s}{W_s} + \frac{V K_2}{W_s} \quad \text{where } \alpha = \frac{2\ell}{H_1^2} \text{ which is also known as a 'Balance constant'}
\]

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.

\( W_s = \text{weight of a sample (material)} \)

\( V = \text{volume of the material gives the magnetic mass susceptibility} \chi \)

\( K_2 = \text{volume susceptibility of air} = + 0.029 \times 10^{-6} \text{ c.g.s. e.m.u.} \)

if nitrogen is used = \( 0.0004 \times 10^{-6} \text{ c.g.s. e.m.u.} \)

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 \( \omega_g \cdot \ell \) in cm.
\[
\chi = \frac{K_2V + (2g\mu) x F_s}{W_s} = \frac{(2g\mu) x F_s}{W_s} + K_2V
\]

\[
= \frac{\alpha x F_s}{W_s} + K_2V \text{ where } \alpha = \frac{2g\mu}{H^2}
\]

\[
\chi = \frac{2 x g x \mu}{W_s x H^2} x F_s \text{ (if nitrogen is used } K_2V \text{ zero negligible)}
\]

\[
\chi_M = \frac{\alpha x F_s}{W_s} x M \text{ where } M = \text{molecular weight of a sample}
\]

\[
\text{ and } \alpha = \text{balance constant}
\]

\[
= 2 x g \frac{\ell}{H^2}
\]

\(\chi_M\) 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

\[
\chi = \frac{2 x g x \ell x F_s}{W_s x H^2} + K_2V
\]

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. 3. To maintain a reasonable field with such dimensions the Humphry'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. 3. It is very similar to that used by Earnshaw, Figgis and Nyholm. 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
A CRYOSTAT ALLOWING AUTOMATIC TEMPERATURE CONTROL FOR A GOUY BALANCE

FIGURE 3-36

- Ground Glass Joint
- Vacuum Pump
- P.T.F.E. Shield
- Copper Chamber
- Asbestos Pad
- Outlets for leads to Pt Resistance, Heating Coil and Thermocouple
- Gaseous N₂
- Liquid Nitrogen
- Specimen

N
S
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 on 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 essentially 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
CONTROL OF THE LEVEL OF LIQUID NITROGEN BY SUNVIC RELAY

Cryostat

Thermistor

Liquid Nitrogen

Leak

Compressed Air

To Compressor

Sunvic Relay

Mains
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 $\pm 0.000005$ 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. Among solid calibrants, $\text{Hg}[\text{Co(CNS)}_4]$ with $X_g = 16.44 \times 10^6$ at $20^\circ\text{C}$ (decreasing approximately $0.05 \times 10^{-6}$ per degree Centigrade rise) and $[\text{Ni(en}_2\text{)}]_2\text{S}_2\text{O}_3$ with $X_g = 11.04 \times 10^{-6}$ at $20^\circ\text{C}$ (decreasing by approximately $0.04 \times 10^{-6}$ per degree Centigrade rise) are common.
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 page 159).

2. Effect of altering length of a specimen and current was found by plotting graphs of length "1 cm" $\rightarrow$ (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 \(\text{Ni}_{\text{2}}\text{S}_{\text{2}}\text{O}_{\text{3}}\) 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 used were: (1) nickel chloride solution; (2) Hg[CO(CNS)$_4$]; (3) Ni$_2$(S$_2$O$_3$)$_3$. 
Figure 38

The optimum position for the base of a tube between the poles of a magnet

Figure 39

Sensitivity of the magnet between the poles pieces
Figure 40. Effect of Altering Length of Specimen and Current on $\text{Ni}_{2n_3} (\text{S}_2\text{O}_3)$

- 17 Amps Current
- 10 Amps Current
- 8 Amps Current
- 4 Amps Current

Pull (Force) – F in Grams

Length – $L$ in cm.
Using the equation (of the susceptibility) where

\[ \chi = \frac{2 \times F_s \times l_s \times g}{W_s \times H^2} \]

- \( F_s = \) Pull in dynes/mg
- \( W_s = \) Weight of a substance in g
- \( l_s = \) Length of a substance in cm
- \( g = \) Gyromagnetic constant = 98
- \( \chi = \) Susceptibility of a (calibrant) substance

\[ = \frac{2 \times g \times l_s}{H^2} \times \frac{F_s}{W_s} = \alpha \times \frac{F_s}{W_s} \]

where \( \alpha = \) balance constant

\[ = \frac{2 \times g \times l_s}{H^2} \]

\[ \therefore H^2 = \frac{2 \times g \times l_s}{\chi \times W_s} \times F_s \]

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

Field calibrations were carried out at 2 amps, 3 amps, 4 amps, 5 amps, 10 amps (see Fig 41, 42, page 162, ).
FIGURE - 42

FIELD CALIBRATION AT 10 AMPS

FIGURE - 43

FIELD CALIBRATION AT 3 AMPS
Results and Discussion of Magnetic Susceptibility Measurements

The variation with temperature in the range 80-300°K of $X_A$ and $\mu_{\text{eff}}$ 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 $t^2g^6e^1$ 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 $^4T_1g - ^2E_g$ cross over point. For $^2E_g (t^2g^6e^1)$ ground state we have a single electron in a doubly degenerate 'g' level which would give rise to substantial Jahn-Teller configurational instability. The inclusion of spin-orbit coupling does not affect this conclusion since $^2E_g$ 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 $[\text{Ni}_2en_4\text{Cl}_2]\text{Cl}_2$. 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)

<table>
<thead>
<tr>
<th>Compound Nien(^2)Cl(_3)</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>(X'_H\times 10^6)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>297.1</td>
<td>1434.0</td>
</tr>
<tr>
<td>284.5</td>
<td>1505.0</td>
</tr>
<tr>
<td>269.1</td>
<td>1592.0</td>
</tr>
<tr>
<td>242.0</td>
<td>1787.0</td>
</tr>
<tr>
<td>221.7</td>
<td>2066.0</td>
</tr>
<tr>
<td>180.3</td>
<td>2463.0</td>
</tr>
<tr>
<td>142.7</td>
<td>3116</td>
</tr>
<tr>
<td>126.1</td>
<td>3528</td>
</tr>
<tr>
<td>107.0</td>
<td>4148</td>
</tr>
<tr>
<td>86.0</td>
<td>5030</td>
</tr>
</tbody>
</table>

\(\theta = -5^\circ\)

Dia. corr. \(10^6 = -162.2\)

### Compound en\(^2\)Br\(_3\)\(\frac{1}{2}\)H\(_2\)O

| Temp °K | \(X'_H\times 10^6\) | \(X'_A\times 10^6\) | \(1/X'_A\times 10^{-2}\) | \(\mu\text{eff B.M.}\) |
|-----------------------------|-------------|
| 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. corr. \(10^6 = -202.3\)
## Table 20

**Variation of Magnetic Moments with Temperature (85 - 300°K)**

### Compound en$_2$ICl$_2$

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{eff}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.8</td>
<td>1398</td>
<td>1587.4</td>
<td>6.30</td>
<td>1.949</td>
</tr>
<tr>
<td>280.7</td>
<td>1477</td>
<td>1666.4</td>
<td>6.0</td>
<td>1.942</td>
</tr>
<tr>
<td>244.0</td>
<td>1722</td>
<td>1916.4</td>
<td>5.22</td>
<td>1.941</td>
</tr>
<tr>
<td>224.3</td>
<td>1890</td>
<td>2079.4</td>
<td>4.81</td>
<td>1.939</td>
</tr>
<tr>
<td>210.3</td>
<td>2009</td>
<td>2198.4</td>
<td>4.55</td>
<td>1.931</td>
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<tr>
<td>180.3</td>
<td>2369</td>
<td>2558.4</td>
<td>3.91</td>
<td>1.929</td>
</tr>
<tr>
<td>140.6</td>
<td>3089</td>
<td>3278.4</td>
<td>3.05</td>
<td>1.928</td>
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<tr>
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<td>3978</td>
<td>4167.4</td>
<td>2.40</td>
<td>1.923</td>
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<tr>
<td>88.0</td>
<td>4938</td>
<td>4927.4</td>
<td>2.03</td>
<td>1.849</td>
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</table>

$\theta = -8°$

Dia. Corrn. $\times 10^{-6} = -189.4$

### Compound en$_2$IBr$_2$

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{eff}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.3</td>
<td>1422.0</td>
<td>1623.8</td>
<td>6.162</td>
<td>1.970</td>
</tr>
<tr>
<td>280.1</td>
<td>1544.0</td>
<td>1745.8</td>
<td>5.731</td>
<td>1.950</td>
</tr>
<tr>
<td>234.0</td>
<td>1799.0</td>
<td>2000.8</td>
<td>5.00</td>
<td>1.943</td>
</tr>
<tr>
<td>201.3</td>
<td>2119.0</td>
<td>2320.8</td>
<td>4.31</td>
<td>1.941</td>
</tr>
<tr>
<td>173.0</td>
<td>2487.0</td>
<td>2688.8</td>
<td>3.72</td>
<td>1.936</td>
</tr>
<tr>
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</tr>
<tr>
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<td>5263.8</td>
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<td>1.910</td>
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$\theta = -12°$

Dia. Corrn $\times 10^{-6} = -201.80$
### TABLE 21
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

#### Compound \(Ni_{2}Cl_{3} \cdot 2H_{2}O\)

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>(X' \times 10^6)</th>
<th>(X'_{A} \times 10^6)</th>
<th>(1/X'_{A} \times 10^{-2})</th>
<th>(\mu_{eff} B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>297.0</td>
<td>1285</td>
<td>1473.3</td>
<td>6.799</td>
<td>1.878</td>
</tr>
<tr>
<td>282.4</td>
<td>1350</td>
<td>1538.3</td>
<td>6.503</td>
<td>1.869</td>
</tr>
<tr>
<td>270.3</td>
<td>1404</td>
<td>1592.3</td>
<td>6.281</td>
<td>1.863</td>
</tr>
<tr>
<td>245.0</td>
<td>1566</td>
<td>1754.3</td>
<td>5.701</td>
<td>1.862</td>
</tr>
<tr>
<td>210.0</td>
<td>1853</td>
<td>2154.3</td>
<td>4.913</td>
<td>1.858</td>
</tr>
<tr>
<td>171.0</td>
<td>2312</td>
<td>2500.3</td>
<td>4.0</td>
<td>1.857</td>
</tr>
<tr>
<td>145.8</td>
<td>2669</td>
<td>2857.3</td>
<td>3.50</td>
<td>1.846</td>
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<tr>
<td>110.0</td>
<td>3488</td>
<td>3676.3</td>
<td>2.720</td>
<td>1.805</td>
</tr>
<tr>
<td>88.2</td>
<td>4276</td>
<td>4464.3</td>
<td>2.240</td>
<td>1.782</td>
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</table>

\(\theta = -12^\circ\)

Diac. Corrn. \(x \times 10^{-6} = -188.28\)

#### Compound \(en_{2}Br_{2}Cl_{1} \cdot \frac{1}{2} H_{2}O\)

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>(X' \times 10^6)</th>
<th>(X'_{A} \times 10^6)</th>
<th>(1/X'_{A} \times 10^{-2})</th>
<th>(\mu_{eff} B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.3</td>
<td>1347.0</td>
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<td>6.503</td>
<td>1.921</td>
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<tr>
<td>280.1</td>
<td>1427</td>
<td>1618.1</td>
<td>6.182</td>
<td>1.912</td>
</tr>
<tr>
<td>263.0</td>
<td>1533</td>
<td>1724.1</td>
<td>5.801</td>
<td>1.911</td>
</tr>
<tr>
<td>243.0</td>
<td>1668</td>
<td>1859.1</td>
<td>5.379</td>
<td>1.865</td>
</tr>
<tr>
<td>210.3</td>
<td>1959</td>
<td>2150.1</td>
<td>4.651</td>
<td>1.864</td>
</tr>
<tr>
<td>172.0</td>
<td>2309</td>
<td>2500.1</td>
<td>4.00</td>
<td>1.862</td>
</tr>
<tr>
<td>136.9</td>
<td>2934</td>
<td>3125.1</td>
<td>3.20</td>
<td>1.859</td>
</tr>
<tr>
<td>(137.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110.3</td>
<td>3874</td>
<td>4065.1</td>
<td>2.46</td>
<td>-</td>
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<td>86.0</td>
<td>4736</td>
<td>4927.1</td>
<td>2.030</td>
<td>1.848</td>
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</tbody>
</table>

\(\theta = -8^\circ\)

Diac. Corrn. \(x \times 10^{-6} = -191.10\)
TABLE 22
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>μeff B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.0</td>
<td>1391</td>
<td>1539</td>
<td>6.498</td>
<td>1.92</td>
</tr>
<tr>
<td>282.1</td>
<td>1455</td>
<td>1603</td>
<td>6.239</td>
<td>1.914</td>
</tr>
<tr>
<td>272.8</td>
<td>1518</td>
<td>1666</td>
<td>6.002</td>
<td>1.914</td>
</tr>
<tr>
<td>244</td>
<td>1690</td>
<td>1838</td>
<td>5.441</td>
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<td>222.5</td>
<td>1893</td>
<td>2041</td>
<td>4.900</td>
<td>1.90</td>
</tr>
<tr>
<td>196.1</td>
<td>2161</td>
<td>2309</td>
<td>4.332</td>
<td>1.90</td>
</tr>
<tr>
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<td>1.893</td>
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<tr>
<td>126.8</td>
<td>3398</td>
<td>3546</td>
<td>2.82</td>
<td>1.891</td>
</tr>
<tr>
<td>112.8</td>
<td>3852</td>
<td>4000</td>
<td>2.50</td>
<td>1.884</td>
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<tr>
<td>88.0</td>
<td>4716</td>
<td>4864</td>
<td>2.056</td>
<td>1.852</td>
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</table>

$\theta = -12°$

Dia. Corrn. x $10^{-6}$ = -148

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>μeff B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.0</td>
<td>1380</td>
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<td>6.602</td>
<td>1.920</td>
</tr>
<tr>
<td>282.0</td>
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<td>1587</td>
<td>6.300</td>
<td>1.912</td>
</tr>
<tr>
<td>272.3</td>
<td>1504</td>
<td>1639</td>
<td>6.102</td>
<td>1.900</td>
</tr>
<tr>
<td>243.8</td>
<td>2107</td>
<td>2242</td>
<td>4.460</td>
<td>1.898</td>
</tr>
<tr>
<td>223.8</td>
<td>2107</td>
<td>2242</td>
<td>5.00</td>
<td>1.898</td>
</tr>
<tr>
<td>196.6</td>
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<td>2270</td>
<td>4.405</td>
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<td>3462</td>
<td>2.888</td>
<td>1.892</td>
</tr>
<tr>
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<td>3922</td>
<td>2.550</td>
<td>1.882</td>
</tr>
<tr>
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<td>4673</td>
<td>4808</td>
<td>2.080</td>
<td>1.847</td>
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</tbody>
</table>

$\theta = -10°$

Dia. Corrn. x $10^{-6}$ = -135.0
FIG. 45

- $\text{Ni}_2\text{Cl}_3$
- $\text{Ni}_2\text{Cl}_2(\text{ClO}_4)$
- $\text{Ni}_2\text{Cl}_2(\text{NO}_3)$

Radawod monomer susceptibility ordinate temperature and magnetic moments against temperature for:

- $\text{NiP}_2\text{BrCl}_2$
- $\text{NiP}_2\text{Br}_3$
- $\text{NiP}_2\text{Cl}_3$
<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_N \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>(\mu_{\text{eff}}\text{ B.M.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>297.1</td>
<td>1263</td>
<td>1506</td>
<td>6.638</td>
<td>1.902</td>
</tr>
<tr>
<td>284.5</td>
<td>1344</td>
<td>1587.8</td>
<td>6.30</td>
<td>1.901</td>
</tr>
<tr>
<td>269.1</td>
<td>1396</td>
<td>1639.8</td>
<td>6.11</td>
<td>1.901</td>
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<td>5.489</td>
<td>1.891</td>
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<td>2222.8</td>
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<td>-</td>
</tr>
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<td>2500.8</td>
<td>4.00</td>
<td>1.884</td>
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<td>3.21</td>
<td>1.884</td>
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</table>

$\phi = -12^\circ$  
\(\text{Dia Corrn. } \times 10^{-6} = -243.80\)
### Table 24

Variation of Magnetic Moments with Temperature (85 - 300°K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pn}_2\text{Cl}_3$</td>
<td></td>
</tr>
<tr>
<td><strong>Temp °K</strong></td>
<td>$X_M' x 10^6$</td>
</tr>
<tr>
<td>298.0</td>
<td>1286.0</td>
</tr>
<tr>
<td>280.0</td>
<td>1361</td>
</tr>
<tr>
<td>246.1</td>
<td>1568</td>
</tr>
<tr>
<td>210.0</td>
<td>1841</td>
</tr>
<tr>
<td>182.0</td>
<td>2138</td>
</tr>
<tr>
<td>144.3</td>
<td>2670</td>
</tr>
<tr>
<td>110.2</td>
<td>3465</td>
</tr>
<tr>
<td>90.3</td>
<td>4076</td>
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</tbody>
</table>

$\theta = -18^\circ$

Dia. corr. x $10^{-6} = -187.08$

<table>
<thead>
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<th>Field 5 amps</th>
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</thead>
<tbody>
<tr>
<td>$\text{Pn}_2\text{Br}_3$</td>
<td></td>
</tr>
<tr>
<td><strong>Temp °K</strong></td>
<td>$X_M' x 10^6$</td>
</tr>
<tr>
<td>296.1</td>
<td>1328</td>
</tr>
<tr>
<td>280.3</td>
<td>1406</td>
</tr>
<tr>
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<tr>
<td>207.0</td>
<td>1926</td>
</tr>
<tr>
<td>180.3</td>
<td>2231</td>
</tr>
<tr>
<td>146.3</td>
<td>2783</td>
</tr>
<tr>
<td>110.2</td>
<td>3597</td>
</tr>
<tr>
<td>88.4</td>
<td>4350</td>
</tr>
</tbody>
</table>

$\theta = -22^\circ$

Dia. corr. x $10^{-6} = -220.68$
### TABLE 25

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

<table>
<thead>
<tr>
<th>Compound $\text{Pn}_2\text{BrCl}_2$</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp °K</strong></td>
<td>$X'_N \times 10^6$</td>
</tr>
<tr>
<td>296.1</td>
<td>1415.0</td>
</tr>
<tr>
<td>280.1</td>
<td>1497.0</td>
</tr>
<tr>
<td>244.3</td>
<td>1726</td>
</tr>
<tr>
<td>210.1</td>
<td>2024</td>
</tr>
<tr>
<td>180.0</td>
<td>2366</td>
</tr>
<tr>
<td>144.2</td>
<td>2917</td>
</tr>
<tr>
<td>110.0</td>
<td>3786</td>
</tr>
<tr>
<td>90.0</td>
<td>4466</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound $\text{Pn}_2\text{ICl}_2\cdot 2\text{H}_2\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp °K</strong></td>
</tr>
<tr>
<td>298.0</td>
</tr>
<tr>
<td>279.0</td>
</tr>
<tr>
<td>268.0</td>
</tr>
<tr>
<td>244.0</td>
</tr>
<tr>
<td>210.0</td>
</tr>
<tr>
<td>180.0</td>
</tr>
<tr>
<td>142.0</td>
</tr>
<tr>
<td>110.1</td>
</tr>
<tr>
<td>88.6</td>
</tr>
</tbody>
</table>

$\theta = -20^\circ$ Dia. corrn. $\times 10^{-6} = -235.28$
# TABLE 26

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pn}_2\text{Cl}_2(\text{ClO}_4)$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.0</td>
<td>1370</td>
<td>1544</td>
<td>6.477</td>
<td>1.921</td>
</tr>
<tr>
<td>283.1</td>
<td>1439</td>
<td>1613</td>
<td>6.200</td>
<td>1.917</td>
</tr>
<tr>
<td>274.0</td>
<td>1493</td>
<td>1667</td>
<td>5.998</td>
<td>1.917</td>
</tr>
<tr>
<td>244.0</td>
<td>1678</td>
<td>1852</td>
<td>5.400</td>
<td>1.910</td>
</tr>
<tr>
<td>223.1</td>
<td>1851</td>
<td>2025</td>
<td>4.938</td>
<td>1.910</td>
</tr>
<tr>
<td>196.8</td>
<td>2172</td>
<td>2346</td>
<td>4.230</td>
<td>1.900</td>
</tr>
<tr>
<td>151.0</td>
<td>2711</td>
<td>2885</td>
<td>3.466</td>
<td>1.869</td>
</tr>
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<td>3159</td>
<td>3333</td>
<td>3.00</td>
<td>1.855</td>
</tr>
<tr>
<td>112.0</td>
<td>3585</td>
<td>3759</td>
<td>2661</td>
<td>1.841</td>
</tr>
<tr>
<td>88.4</td>
<td>4088</td>
<td>4262</td>
<td>2.346</td>
<td>1.748</td>
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</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$\text{Pn}_2\text{Cl}_2(\text{NO}_3)$</th>
<th>Field 5 amps</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.0</td>
<td>1379</td>
<td>1541</td>
<td>6.490</td>
<td>1.921</td>
</tr>
<tr>
<td>283.1</td>
<td>1454</td>
<td>1616</td>
<td>6.189</td>
<td>1.928</td>
</tr>
<tr>
<td>274.0</td>
<td>1504</td>
<td>1666</td>
<td>6.002</td>
<td>1.918</td>
</tr>
<tr>
<td>244.0</td>
<td>1705</td>
<td>1867</td>
<td>5.356</td>
<td>1.917</td>
</tr>
<tr>
<td>221.3</td>
<td>1883</td>
<td>2045</td>
<td>4.890</td>
<td>1.911</td>
</tr>
<tr>
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<td>2119</td>
<td>2281</td>
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<td>1.900</td>
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<tr>
<td>150.0</td>
<td>2779</td>
<td>2941</td>
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<td>1.891</td>
</tr>
<tr>
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<td>3300</td>
<td>3462</td>
<td>2.888</td>
<td>1.868</td>
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<tr>
<td>112.0</td>
<td>3615</td>
<td>3777</td>
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<td>1.847</td>
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<tr>
<td>85.1</td>
<td>4105</td>
<td>4267</td>
<td>2.344</td>
<td>1.716</td>
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$\theta = -22^\circ$  
Dia. Corrn. $x 10^{-6} = -162$.  

$e = -24^\circ$  
Dia. Corrn. $x 10^{-6} = -174$
FIG. 46

\[ \chi_A^{-1} \times 10^2 \]

Temperature and magnetic moment for:

- NiPn\(_2\)Cl\(_2\) \(2\)H\(_2\)O
- NiPn\(_2\)Cl\(_2\)(NO\(_3\))
- NiPn\(_2\)IBr\(_2\)
- NiPn\(_2\)Cl\(_2\)(ClO\(_4\))
<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_m \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>297.3</td>
<td>1361</td>
<td>1587.7</td>
<td>6.3</td>
<td>1.951</td>
</tr>
<tr>
<td>280.0</td>
<td>1423</td>
<td>1653.7</td>
<td>6.05</td>
<td>1.932</td>
</tr>
<tr>
<td>270.3</td>
<td>1489</td>
<td>1715.7</td>
<td>5.832</td>
<td>1.932</td>
</tr>
<tr>
<td>246.1</td>
<td>1682</td>
<td>1908.7</td>
<td>5.342</td>
<td>1.926</td>
</tr>
<tr>
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<td>1942</td>
<td>2173.7</td>
<td>4.601</td>
<td>1.918</td>
</tr>
<tr>
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<td>2274</td>
<td>2500.7</td>
<td>4.00</td>
<td>1.905</td>
</tr>
<tr>
<td>146.3</td>
<td>3758</td>
<td>3984.7</td>
<td>2.35</td>
<td>1.900</td>
</tr>
<tr>
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<td>4255.7</td>
<td>2.51</td>
<td>1.900</td>
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<td>90.0</td>
<td>4340</td>
<td>4566.7</td>
<td>2.19</td>
<td>1.823</td>
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</tbody>
</table>

$Q = -24^\circ$  
Dia Courn. $\times 10^{-6} = -226.68$
### TABLE 28

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>en$_3$Cl$_3$HCl,2H$_2$O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_H \times 10^6$</td>
<td>$X'_A \times 10^6$</td>
</tr>
<tr>
<td>296.1</td>
<td>1212.0</td>
<td>1470.6</td>
</tr>
<tr>
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<td>1280.0</td>
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<tr>
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<td>1355.0</td>
<td>1613.6</td>
</tr>
<tr>
<td>243.9</td>
<td>1525.0</td>
<td>1783.6</td>
</tr>
<tr>
<td>224.1</td>
<td>1665.0</td>
<td>1923.6</td>
</tr>
<tr>
<td>180.0</td>
<td>2117.0</td>
<td>2375.6</td>
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<tr>
<td>144.2</td>
<td>2615</td>
<td>2873.6</td>
</tr>
<tr>
<td>125.3</td>
<td>3075</td>
<td>3333.6</td>
</tr>
<tr>
<td>110.0</td>
<td>3418</td>
<td>3676.6</td>
</tr>
<tr>
<td>88.0</td>
<td>4237.0</td>
<td>4495.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>en$_3$Br$_3$HBr,2H$_2$O</th>
<th>Field 5 amp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_H \times 10^6$</td>
<td>$X'_A \times 10^6$</td>
</tr>
<tr>
<td>296.0</td>
<td>1088.0</td>
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</tr>
<tr>
<td>280.4</td>
<td>1667.0</td>
<td>1370.4</td>
</tr>
<tr>
<td>246.3</td>
<td>1230</td>
<td>1543.4</td>
</tr>
<tr>
<td>224.1</td>
<td>1363.0</td>
<td>1666.4</td>
</tr>
<tr>
<td>180.2</td>
<td>1760.0</td>
<td>2063.4</td>
</tr>
<tr>
<td>145.3</td>
<td>2197.0</td>
<td>2500.4</td>
</tr>
<tr>
<td>125.4</td>
<td>2554.0</td>
<td>2857.4</td>
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<tr>
<td>110.0</td>
<td>2877</td>
<td>3180.4</td>
</tr>
<tr>
<td>90.0</td>
<td>3543</td>
<td>3846.4</td>
</tr>
</tbody>
</table>

$\theta = 0°$  
Dia. Corrn. x $10^{-6} = 303.4$
Reciprocal magnetic susceptibility against temperature for:

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

$\chi^{-1} \times 10^{-2}$ vs. $\mu_0$ (B.M.)

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

$\chi^{-1} \times 10^{-2}$ vs. $\mu_0$ (B.M.)

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

$\chi^{-1} \times 10^{-2}$ vs. $\mu_0$ (B.M.)

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

$\chi^{-1} \times 10^{-2}$ vs. $\mu_0$ (B.M.)
TABLE 29
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

<table>
<thead>
<tr>
<th>Compound en$_3$I$_3$,HI,2H$_2$O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_M x 10^6$</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>298.1</td>
<td>1148.0</td>
</tr>
<tr>
<td>280.0</td>
<td>1113.0</td>
</tr>
<tr>
<td>260.0</td>
<td>1114.0</td>
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<tr>
<td>246.0</td>
<td>1195.0</td>
</tr>
<tr>
<td>222.1</td>
<td>1357.0</td>
</tr>
<tr>
<td>180.2</td>
<td>1716.0</td>
</tr>
<tr>
<td>144.1</td>
<td>2197.0</td>
</tr>
<tr>
<td>123.9</td>
<td>2574.0</td>
</tr>
<tr>
<td>88.9</td>
<td>3665.0</td>
</tr>
</tbody>
</table>

$\theta = 0^\circ$

Dia. Corrn. x $10^{-6} = -367.40$

<table>
<thead>
<tr>
<th>Compound en$_3$Cl$_3$,3H$_2$O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_M x 10^6$</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>296.3</td>
<td>1263</td>
</tr>
<tr>
<td>280.0</td>
<td>1340</td>
</tr>
<tr>
<td>273.8</td>
<td>1366</td>
</tr>
<tr>
<td>243.2</td>
<td>1565</td>
</tr>
<tr>
<td>210.1</td>
<td>1832</td>
</tr>
<tr>
<td>180.3</td>
<td>2163</td>
</tr>
<tr>
<td>146.1</td>
<td>2703</td>
</tr>
<tr>
<td>124.1</td>
<td>3201</td>
</tr>
<tr>
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<td>3599</td>
</tr>
<tr>
<td>88.0</td>
<td>4340</td>
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$\theta = 0^\circ$

Dia. Corrn. x $10^{-6} = -247.2$
TABLE 30
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 – 300°K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{en}_3\text{Br}_2\text{H}_2\text{O}$</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp °K</strong></td>
<td>$X'_M \times 10^6$</td>
<td>$X'_A \times 10^6$</td>
</tr>
<tr>
<td>296</td>
<td>1295</td>
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</tr>
<tr>
<td>281.6</td>
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<td>242.1</td>
<td>1609</td>
<td>1876.8</td>
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<tr>
<td>226.3</td>
<td>1733</td>
<td>2000.8</td>
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<td>1842</td>
<td>2119.8</td>
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<tr>
<td>178.0</td>
<td>2233</td>
<td>2500.8</td>
</tr>
<tr>
<td>146.2</td>
<td>2736</td>
<td>3003.8</td>
</tr>
<tr>
<td>112.3</td>
<td>3279</td>
<td>3546.8</td>
</tr>
<tr>
<td>110.0</td>
<td>3609</td>
<td>3876.8</td>
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<td>4652.8</td>
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</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{en}_3\text{I}_3$</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp °K</strong></td>
<td>$X'_M \times 10^6$</td>
<td>$X'_A \times 10^6$</td>
</tr>
<tr>
<td>298.0</td>
<td>1248.0</td>
<td>1537.8</td>
</tr>
<tr>
<td>280.4</td>
<td>1203</td>
<td>1492.8</td>
</tr>
<tr>
<td>262.4</td>
<td>1248</td>
<td>1537.8</td>
</tr>
<tr>
<td>242.0</td>
<td>1377</td>
<td>1666.8</td>
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<tr>
<td>222.0</td>
<td>1503</td>
<td>1792.8</td>
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<td>180.2</td>
<td>1884</td>
<td>2173.8</td>
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<td>146.2</td>
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<td>2632.8</td>
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<td>110.0</td>
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<td>3333.8</td>
</tr>
<tr>
<td>90.0</td>
<td>3743</td>
<td>4032.8</td>
</tr>
</tbody>
</table>

$\theta = -4^\circ$  
Dia. Corrn. $x 10^{-6} = -289.8$
TABLE 31

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pn₃Br₃</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>X'Mx10⁶</td>
<td>X'Ax10⁶</td>
</tr>
<tr>
<td>297.0</td>
<td>1264</td>
<td>1543</td>
</tr>
<tr>
<td>270.0</td>
<td>1415</td>
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</tr>
<tr>
<td>246.3</td>
<td>1566</td>
<td>1845</td>
</tr>
<tr>
<td>210.0</td>
<td>1858</td>
<td>2137</td>
</tr>
<tr>
<td>180.4</td>
<td>2172</td>
<td>2451</td>
</tr>
<tr>
<td>146.1</td>
<td>2654</td>
<td>2933</td>
</tr>
<tr>
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<td>3968</td>
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<tr>
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</table>

θ = -5°

Dia. Corrn. x 10⁻⁶ = -279.12

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pn₃Br₃·2H₂O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>X'Mx10⁶</td>
<td>X'Ax10⁶</td>
</tr>
<tr>
<td>297.0</td>
<td>1231</td>
<td>1536.1</td>
</tr>
<tr>
<td>280.3</td>
<td>1318</td>
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</tr>
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<td>1666.1</td>
</tr>
<tr>
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<td>2146</td>
<td>2452.1</td>
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<td>4624.1</td>
</tr>
</tbody>
</table>

θ = -5°

Dia. Corrn. x 10⁻⁶ = -305.12
FIG. 48

- Ni(N-meen)$_2$Br$_3$
- Ni(N-meen)$_2$Cl$_3$2H$_2$O
- Ni(N-meen)$_2$I$_3$
- Ni(N-meen)$_2$Br$_3$2H$_2$O
### TABLE 32

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

<table>
<thead>
<tr>
<th>Compound (N-Meen) $\mathrm{Cl}_3\mathrm{H}_2\mathrm{O}$</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp $^\circ\mathrm{K}$</td>
<td>$X'_M \times 10^6$</td>
</tr>
<tr>
<td>296.2</td>
<td>1326.0</td>
</tr>
<tr>
<td>282.1</td>
<td>1400</td>
</tr>
<tr>
<td>272.8</td>
<td>1454</td>
</tr>
<tr>
<td>244.3</td>
<td>1635</td>
</tr>
<tr>
<td>210.3</td>
<td>1888</td>
</tr>
<tr>
<td>180.0</td>
<td>2226</td>
</tr>
<tr>
<td>146.2</td>
<td>2720</td>
</tr>
<tr>
<td>110.0</td>
<td>3591</td>
</tr>
<tr>
<td>90.0</td>
<td>4097</td>
</tr>
</tbody>
</table>

(Meen = Methylethylenediamine)  
Dia. Corrn $\times 10^{-6} = -213.08$  
$\theta = -12^\circ$

<table>
<thead>
<tr>
<th>Compound (N-Meen)$_2\mathrm{Br}_3$</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp $^\circ\mathrm{K}$</td>
<td>$X'_M \times 10^6$</td>
</tr>
<tr>
<td>293.6</td>
<td>1319</td>
</tr>
<tr>
<td>282.0</td>
<td>1372</td>
</tr>
<tr>
<td>270.1</td>
<td>1447</td>
</tr>
<tr>
<td>244.3</td>
<td>1598</td>
</tr>
<tr>
<td>210.1</td>
<td>1859</td>
</tr>
<tr>
<td>180.3</td>
<td>2161</td>
</tr>
<tr>
<td>110.1</td>
<td>3430</td>
</tr>
<tr>
<td>88.9</td>
<td>4128.0</td>
</tr>
</tbody>
</table>

$\theta = -18^\circ$  
Dia. Corrn $\times 10^{-6} = -220.68$
TABLE 33
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(N-Meen)\textsubscript{2}I₃</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>X'_M \times 10^6</td>
<td>X'_A \times 10^6</td>
</tr>
<tr>
<td>296</td>
<td>1270</td>
<td>1538.6</td>
</tr>
<tr>
<td>280.3</td>
<td>1369</td>
<td>1637.6</td>
</tr>
<tr>
<td>246.3</td>
<td>1550</td>
<td>1818.6</td>
</tr>
<tr>
<td>210.0</td>
<td>1837</td>
<td>2105.6</td>
</tr>
<tr>
<td>180.8</td>
<td>2171</td>
<td>2439.6</td>
</tr>
<tr>
<td>110.0</td>
<td>3436</td>
<td>3704.6</td>
</tr>
<tr>
<td>90.0</td>
<td>4080</td>
<td>4348.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>(NN-2Meen)\textsubscript{2}Cl₃\textsubscript{2}H₂O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>X'_M \times 10^6</td>
<td>X'_A \times 10^6</td>
</tr>
<tr>
<td>296.0</td>
<td>1268</td>
<td>1502.8</td>
</tr>
<tr>
<td>283.0</td>
<td>1321</td>
<td>1555.8</td>
</tr>
<tr>
<td>273.0</td>
<td>1377</td>
<td>1611.8</td>
</tr>
<tr>
<td>244.0</td>
<td>1550</td>
<td>1784.8</td>
</tr>
<tr>
<td>223.2</td>
<td>1700</td>
<td>1934.8</td>
</tr>
<tr>
<td>196.1</td>
<td>1931</td>
<td>2165.8</td>
</tr>
<tr>
<td>150.3</td>
<td>2485</td>
<td>2719.8</td>
</tr>
<tr>
<td>128.7</td>
<td>2841</td>
<td>3075.8</td>
</tr>
<tr>
<td>112.0</td>
<td>3181</td>
<td>3415.8</td>
</tr>
<tr>
<td>90.2</td>
<td>3933</td>
<td>4167.8</td>
</tr>
</tbody>
</table>

\theta = -20°
Dia. Corrn. x 10^{-6} = -234.8
TABLE 34
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85-300°K)

* Compound (NN-2Meen)$_2$Br$_2$,2H$_2$O

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.1</td>
<td>1231.0</td>
<td>1499.5</td>
<td>6.70</td>
<td>1.892</td>
</tr>
<tr>
<td>282.5</td>
<td>1292.0</td>
<td>1560.5</td>
<td>6.418</td>
<td>1.887</td>
</tr>
<tr>
<td>273.0</td>
<td>1348</td>
<td>1616.5</td>
<td>6.19</td>
<td>1.887</td>
</tr>
<tr>
<td>243.9</td>
<td>1513</td>
<td>1781.5</td>
<td>5.615</td>
<td>1.872</td>
</tr>
<tr>
<td>223.1</td>
<td>1653</td>
<td>1921.5</td>
<td>5.188</td>
<td>1.862</td>
</tr>
<tr>
<td>196.3</td>
<td>1906</td>
<td>2174.5</td>
<td>4.620</td>
<td>1.813</td>
</tr>
<tr>
<td>150.1</td>
<td>2135</td>
<td>2703.5</td>
<td>3.699</td>
<td>1.809</td>
</tr>
<tr>
<td>128.5</td>
<td>2753</td>
<td>3021.5</td>
<td>3.30</td>
<td>1.770</td>
</tr>
<tr>
<td>112.5</td>
<td>3142</td>
<td>3410.5</td>
<td>2.933</td>
<td>1.756</td>
</tr>
<tr>
<td>90.0</td>
<td>3881</td>
<td>4149.5</td>
<td>2.41</td>
<td>1.735</td>
</tr>
</tbody>
</table>

$\theta = -22^\circ$  
Dia. Corrn. x $10^{-6} = -268.48$

* Compound (NN-2Meen)$_2$I$_3$,2H$_2$O

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.0</td>
<td>1188</td>
<td>1504.4</td>
<td>6.65</td>
<td>1.894</td>
</tr>
<tr>
<td>283.0</td>
<td>1239</td>
<td>1555.4</td>
<td>6.43</td>
<td>1.884</td>
</tr>
<tr>
<td>273.1</td>
<td>1294</td>
<td>1610.4</td>
<td>6.211</td>
<td>1.883</td>
</tr>
<tr>
<td>244.0</td>
<td>1469</td>
<td>1785.4</td>
<td>5.602</td>
<td>1.874</td>
</tr>
<tr>
<td>223.1</td>
<td>1619</td>
<td>1935.4</td>
<td>5.168</td>
<td>1.866</td>
</tr>
<tr>
<td>196.0</td>
<td>1858</td>
<td>2174.4</td>
<td>4.600</td>
<td>1.854</td>
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<tr>
<td>150.0</td>
<td>2127</td>
<td>2443.4</td>
<td>3.645</td>
<td>-</td>
</tr>
<tr>
<td>128.6</td>
<td>2809</td>
<td>3125.4</td>
<td>3.200</td>
<td>1.801</td>
</tr>
<tr>
<td>112.4</td>
<td>3161</td>
<td>3477.4</td>
<td>2.876</td>
<td>1.781</td>
</tr>
<tr>
<td>90.0</td>
<td>3851</td>
<td>4167.4</td>
<td>2.40</td>
<td>1.740</td>
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</tbody>
</table>

$\theta = -22^\circ$  
Dia. Corrn. x $10^{-6} = -316.4$
### Table 33

**Variation of Magnetic Moments with Temperature (83 - 300 K)**

<table>
<thead>
<tr>
<th>Compound (N,N'-2Meen)$_2$Cl$_3$2H$_2$O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_M \times 10^6$</td>
</tr>
<tr>
<td>296.0</td>
<td>1281</td>
</tr>
<tr>
<td>283.1</td>
<td>1329</td>
</tr>
<tr>
<td>273.1</td>
<td>1378</td>
</tr>
<tr>
<td>246.5</td>
<td>1545</td>
</tr>
<tr>
<td>208.3</td>
<td>1871</td>
</tr>
<tr>
<td>190.0</td>
<td>2021</td>
</tr>
<tr>
<td>149.6</td>
<td>2473</td>
</tr>
<tr>
<td>128.5</td>
<td>2807</td>
</tr>
<tr>
<td>112.0</td>
<td>3191</td>
</tr>
<tr>
<td>90.3</td>
<td>3831</td>
</tr>
</tbody>
</table>

$\theta = -25^\circ$

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

<table>
<thead>
<tr>
<th>Compound (N,N'-2Meen)$_2$Br$_3$2H$_2$O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_M \times 10^6$</td>
</tr>
<tr>
<td>296.0</td>
<td>1229</td>
</tr>
<tr>
<td>284.4</td>
<td>1311</td>
</tr>
<tr>
<td>276.0</td>
<td>1355</td>
</tr>
<tr>
<td>244.0</td>
<td>1533</td>
</tr>
<tr>
<td>223.0</td>
<td>1692</td>
</tr>
<tr>
<td>196.3</td>
<td>1928</td>
</tr>
<tr>
<td>150.1</td>
<td>2583</td>
</tr>
<tr>
<td>112.4</td>
<td>3281</td>
</tr>
<tr>
<td>90.2</td>
<td>3920</td>
</tr>
</tbody>
</table>

$\theta = -25^\circ$

Dia. Corrn. x $10^{-6} = -268.48$
FIG. 48(a)

- Ni(N-meen)$_2$Br$_3$
- Ni(N,meeen)$_2$Br$_3$·2H$_2$O
- Ni(N,meeen)$_2$I$_3$·2H$_2$O

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

- Ni(N,meeen)$_2$Cl$_3$·2H$_2$O
- Ni(N,N'-meen)$_2$Br$_3$·2H$_2$O
TABLE 36
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(N,N'-2Meen)I₃,2H₂O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>X'M x10⁶</td>
<td>X'A x10⁶</td>
</tr>
<tr>
<td>296.0</td>
<td>1179</td>
<td>1495</td>
</tr>
<tr>
<td>283.0</td>
<td>1247</td>
<td>1563</td>
</tr>
<tr>
<td>273.1</td>
<td>1298</td>
<td>1614</td>
</tr>
<tr>
<td>244.0</td>
<td>1470</td>
<td>1786</td>
</tr>
<tr>
<td>222.8</td>
<td>1620</td>
<td>1936</td>
</tr>
<tr>
<td>196.1</td>
<td>1859</td>
<td>2175</td>
</tr>
<tr>
<td>148.8</td>
<td>2462</td>
<td>2778</td>
</tr>
<tr>
<td>128.5</td>
<td>2818</td>
<td>3134</td>
</tr>
<tr>
<td>112.3</td>
<td>3211</td>
<td>3527</td>
</tr>
<tr>
<td>90.1</td>
<td>3851</td>
<td>4167</td>
</tr>
</tbody>
</table>

θ = -30°

Dia. Corrn. x 10⁻⁶ = -316.4

* These are nickel complexes
### TABLE 37
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>μeff B.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.3</td>
<td>1178</td>
<td>1543</td>
<td>6.51</td>
<td>1.915</td>
</tr>
<tr>
<td>284.2</td>
<td>1248</td>
<td>1613</td>
<td>6.301</td>
<td>1.907</td>
</tr>
<tr>
<td>273.1</td>
<td>1302</td>
<td>1667</td>
<td>6.056</td>
<td>1.907</td>
</tr>
<tr>
<td>244.1</td>
<td>1483</td>
<td>1848</td>
<td>5.49</td>
<td>1.92</td>
</tr>
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<td>223</td>
<td>1635</td>
<td>2000</td>
<td>5.088</td>
<td>1.882</td>
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<td>1857</td>
<td>2222</td>
<td>4.466</td>
<td>1.882</td>
</tr>
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<td>1489</td>
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<td>2857</td>
<td>3.50</td>
<td>1.852</td>
</tr>
<tr>
<td>128.5</td>
<td>2861</td>
<td>3226</td>
<td>3.05</td>
<td>1.843</td>
</tr>
<tr>
<td>112.5</td>
<td>3240</td>
<td>3605</td>
<td>2750</td>
<td>1.816</td>
</tr>
<tr>
<td>90.0</td>
<td>3904</td>
<td>4269</td>
<td>2.322</td>
<td>1.769</td>
</tr>
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</table>

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

### Compound (NN'-2eten)$_2$I$_3$·2H$_2$O

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>μeff B.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>1243</td>
<td>1527</td>
<td>6.55</td>
<td>1.908</td>
</tr>
<tr>
<td>282.1</td>
<td>1303</td>
<td>1587</td>
<td>6.30</td>
<td>1.900</td>
</tr>
<tr>
<td>272.0</td>
<td>1355</td>
<td>1639</td>
<td>6.10</td>
<td>1.896</td>
</tr>
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<td>244.0</td>
<td>1527</td>
<td>1811</td>
<td>5.523</td>
<td>1.883</td>
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<tr>
<td>223.2</td>
<td>1673</td>
<td>1957</td>
<td>5.11</td>
<td>1.876</td>
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<tr>
<td>196.0</td>
<td>1924</td>
<td>2208</td>
<td>4.53</td>
<td>1.868</td>
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<tr>
<td>148.2</td>
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<td>2817</td>
<td>3.53</td>
<td>1.835</td>
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<td>130</td>
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<td>3125</td>
<td>3.20</td>
<td>1.810</td>
</tr>
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<td>112.1</td>
<td>3262</td>
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<td>1.790</td>
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<tr>
<td>88.6</td>
<td>3916</td>
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$\theta = -26°$  
Dia. Corrn. $x 10^{-6} = -284.34$
### TABLE 38
VARIATION OF MAGNETIC MOMENTS WITH TEMPERATURE (85 - 300°K)

<table>
<thead>
<tr>
<th>Compound Ni(N,N-2eten)$_2$Cl$_3$·2H$_2$O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_M \times 10^6$</td>
</tr>
<tr>
<td>296.0</td>
<td>1259</td>
</tr>
<tr>
<td>283</td>
<td>1329</td>
</tr>
<tr>
<td>273</td>
<td>1393</td>
</tr>
<tr>
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</tr>
<tr>
<td>223</td>
<td>1716</td>
</tr>
<tr>
<td>196.1</td>
<td>1938</td>
</tr>
<tr>
<td>148.8</td>
<td>2573</td>
</tr>
<tr>
<td>128.8</td>
<td>2941</td>
</tr>
<tr>
<td>112.5</td>
<td>3321</td>
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<td>90.2</td>
<td>3985</td>
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</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound Ni(N,N-2eten)$_2$Br$_3$·2H$_2$O</th>
<th>Field 5 amps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °K</td>
<td>$X'_M \times 10^6$</td>
</tr>
<tr>
<td>296.4</td>
<td>1246</td>
</tr>
<tr>
<td>283.0</td>
<td>1297</td>
</tr>
<tr>
<td>276.0</td>
<td>1330</td>
</tr>
<tr>
<td>244.3</td>
<td>1530</td>
</tr>
<tr>
<td>223.2</td>
<td>1683</td>
</tr>
<tr>
<td>196.0</td>
<td>1910</td>
</tr>
<tr>
<td>150.0</td>
<td>2498</td>
</tr>
<tr>
<td>128.8</td>
<td>2909</td>
</tr>
<tr>
<td>112.5</td>
<td>3252</td>
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<tr>
<td>90.0</td>
<td>3871</td>
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</table>

$\Theta = -23^\circ$ Dia. Corrn. x $10^{-6}$ 317.22
**TABLE 39**

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

*Compound (NN'-2eten)₂Br₃,2H₂O*  
Field 5 amps

<table>
<thead>
<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1350</td>
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$\theta = -26^\circ$  
Dia. Corrn. x $10^{-6} = -317.22$

*Compound (NN'-2eten)₂I₃,2H₂O*  
Field 5 amps

<table>
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<tr>
<th>Temp °K</th>
<th>$X'_M \times 10^6$</th>
<th>$X'_A \times 10^6$</th>
<th>$1/X'_A \times 10^{-2}$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
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$\theta = -30^\circ$  
Dia. Corrn. x $10^{-6} = -365.84$
FIG. 49

$\chi_A^{-1} \times 10^{-2}$

Temperature vs. Magnetic Moment

- $\bullet$ Ni(N,N-2eten)$_2$Cl$_3$2H$_2$O
- $\Delta$ Ni(N,N-2eten)$_2$I$_3$2H$_2$O
- $+$ Ni(N,N-2eten)$_2$Br$_3$2H$_2$O
- $-\times$ Ni(N,N'-2eten)$_2$I$_3$2H$_2$O

Radial magnetic susceptibility against temperature and magnetic moment 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 \( \mu_{\text{eff}} = \mu_{\text{S.O.}} \left( 1 - \frac{2\Lambda}{\Delta} \right) \), where \( \mu_{\text{S.O.}} \) = spin-only value (magnetic moment)

\( \Delta \) = separation between the ground level and level being "mixed in".

\( \Lambda \) = spin-orbit-coupling constant.

For compounds in which intramolecular antiferromagnetic interactions occur, the magnetic susceptibility (or \( X_A \)) can be calculated on the basis of spin-spin coupling theory. Figgis and Martin 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 have made similar calculations for the spin system \( (\frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}) \). Wojciechowski has derived the magnetic susceptibility equation for the following spin systems:

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

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 \( (\frac{1}{2}, \frac{1}{2}), (\frac{3}{2}, \frac{1}{2}), (\frac{3}{2}, \frac{3}{2}) \). 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

\[ \mu = 2\sqrt{S(S+1)} \mu B \]

The magnetic moment calculated from the Curie equation

\[ \mu = 2.84\sqrt{X_M T} \mu B \]
decreases with temperature.

(2) The Neel 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^m 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 arithmetic mean of the moment for each metal ion of M-M system. This means that

\[ \mu \approx \sqrt{S_1 (S_1+1)} + \sqrt{S_2 (S_2+1)} \mu B \]

For high value of -J determined by the equation

\[ \mu = 2\sqrt{(|S_1 - S_2|)(|S_1 - S_2| + 1)} \mu B \]

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

The magnetic moment \( \mu_{eff} \) calculated from the Curie law for the magnetic susceptibilities calculated at different values of J is changed with temperature from

\[ \mu = 2\sqrt{|S_1 - S_2| (|S_1 - S_2| + 1)} \mu B \]
to

\[ \mu = \sqrt{2} \left( \sqrt{S_1 (S_1+1)} + \sqrt{S_2 (S_2+1)} \right) \mu B \]
These equations show that the two straight lines which represent the relationship reciprocals of magnetic susceptibilities \( \rightarrow \) 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 \( d^nd^m \) electron structure. If \( J \) is +ve for all electron configurations of the M-M system, that is for the \( d^nd^n \) and \( d^nd^m \) electron configurations the magnetic moment increases. For high values of the exchange integral \( J \) the curve reciprocal magnetic susceptibility \( \rightarrow \) temperature is a straight line with the Weiss constant \( \Theta \) 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 \( \Theta \).

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

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

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

\[
\mu = \sqrt{2 \left( \sqrt{S_1 (S + 1)} + \sqrt{S_2 (S_2 + 1)} \right)} \mu_B
\]

to

\[
\mu = 2 \sqrt{S(S + 1)} \mu_B \quad \text{where} \quad S = S_1 + \frac{S_2}{2}
\]

According to Kanamori 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 \( 90^\circ \), 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. 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 that the atomic susceptibility $\chi_A$ of the metal atom can be calculated by using equation

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

where

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

$g =$ spectroscopic splitting factor

$\beta =$ Bohr magneton $= 0.9174 \times 10^{-20}$ erg/gauss$^{-1}$

$N =$ Avogadro number $= 6.023 \times 10^{23}$ mole$^{-1}$

$N\chi =$ temperature independent paramagnetism

$J =$ exchange integral.

$T =$ Absolute temperature

$k =$ Boltzmann's constant

$= 1.380 \times 10^{-16}$ erg degree

$= 0.6950$ cm$^{-1}$

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

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

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

where

$k = \frac{g^2 N \beta^2}{3k}$ and $x = -\frac{J}{kT}$
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.

<table>
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<th>$S'$</th>
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<th>Energy =</th>
</tr>
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<tbody>
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<td></td>
<td>$2S' + 1$</td>
<td>$J[S'(S' + 1)]$</td>
</tr>
<tr>
<td>2S</td>
<td>4S + 1</td>
<td>$J[2S(2S + 1)]$</td>
</tr>
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<td>0</td>
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</table>

(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 equation.

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

(1)

where

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

$E_i(1)$ is the coefficient of the first order Zeeman effect

$E_i(2)$ 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 $-g\mu_BS'$ to $+g\mu_BS'$

$$\frac{E_i^2(1)}{kT} \text{ becomes } \frac{g^2\mu^2}{kT} [S']^2 + (S' + 1)^2 + ... 0 ... (-S')^2$$

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

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 $N\chi$ term, equation (1) reduced to

$$X_M = N \frac{g^2\mu^2}{2kT} \frac{\Sigma S'(S' + 1)(2S' + 1) \exp \left( -\frac{E_i(0)}{kT} \right)}{\Sigma (2S' + 1) \exp \left( -\frac{E_i(0)}{kT} \right)} + N\chi$$

(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 $S = \frac{3}{2}$. Four levels occur corresponding to $S^\prime = 0, 1, 2$ and 3 with energies of $0, 2J, 6J$ and $12J$.

\[ \chi_M = \frac{N^2 \beta^2}{2kT} \left[ 0 + 1.23 \exp \left( -\frac{2J}{kT} \right) + 2.35 \exp \left( -\frac{6J}{kT} \right) + 3.47 \exp \left( -\frac{12J}{kT} \right) \right] + M \]

Multiplying through $x^{12}$ where $x = \exp \left( \frac{J}{kT} \right)$ and substituting $\chi_A = \frac{1}{2} \chi_M$

\[ \chi_A = \frac{N^2 \beta^2}{3kT} \left[ \frac{42 + 15x^6 + 3x^{10}}{7 + 5x^6 + 3x^{10} + x^{12}} \right] + Nx \]

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

For $S = \frac{1}{2}$

\[ \chi_A = \frac{3k}{T} \left[ \frac{5 + 4x}{5 + 3x^4 + x^6} \right] + Nx \]

For $S = \frac{3}{2}$

\[ \chi_A = \frac{3k}{T} \left[ \frac{14 + 5x^6 + x^{10}}{7 + 5x^6 + 3x^{10} + x^{12}} \right] + Na \]

For $S = 2$

\[ \chi_A = \frac{6k}{T} \left[ \frac{30 + 14x^8 + 5x^{14} + x^{18}}{9 + 7x^8 + 5x^{14} + 3x^{18} + x^{20}} \right] + Na \]

For $S = \frac{5}{2}$

\[ \chi_A = \frac{3k}{T} \left[ \frac{55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28}}{11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}} \right] + Na \]

Where $x = \exp \left( \frac{J}{kT} \right)$ and \( \kappa = \frac{N^2 \beta^2}{3k} = 0.1251 \text{ g}^2 \)

If $Na$ is neglected then substitution of $J = 0$ (i.e. $x = 1$) and $g = 2$, followed by insertion of the values of $\chi_A$ in Langevin's 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
\[ \frac{J}{kT} = J \text{ (in cm}^{-1}) \]
\[ 0.69503 \times T \text{ (in degrees)} \]

Also frequently measured in degrees by incorporating \( k \), when

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

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 \( \text{Ni}^2\text{Cl}_3 \):

A graph of \( \frac{1}{X_A} \rightarrow T \) was plotted. From the graph two convenient temperatures were taken and inserted into the equation.

\[ X_{Ni} = \frac{k}{T} \left[ \frac{1}{1 + \frac{1}{3} \exp \left( \frac{-J}{kT} \right)} \right] + N \]

Thus at

\[ 280^\circ K = 5.931 \times 10^{-2} = \frac{k}{280} \left[ \frac{1}{1 + \frac{1}{3} \exp \left( \frac{-J}{280 k} \right)} \right] + N \text{ and} \]

\[ 120^\circ K = 265.0 \times 10^{-6} = \frac{k}{120} \left[ \frac{1}{1 + \frac{1}{3} \exp \left( \frac{-J}{120 k} \right)} \right] + N \]

Now solving the simultaneous equation we get

\[ \frac{593.1 \times 10^{-6}}{265.0 \times 10^{-6}} = \frac{k}{280} \left[ \frac{1}{1 + \frac{1}{3} \exp \left( \frac{-J}{280 k} \right)} \right] + N \]

\[ \frac{k}{120} \left[ \frac{1}{1 + \frac{1}{3} \exp \left( \frac{-J}{120 k} \right)} \right] + N \]

\[ 2.238 = \frac{3 + \exp \left( \frac{-J}{120 k} \right)}{7 + 2.333 \exp \left( \frac{-J}{280 k} \right)} \]

\[ 15.666 + 5.221 \exp \left( \frac{-J}{280 k} \right) = 3 + \exp \left( \frac{-J}{120 k} \right) \]

\[ 12.666 + 5.221 \exp \left( \frac{-J}{280 k} \right) = \exp \left( \frac{-J}{120 k} \right) \]
Substituting the different value of J, the value giving the best fit was found, e.g.

If we take \( J = 360 \text{ k} \)

\[
\text{L.H.S.} = 5.983 \quad \text{and} \quad \text{R.H.S.} = 3.0
\]

It can be seen that these are not equal.

If, however, \( J = 400 \text{ k} \)

then \( \text{L.H.S.} = 5.25 \) and \( \text{R.H.S.} = 3.33 \)

If \( J = 460 \text{ k} \)

\( \text{L.H.S.} = 4.20 \) and \( \text{R.H.S.} = 3.83 \)

If \( J = 500 \text{ k} \)

\( \text{L.H.S.} = 3.37 \) and \( \text{R.H.S.} = 4.16 \)

The best fit value of \( J \) was found as \(-470 \text{ k} \) as

\[
12.666 + 5.221 \exp \left( \frac{-470}{280} \right) = \exp \left( \frac{-470}{120} \right)
\]

\[
3.94 = 3.91
\]

\[ \therefore \quad \text{L.H.S.} = \text{R.H.S.} \]

Having found the value of \( J \) the values of \( k \) and \( g \) were found

\[
265.1 \times 10^{-6} = \frac{k}{120} \left[ \frac{1}{1 + \frac{1}{3} \exp (3.9 \text{ k})} \right]
\]

\[
265.1 \times 10^{-6} = \frac{k}{120} \left[ \frac{1}{1 + \frac{1}{3} \times (3.9 \times 0.6949)} \right] \quad ( \therefore \quad k = 0.6949 \text{ cm}^{-1} )
\]

\[ \therefore \quad k = 0.6040 \]

\[ \therefore \quad k = \frac{g^2 \mu B^2}{3k} = \frac{g^2 \times (6.023 \times 10) \times (0.9174 \times 10)^2}{3 \times 1380 \times 10^{-16}} \]

\[ \therefore \quad g = \sqrt{\frac{k}{1.250}} = \sqrt{\frac{0.6040}{0.1250}} = 2.19 \]
For \( \text{Ni}_{2}\text{Cl}_3 \)

\[ g = 2.19 \]

\[ \kappa = 0.6040 \]

\[ J = -470 \text{ k} \text{ which corresponds to} \]

\[ = -327 \text{ cm}^{-1} \text{ (326.60 cm}^{-1}) \]

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 \( \chi_M^{-1} \) versus \( T \) plotted. Fig. 45 page 171 illustrates the type of curves resulting from the theoretical equation using \( J = 327 \text{ cms and} \)

\[ g = 2.19 \text{ values} \]

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 \( \mu \text{ S.O. then} \)

\[ g = 2 \text{ but} \ g \text{ will depart from this value depending on} \]

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. Foster and Ballhansen\(^{102}\) on the other hand used the molecular orbital approach and concluded that \(\sigma\) bonding between singly occupied \(3d^2\) 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. 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 binuclear (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.
Appendix - E.S.R. Spectroscopy

Introduction

Complexes containing large organic chelating ligands were difficult to assign the true valency state of the metal ion. Therefore there had been (and has been) a controversy over the identification of Ni(III) and Ni(IV) species in solution. The critics of the Ni(III) assignment base their arguments on the expected difference between a free radical type and a 3d⁷ 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 made, however, attempts to observe the epr signal either failed or were not reported. During studies of some physical properties in solution of the iron through zinc tetra phenyl porphyrins Wolberg et al. 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 ones the g factor for the symmetric signal was measured directly from the experimental spectrum.

<table>
<thead>
<tr>
<th>Species</th>
<th>Temp.</th>
<th>g aver.</th>
<th>g 1</th>
<th>g 2</th>
<th>g 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(III)TPP⁺</td>
<td>77</td>
<td>2.235</td>
<td>2.116</td>
<td>2.295</td>
<td></td>
</tr>
</tbody>
</table>

These two epr signals were interpreted for a square planar d⁷ configuration.

Preparation of epr study of solution of oxidized nickel di-thiocarbonato complexes were made by Solozenkin, P.M. Kopitsya. Here epr spectrum was measured at 20⁰ with singlet gₛ = 2.100 ± 0.001 and ΔH = 63 ± 4. At 77⁰K the spectrum was anisotropic with g₁ = 2.032, g₂ = 2.127 and g₃ = 2.137 and can be described by spin corresponding to orthoxombic symmetry which points low spin - S = ½ Ni(III) with a
rectangular pyramid structure. The temperature dependent spectra is reminiscent of the behaviour predicted by Liher and Ballhausen for an octahedral complex with tetragonal Jahn-Teller 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 Eleany.

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. al. Relationship between e.s.r. g-values and covalent bonding in tetragonal copper (II) compounds were studied by Smith.

For d⁷ in a strong octahedral field we have just one electron in eg orbital outside the closed sub shell (t²g⁶). The configuration is therefore (t²)⁶(e), S = ½. With one electron more than can be accommodated in the (t²) shell the extra electron must enter the (e) shell giving net spin = ½. 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 d⁷ (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 Ni²⁺ 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**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Host lattice</th>
<th>$g_{1}$</th>
<th>$g_{2}$</th>
<th>$g_{3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3d^7$Ni$^{3+}$</td>
<td>MgO</td>
<td></td>
<td></td>
<td>2.1693</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td></td>
<td></td>
<td>2.282</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>2.045</td>
<td></td>
<td>2.146</td>
</tr>
<tr>
<td></td>
<td></td>
<td>powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$4d^7$Rh$^{2+}$</td>
<td>ZnWO$_4$</td>
<td>2.375</td>
<td>2.12</td>
<td>(average)</td>
</tr>
<tr>
<td>$5d^7$Pt$^{3+}$</td>
<td>Al$_2$O$_3$</td>
<td>2.011</td>
<td>2.328</td>
<td>2.220</td>
</tr>
<tr>
<td></td>
<td>BaTiO$_3$</td>
<td>1.950</td>
<td>2.459</td>
<td></td>
</tr>
</tbody>
</table>

Spin orbit coupling mixes some of the $(4T_i)_{T_2}$ 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 A (ligand field splitting parameter)

\[ h\nu = g\beta H \]
\[ \therefore \mu = gH \frac{\beta}{H} \]
\[ \nu = gH \times \text{constant} \]

We know that at 3 cm radiation, resonance frequency = 9500 Mc/sec

\[ h = \text{Planck's constant} = 6.624 \times 10^{-27} \]
\[ \beta = \text{Bohr magneton} = 0.917 \times 10^{-20} \text{ ergs} \]
\[ g = \text{spin only value} = 2.0023 \]

The resonance in this case

\[ H = \frac{h\nu}{g^3} = \frac{6.624 \times 10^{-27} \times 9.5 \times 10^7}{2.0023 \times 0.917 \times 10^{-20}} \]
\[ \therefore H = 3.427 \text{ gauss} \]
\[ \therefore g = \frac{3.427 \times 2.0023}{3.140 \times 1} = 2.185 \]

Using this g value we may be able to calculate ligand field splitting parameter A, neglecting other effects from the following equation.

\[ g = 2[1 - \left( \frac{\lambda + 2\lambda}{\Delta} \right)] \quad \text{where} \quad \lambda = \text{spin-orbit coupling constant} \]

The free ion value (cm\(^{-1}\)) of spin-orbit coupling constant for \( d^7 \) in strong field 2E state = -715

\[ g = 2\left[1 - \left( \frac{2 \times -715}{\Delta} \right) \right] \]
\[ 2.185 = 2 + \left[1 + \frac{1430}{\Delta} \right] \]
\[ 2.185 = 2 + \frac{2860}{\Delta} \]
\[ \therefore \Delta = 15490 \text{ cm}^{-1} \]

The g value for Ni(II)Cl\(_3\) from magnetic moments is also near this value (see page ___)
Crystalline Powder R.T.
Ni(II)Br3 + 1/2 H2O
E.S.R. Spectrum of
FIG. 53

ESR Spectrum of
Ni(C₂Cl₂·3H₂O)
Powder R.T.

3.6 Kg
3.1 Kg
REFERENCES

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