ALIPHATIC AMINES: A STUDY OF THEIR SPECTROCHEMICAL SERIES AND OF SOME OF THEIR REACTIONS WITH ANHYDROUS METAL HALIDES

by

JOHN F. KILMARTIN

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SUMMARY.

Monomeric tetrahedral complexes $MX_2 \cdot 2NMe_3$, X = halogen, pseudohalogen are formed with nickel(11) and cobalt(11). The chloro-complex of nickel(11) exists in two forms, α-$NiCl_2 \cdot 2NMe_3$ (blue), which has been assigned a tetrahedral structure, and β-$NiCl_2 \cdot 2NMe_3$ (red), which has been assigned a halogen-bridged polymeric octahedral structure. Monomeric octahedral complexes ML_4X_2, L = iso-butylamine, formed with nickel(11) have trans-configurations. Splitting of the $^3T_{2g} \leftarrow {}^3A_{2g}$ transition in the halo-complexes has been interpreted to indicate tetragonal distortion caused by lattice requirements in the solid state.

Monomeric octahedral complexes ML_4X_2, L = iso-butylamine, iso-propylamine, sec-butylamine, cyclohexylamine, are formed with cobalt(11). The stability of the halo-complexes at ambient temperature and pressure follow the polarizability sequence Cl < Br < I but are significantly less stable than the complexes CoL_4X_2, L = pyridine, substituted pyridine. The instability of the complexes is considered to be a consequence of the Electroneutrality Principle. In solution the complexes undergo a structural transformation and give tetrahedral species ML_2X_2. Mean values of $10D_q$ suggest that the ligand field perturbing power of the amine is almost independent of its steric nature and that the amines occupy a similar position to that of ammonia in the spectrochemical series.

Monomeric tetrahedral complexes ML_2X_2 are also formed by cobalt (11) with the same aliphatic amines. Pronounced splitting of the $^4T_1 \leftarrow {}^4A_2$ transition in the reflectance

spectrum of these complexes is interpreted to indicate a lowering of C_{2v} symmetry. Tetrahedral stereochemistry is retained in solution but the absence of splitting in the $^4T_1 \leftarrow {}^4A_2$ transition indicates that the complexes are less severely distorted than in the solid state.

The two complexes $CoL_2(CNS)_2$, L = iso-butylamine, cyclohexylamine, form polymeric octahedral structures which contain bridging thiocyanate, as deduced from the positions of $\nu(C{\equiv}N)$, $\nu(C{-}S)$ and $\nu(M{-}NCS)$ in the infrared spectra. A weak band on the high energy side of the $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transition in the electronic spectra of these complexes is attributed to the greater asymmetry of their polymeric structure in comparison to that for monomeric octahedral species. These complexes also undergo a structural transformation in solution and give tetrahedral species $CoL_2(CNS)_2$.

A number of complexes of chromium(111) chloride with aliphatic ketones have been studied. The shift in the carbonyl stretching frequency upon coordination of these ketones has been clearly demonstrated. An unexpected band, situated at 2300 cm^{-1} has been observed in the infrared spectrum of chloropentakis-(ethylamine)chromium(111) chloride when the complex is prepared under open-air conditions. This observation has been tentatively inferred to indicate that the reactivity of ethylamine becomes enhanced upon coordination and it may be oxidized to acetonitrile.

This work was carried out between 1971 and 1973 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

John F. Kilmartin

JOHN F. KILMARTIN

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CONTENTS

1. INTRODUCTION

1.1. Object of the Study

Complexes of ammonia are well known and the position of this ligand in the spectrochemical series is well established. In contrast the chemistry of the complexes containing simple aliphatic amines has been studied to a much lesser extent. In the present work it was decided to attempt the preparation of some complexes containing the latter type ligands with selected first row metal halides, to characterize these complexes, and to establish the position of the amines relative to ammonia in the spectrochemical series.

Of the metals having an oxidation state of +2, cobalt(11) and nickel(11) were chosen. While the chemistry of these two metals might be expected to be rather similar, very often striking differences are apparent. Chromium(111) is a good example of a metal from the first transition series having an oxidation state of +3 because in many cases the chemistry of chromium(111) parallels the chemistry of other metals such as titanium and vanadium in similar oxidation states, e.g. the existence of isostructural complexes $MX_3.2NMe_3$ [1] (X = Cl, Br; M = titanium, vanadium, chromium) - but Cr(111) is frequently distinguished by its kinetic inertness.

It is instructive to observe how the major interests of

inorganic chemists in the halide compounds of the first row transition metals have evolved over the past fifteen years. Before 1958 the apparent non-existence of tetrahedral nickel(11) complexes was generally assumed to be in accord with crystal field theory,[2] which predicts a gain in crystal field energy of 3.6 - 7.2 kilojoules $mole^{-1}$ on going from a tetrahedral to an octahedral complex.[2] More detailed examination[3] showed however, that crystal field stabilization energy is only a minor component of lattice energy and may be swamped by the electrostatic interaction between metal and ligands.

In 1958 Venanzi[4] suggested on the basis of spectroscopic and magnetic evidence that the complexes $Ni(PPh_3)_2X_2$ (X = Cl, Br, I) were pseudotetrahedral. He attributed the formation of the complexes to steric repulsions between the triphenylphosphine molecules which prevent polymerization of the $Ni(PPh_3)_2X_2$ units and consequently, the formation of an octahedral complex. Later, a complete x-ray crystallographic study[5] established this structure in detail.

In the following years many more tetrahedral complexes containing monodentate and polydentate ligands were prepared. Furthermore, Venanzi and co-workers have shown[6,4,7] that as the alkyl groups of tertiary phosphines in complexes NiL_2X_2 (L = tertiary phosphine, X = halogen) are replaced by phenyl groups there is a change of structure from square planar to tetrahedral.

The study and characterization of five-coordinate complexes proved just as interesting as the earlier work on

tetrahedral stereochemistry of nickel(11). Antler and Laubengayer[8] first obtained evidence for the existence of the complex $TiCl_3 \cdot 2NMe_3$ in the gas phase reaction of titanium tetrachloride with trimethylamine. It was also synthesised directly from the trichloride, and the corresponding tribromide[9] may be prepared by direct interaction of the components. Trimethylamine is the only solvent in which the complexes dissolve without reaction. At first they were considered to be halogen-bridged dimers but the x-ray structural determination of the complex $TiBr_3 \cdot 2NMe_3$ by Russ and Wood[10], clearly established that the complex is a trigonal bipyramidal molecule with essentially D_{3h} symmetry.

Despite the considerable interest shown by workers in the various stereochemical forms of these metal halide complexes, no systematic study of the chemistry involving the adducts formed by simple molecules, especially amines, has been undertaken. In contrast the chemistry of the reactions involving liquid or gaseous ammonia with metal halides has been extensively studied over a period of years. Much of the earlier work has been reviewed by Fernelius and Bowman[11] and more recently by Fowles,[12] Garner and House.[13]

A study of the literature indicated that adducts prepared with trialkylamines were in a minority. Invariably the stereochemical requirements of the ligand were considered responsible for the non-formation of this type of adduct. The absence of a large number of mono-aliphatic amine complexes of cobalt(11) dihalides was also very noticeable. For purposes of comparison some adducts were prepared which have been prepared and

characterized previously.

It should be borne in mind that chemistry is an experimental subject and as such has many diversified fields and applications. For this reason alone it is seldom possible (and rarely fully beneficial) to study an isolated topic without making reference and investigating certain aspects of chemistry outside the topic. In general this always imparts a unifying understanding of the subject, not obtainable from an isolated study within the limits of the topic itself. During the course of this work a number of adducts formed by simple ketones with chromium(111) were isolated. These adducts were fully characterized and the results are included in this topic.

1.2. Complexes of Metal Halides with Simple Aliphatic Amines

1.2.1. Complexes of Nickel(11)

Uhlig and Staiger[14] have shown that nickel(11) halides react readily with primary aliphatic amines forming coordination compounds of the type NiL_6X_2 (L = $MeNH_2$, $EtNH_2$, $n\text{-}PrNH_2$; X = Cl, Br, I). Many of the complexes have been prepared previously by Ephraim and Linn[15] but not fully characterized by them. Thermal decomposition studies on the series NiL_6X_2[15] showed that complexes having 4, 3, 2 and 1.5 amine molecules per central atom were formed. For all these compounds magnetic and spectrophotometric measurements indicated a coordination

number of 6. Therefore the 1:2 and the 1:1.5 complexes are discussed as having highly polymeric structures.

Uhlig and Staiger[16] have also prepared a series of complexes formed by nickel(11) halides with secondary and tertiary amines. In this case the reaction between metal halide and amine was much slower than reactions with primary amines. Dimethylamine and diethylamine formed coordination compounds having metal to amine ratios of 1:4, 1:3 and 1:2. Binuclear octahedral structures are suggested for the 1:3 complexes, whereas tetrahedral or square planar configurations are proposed for the 1:2 compounds.

The complex $NiI_2.2NMe_3$ is formed with trimethylamine. It has been prepared by condensing trimethylamine on to anhydrous nickel iodide and allowing the reactants to stand at 0^o for one week.[16] Under the same conditions nickel bromide showed only partial reaction after five weeks, while nickel chloride showed no reaction. When $NiI_2.2NMe_3$ is dissolved in benzene there is a structural alteration.[16] The spectrum of the solution has peaks suggesting the presence of the NiI_4^{2-} anion. Lever and co-workers have shown[17] that $NiI_2.2Mp$ (Mp = Methylpyrazine) tends to rearrange to form the anion NiI_4^{2-} when dissolved in acetone in the absence of an excess of methylpyrazine. The presence of this anion was confirmed from its solution spectrum[18] and its conductivity in acetone. Uhlig and Staiger have argued that $NiI_2.2NMe_3$, when dissolved in benzene, behaves similarly to $NiI_2.2Mp$ when dissolved in acetone. By comparing maxima in the spectra and allowing for the bathochromic shift brought about by benzene they propose the formation of NiI_4^{2-}. The

presence of a shoulder at 444 nm is taken as evidence for the existence of the cation $[Ni(NMe_3)_4]^{2+}$, as cations of this type show an absorption maximum at 450 nm.[19, 20] Accordingly the complex is formulated as the ion pair $[Ni(NMe_3)_4][NiI_4]$ in benzene. However flat maxima in the spectra at 900 nm and 1,000 nm suggest the presence of some pseudotetrahedral $NiI_2.2NMe_3$ species also.

Prasad and Krishnan[21] have reacted triethylamine with nickel iodide and report the formation of complexes $NiI_2.NEt_3$ and $NiI_2.4NEt_3$. Very little information is available on the characterization and structure of these complexes. No magnetic measurements or spectra are available, and the analytical data obtained, compares very poorly with theoretical calculations. In view of this the validity of much of their work must be viewed with reservations.

More recently Kartopolova and co-workers[22] report that nickel(11) halides react with triethylamine to give fine crystals having composition $NiX_2(NEt_3)_2nH_2O$ (X = Cl, Br, I). The thermal decomposition of these complexes proceeded in two stages. At first water molecules were eliminated and then each molecule of triethylamine separately. The intermediates $NiX_2(NEt_3)_2$ and $NiX_2.NEt_3$ were isolated and analysed, but further work on the complexes has not been reported.

1.2.2. Complexes of Cobalt(11)

A vast amount of work has been reported on the preparation

and properties of cobalt(11) dihalide adducts with pyridine, substituted pyridines, aniline and closely related nitrogen bases. The chemistry of the two bis(pyridine) isomers α-$CoCl_2(py)_2$ and β-$CoCl_2(py)_2$ has been extensively studied.[23] The reaction of anhydrous ammonia with cobalt(11) dihalides has been equally well studied. Similarly in the case of the chloride an α and β form have been isolated for the complex $CoCl_2(NH_3)_2$.[24] On the other hand, surprisingly little information is available on the adducts formed by simple amines.

Ephraim and Linn[15] were probably the first to examine some of the latter type adducts. More recently Hatfield and Yoke[25] have studied the reactions of mono-, di-, and trimethylamine with cobalt(11) dihalides. Ethylamine forms stable complexes of the type $Co(EtNH_2)_2X_2$ (X = Cl, Br, I). In addition these workers indicate that ethylamine also forms higher complexes having appreciable dissociation pressures at room temperature. No composition is proposed for these higher ethylamine complexes but their stability is in the order I>Br>Cl, while the relatively high dissociation pressures observed is attributed to the relative degree of expansion of the crystal lattice needed in order to accommodate the amine ligands.

Diethylamine also forms 2:1 complexes $Co(Et_2NH)_2X_2$ (X = Cl, Br) but only 1:1 adducts $CoX_2.NEt_3$ have been obtained with triethylamine. Reflectance spectra in the visible region and magnetic moments at room temperature have been recorded for all the above Co(11) complexes. On this evidence it is suggested that in the bis(ethylamine) and bis(diethylamine)

complexes the halide ions are coordinated to give pseudo-tetrahedral geometry. Doubly halogen-bridged dimers or singly halogen-bridged linear polymers are suggested to account for similar tetra-coordinated cobalt(11) in the 1:1 complexes of triethylamine.

Apart from this work reported by Hatfield and Yoke, further information on simple aliphatic amine complexes is scarce. Some work has been done by Bodtker-Naess and Hassel[26] on the hexakis(methyl amine) complex $Co(MeNH_2)_6I_2$, while Bucknall and Wardlaw[27] have prepared the tris(allylamine) complex $Co(C_3H_5NH_2)_3Cl_2$.

1.2.3. Complexes of Chromium(111)

In contrast to nickel(11) or cobalt(11) a considerable number of amine complexes with chromium(111) have been prepared. Compiling a comprehensive review of these complexes is in itself a formidable task. This present summary is confined to the complexes formed by chromium(111) with some simple aliphatic monodentate ligands. By far the most complete and up to date survey of both ammine and amine complexes of chromium(111) is that by Garner and House.[13]

The pentakis(alkylamine) complexes of the type $[Cr(RNH_2)_5X]X_2$ (R = H, Me, Et, allyl, n-Bu, i-Bu; X = monoacido ligand) have been investigated by Mandal,[28] Lang and co-workers[29] and more recently by Rogers and Staples.[30]

Every known member of the family can be prepared, either directly or indirectly, by reaction of the anhydrous amine with anhydrous $CrCl_3$. When $[Cr(MeNH_2)_5Br]Br_2$ is gently refluxed in excess methylamine, coordinated bromide is gradually eliminated and the hexakis(methylamine) complex $Cr(MeNH_2)_6Br_3$ formed.[31] This is the only example of a hexakis(amine) complex reported. No corresponding conversion could be obtained when the chloride anion was present.

Very little information is available on the reaction of chromium(111) halides and dialkylamines. Awakawa and co-workers[32] have reported complexes of formulae $Cr(Me_2NH)_3Cl_3$, $Cr(Me_2NH)_2Cl_3$, $Cr(Et_2NH)_3Cl_3$ and $Cr(Et_2NH)_2Cl_3$ but little chemistry of the complexes has been presented.

One of the most widely studied adducts of chromium trichloride is that formed with trimethylamine[1,33,34] having empirical formula $CrCl_3.2NMe_3$ similar to the analogous complexes of titanium and vanadium (Sect. 1.1.). The complex is monomeric with a trans trigonal-bipyramidal configuration, as indicated by dipole moment, infrared, visible and ultraviolet spectroscopy. This geometry has been confirmed by Fowles and co-workers[1] using single crystal x-ray diffraction techniques.

1.3. Ketone Complexes of Titanium(111) and Chromium(111)

Titanium trichloride dissolves in acetone to give a red solution. Clark and co-workers[35] were not able to precipitate

a complex from this solution but on complete removal of the solvent, a red solid was isolated whose analysis corresponded to the complex $TiCl_3.3Me_2CO$. It is virtually a non-electrolyte in acetone and the absorption spectrum is typical of octahedral titanium(111), containing a single asymmetric peak with maximum at 15.4 kK ($\epsilon = 37$) and a shoulder at 13.3 kK ($\epsilon = 28$). Fowles and co-workers[36] suggest that diethylketone and benzophenone may be restricted to forming 1:2 complexes by steric considerations, but that it seems likely that the titanium atoms will retain their octahedral environment in the solid through chlorine bridging. However, the diethylketone complex dissolves in the ligand as solvent, the spectrum of which closely resembles that of the acetone complex. Thus it is suggested that in solution chlorine bridging is broken down and a 1:3 complex is formed. For all three compounds there is an appreciable lowering of the carbonyl stretching frequency (by ~ 100 cm^{-1}) on coordination, and the magnetic moments (~ 1.6 B.M.) are slightly lower than those expected for titanium(111) complexes.

Surprisingly few complexes involving chromium(111) with ketones or aldehydes have been reported. The complex with acetone has been prepared by Taylor[37] and also by Awakawa and co-workers.[32] The latter workers also prepared complexes $CrCl_3.2MeCOEt$, $CrCl_3.Et_2CO$ and $CrCl_3.2MeCOPh$. Though the lowering of the carbonyl stretching frequency has been observed very little physical data has been presented.

The characteristic change in the carbonyl frequency upon coordination to a metal cation makes it a useful diagnostic tool in certain cases. While investigating the reaction of

toluene with chromyl chloride in carbon disulphide solution (the Etard reaction) Duffin and Tucker[38] were able to show, by a consideration of infrared spectra, that the brown amorphous solid (usually termed the Etard adduct) which precipitates during reaction contains benzaldehyde coordinated with compounds of chromium.

1.4. Comparison of Ammonia with Simple Amines

1.4.1. Physical Properties

The substitution of a hydrogen atom in ammonia by an alkyl group brings about important quantitative changes but leaves the molecule qualitatively very similar. Methylamine boils at -6°, about 27° higher than ammonia, and the methyl group just adds the usual increment to the boiling point resulting from molecular weight increase. Further substitution of ammonia does not produce a simple increase in boiling point: although dimethylamine boils 13° above methylamine, trimethylamine boils only 9.5° above it.

With heavier alkyl groups there is a continuous rise in boiling point from primary to tertiary amine, but it is not quite as steep as would be expected from considerations of molecular weight alone. These phenomena are adequately explained when changes in hydrogen bonding are taken into account. Substitution of the second hydrogen of ammonia by even a methyl group apparently reduces hydrogen bonding

significantly and substitution of all three stops it.

1.4.2. Changes in Basicity

The effect of substitution on the base strength of alkylamines is more complicated and has been the subject of much discussion. Methylamine is a markedly stronger base than ammonia, its ionization constant 4.4×10^{-4} being about twenty times greater. However the general trend is for a second alkyl group to increase the strength only a slight amount over the primary amine and for the third to decrease the base strength compared to the secondary amine, sometimes to a value lower than that of the primary amine.

Although the increased basic strength of primary amines over ammonia can be attributed to the electron donating effect of alkyl groups, it is obvious that such an effect is insufficient to explain the relationship of the basicities of secondary and tertiary amines. The problem has been the subject of much interest[39,40,41] and has invoked two types of explanation, one based on steric crowding, the other on solvation (in which steric effects may also play a role). Brown and co-workers[39] have favoured the propostion that the base-strengthening inductive effect of alkyl groups is opposed by steric crowding. Other workers[40,41] think that solvation is of major importance in determining the differences in base strength among different types of amines.

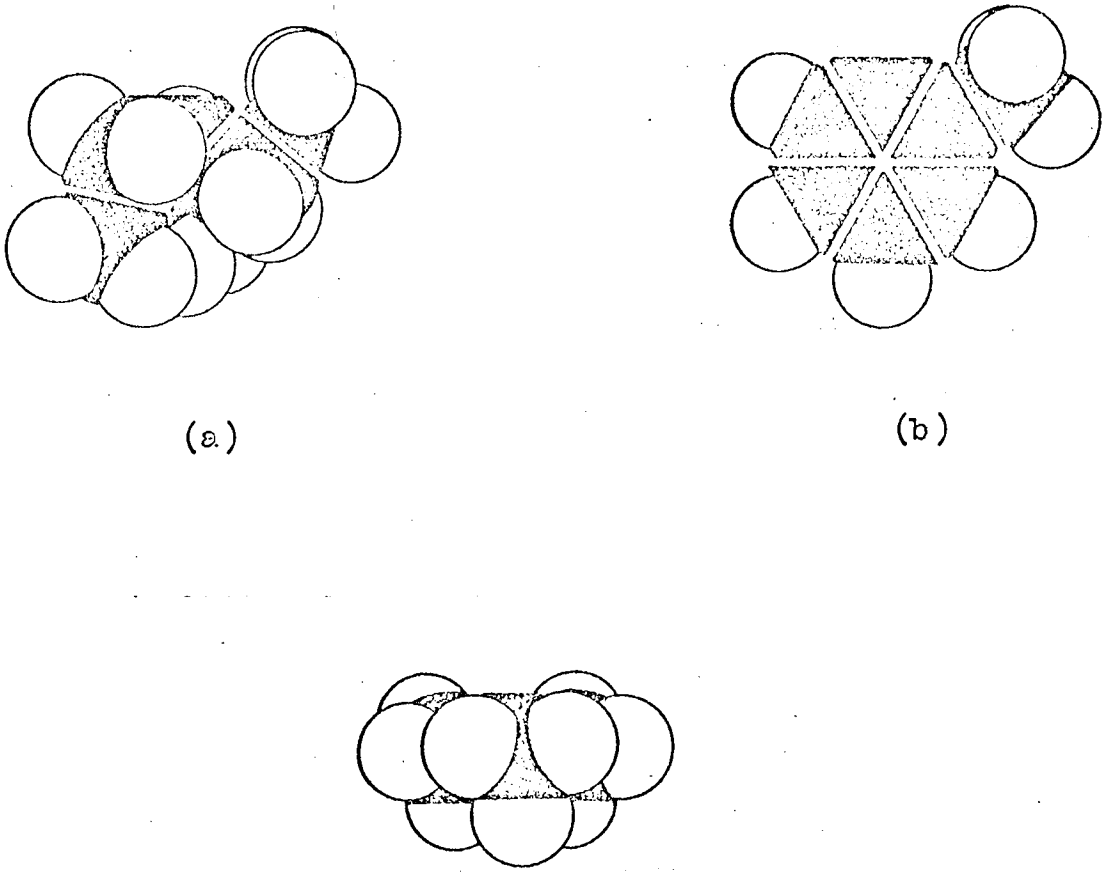
1.4.3. Steric Considerations

Despite the general similarity in structure, trimethylamine and triethylamine exhibit marked differences in their behaviour. For example in aqueous solution triethylamine is a considerably stronger base than trimethylamine.[42] Yet in spite of its greater strength, triethylamine reacts at a much slower rate with alkyl halides and forms a much less stable addition compound with trimethylboron.[43] These differences in behaviour of the two amines have been attributed to the peculiar steric configuration of the triethylamine molecule.[39b] Only two of the three ethyl groups can be removed to the "rear" of the nitrogen atom, away from the group adding or reacting at the vacant position of the nitrogen atom. For steric reasons the third ethyl group cannot be similarly accommodated, but is required to take a position such that the group projects into the region usually assigned to the unshared pair of electrons (Fig.1.1a).

According to Brown and Sujishi,[44] triethylamine therefore resembles a typical hindered amine such as 2-picoline (Fig.1.1b) much more closely than it does a relatively unhindered amine such as trimethylamine (Fig.1.1c).

These workers proved their hypothesis by preparing the adduct of trimethylboron with quinuclidine, the cyclic analogue of triethylamine, but in which the offending ethyl group of triethylamine is absent.

Taft[45] has discussed the steric effects of a series of amines on adduct formation with trimethylboron in terms of free energies, heats and entropies of activation. In Table 1.1



(a) (b)

(c)

Fig. 1.1 Molecular models of (a) triethylamine (b) 2-picoline (c) trimethylamine [44]

the strains are listed in terms of potential energy of activation ($\Delta\Delta Er$) resulting from changes in repulsions between non-bonded atoms.

TABLE 1.1

Steric Strains in 1:1 Amine-Boromethyl Addition Compounds[45]

Amine	Steric Strain, $\Delta\Delta E_r$ joules $mole^{-1}$
NH_3	0.0
CH_3NH_2	0.0
$C_2H_5NH_2$	0.0
$n\text{-}C_3H_7NH_2$	0.0
$i\text{-}C_3H_7NH_2$	0.36
$S\text{-}\ C_4H_9NH_2$	0.38
$t\text{-}C_4H_9NH_2$	1.60
$(CH_3)_2NH$	0.40
$(CH_3)_3N$	1.64
$n\text{-}C_4H_9(CH_3)_2N$	2.43
$(C_2H_5)_2NH$	1.45
$(C_2H_5)_3N$	(4.05)

Even though all these results have been obtained using trimethylboron as a reference acid it is reasonable to assume that similar trends in steric behaviour might be obtained with other reference acids such as metal halides.

1.5. Factors Influencing the Instability of Metal-Amine Complexes

In this context it is necessary to make reference to the coordinating abilities of the phosphorus atom in trialkylphosphines and to those of the nitrogen atom in trialkylamines. In comparison to the number of trialkylphosphine complexes reported, relatively few trialkylamine complexes exist. The unavailability of d-orbitals of suitable energy in the nitrogen atom is well known; as a result of this restriction many compounds of nitrogen have never been prepared. For example NF_5 and $NaNF_6$ are unknown while their second row analogues PF_5 and $NaPF_6$ are relatively stable compounds.

The vacant d-orbitals of suitable energy in the phosphorus atom might be considered to be of prime importance in complex formation with trialkylphosphines. In addition to the normal σ-bond formed by such molecules their π-acidity could give rise to multiple bonding resulting from the drift of electron density from the metal atom to the phosphorus atom.

Sacconi and co-workers[46] have studied the formation constants, heats of reaction, free energy and entropy changes associated with the equilibria between diacetyl - bisbenzoylhydrazine - nickel(11) (NiDBH) and trialkylamines and -phosphines in benzene. They have concluded that the donor tendency of trialkylamines is governed by a competition between steric and inductive effects. While the stability of the adducts of phosphines is 4-11 times that of amines,[46] the heats of formation are practically equal for both series of ligands. Accordingly they postulate that the bonding between nickel and phosphine ligands is essentially σ in character and that the higher stability of the phosphine adducts is entirely due to

the presence of lower steric strains.

However it should be pointed out that these workers fail to emphasise that all their measurements were made using the complex NiDBH as a reference acceptor for both series of trialkyl ligands. The ligand DBH forms a planar complex with Ni(11), the metal cation occupying the centre of a π-bonded system of three chelate rings. Such a ligand many seriously alter the Lewis basicity of the metal towards trialkylphosphines, resulting in little π-dative bonding, even though the Lewis acidity of the phosphines may remain unchanged.

Nyholm and collaborators[3] consider that steric effects as structural determinants are frequently overemphasised in the case of simple ligand atoms and that electrostatic effects and the charge distribution in the complex as a whole can often be the dominant factors. In general the stability of a complex increases with increasing ionic potential (charge/ionic radius) of the metal cation. An example of this increasing stability for some ethylenediaminetetraacetic (E.D.T.A.) complexes is shown in the following table:-

Ion	Ionic Radius, Å	Ionic Potential Charge/Radius	Log β_1 *
Ba^{2+}	1.53	1.31	7.8
Sr^{2+}	1.32	1.51	8.6
Ca^{2+}	1.18	1.70	10.6

* β_1 = Stability Constant for the Reaction

$M + L = ML$

$$\beta_1 = \frac{[ML]}{[M][L]}$$ (M = Ba, Sr, Ca; L = E.D.T.A.)

The ionic potential effect is also well illustrated by the regular rise in stability of the Lanthanide - E.D.T.A. complexes from lanthanum to lutecium due to the "lanthanide contraction", which leads to a steady increase in ionic potential with increasing atomic number.

Irving and Williams[48] have shown that the same order of increasing stability

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$

holds, irrespective of the nature of the ligand and this is also the order of decreasing ionic radius (Cu^{2+} smallest). Similar orders have been observed by other workers.[49, 50]

The extent of electron transfer to the metal depends not only on the ionic potential of the cation but also on the polarizability of the anion: as each of these increases so also must the amount of negative charge accumulating on the metal atom. In general it is found that complex stabilities increase with increasing polarizability of the ligand but there is a limit to the amount of negative charge that can be accepted by a metal ion (Pauling's electroneutrality principle). Accordingly there is the affinity sequence $P < S < N > O > F$ for these donor atoms with transition metals Mn^{2+} to Zn^{2+}, even though the polarizability sequence is $P > S > N > O > F$.[51,52] This illustrates the low affinity of these metals for S and P donor atoms and their high affinity for the less polarizable atoms N, O and F.

The high electronegativity of nitrogen means that N-Metal coordinate bonds will have a considerable ionic character. Reduction of the electronegativity of the nitrogen atom should

therefore enhance the stability on complex formation. This can occur by neutralization of the positive charges which develop on complex formation. It takes place either by transmission of the positive charge to hydrogen atoms as in ammines[53] or by polarization of an aromatic system as in pyridine complexes. No mechanism is available to remove the positive charge from the nitrogen atoms of the tertiary alkylamine complexes and this many be a fundamental cause of their instability.

It would appear therefore that the instability of trialkylamine complexes cannot be identified with any one particular reason. No doubt steric effects are of paramount importance, but the principle of electroneutrality and the unavailability of d-orbitals on the nitrogen atom must also be considered in this context.

1.6. Aspects of Electronic Spectra

1.6.1. Weak Field Complexes

While the foundation of modern inorganic chemistry can be attributed to Werner, the elucidation of the stereochemistry and the structural determination of many complexes has only been accomplished during the past 10 to 15 years. The use of modern techniques, such as x-ray crystallography, magnetic susceptibility measurements and electronic spectroscopy have made this possible.

Of major importance in a transition metal coordination complex is the presence of an incomplete d-shell in which the energies of the d-orbitals are split, the magnitude of splitting being determined by the ligand field strength and the stereochemistry of the complex. The electronic absorption spectrum and hence the colour of the complex depends upon the arrangement and energies of the electrons within the d-shell. Consequently the study of electronic spectra is an invaluable tool in the elucidation of the stereochemistry of inorganic complexes.

The basis for understanding electronic absorption spectra was presented by Bethe[54] in 1929. Since then development has been rapid and there is now an amount of literature dealing with the theoretical aspects and interpretation of the spectra of inorganic complexes. Workers such as Orgel,[55] Jørgensen[56] and Lever[57] have approached the subject in somewhat different ways, which taken together provide a comprehensive survey of this field.

A single d-electron in an octahedral field many occupy either a t_{2g} or an e_g orbital. The lower energy orbital is t_{2g} so that the ground state has the electronic configuration t_{2g}^1; the e_g orbital lies at an energy $10D_q$ (sometimes referred to as Δ) higher than t_{2g}. An electron in this orbital gives rise to the state ^2E_g, lying $10D_q$ above $^2T_{2g}$. A single electronic absorption is expected and is written $^2E_g \leftarrow {}^2T_{2g}$, with an energy $10D_q$.

Similarly the ^2D state arising from a d^9 configuration gives rise to a ^2E_g ground state (the hole formalisation indicates the presence of a "hole" in the e_g orbitals) and

a $^2T_{2g}$ excited state. One transition $^2T_{2g} \leftarrow {}^2E_g$, with the same energy $10D_q$ is predicted.

Whereas the d^1 configuration gives rise to only one free ion term, the d^2 configuration has five (^3F, ^3P, ^1G, ^1D, ^1S). In the presence of a ligand field these split and give rise to the following components:

$$^3F \longrightarrow {}^3A_{2g},\ {}^3T_{2g},\ {}^3T_{1g}$$

$$^3P \longrightarrow {}^3T_{1g}$$

$$^1D \longrightarrow {}^1T_{2g},\ {}^1E_g$$

$$^1G \longrightarrow {}^1A_{1g},\ {}^1T_{2g},\ {}^1T_{1g},\ {}^1E_g$$

$$^1S \longrightarrow {}^1A_{1g}$$

Three spin-allowed transitions are predicted from the ground state i.e.

ν_1 $\quad {}^3T_{2g} \leftarrow {}^3T_{1g}$

ν_2 $\quad {}^3A_{2g} \leftarrow {}^3T_{1g}$

ν_3 $\quad {}^3T_{1g}(P) \leftarrow {}^3T_{1g}$

The actual energies of these transitions are not so readily predicted as in the d^1 situation. They are a function of three quantities:-

(a) The crystal field splitting parameter D_q.

(b) The magnitude of the $^3F - {}^3P$ separation in the free ion. The fact that these two terms do not have the same energy is due to the differing mutual electronic

repulsion within each term. The energy separation between the two terms is 15B, where B is the parameter of interelectronic repulsion, introduced by Racah.

(c) The magnitude of the interaction between the two $^3T_{1g}$ states.

However (c) is a function of D_q and B only, so that these two quantities are all that is needed to interpret a d^2 spectrum. There are two principal ways for determining D_q spectroscopically, the method used depending upon the metal ion in question. With some ions, the lowest energy spin-allowed transition corresponds exactly with $10D_q$, at least to a first order approximation. In this case $10D_q$ is simply the energy of this transition and is therefore obtained without calculation. All other spin-allowed transitions will be functions of $10D_q$ and B. Where $10D_q$ and B cannot be directly estimated from an absorption band, two or more observed transition energies must be used to solve the appropriate secular equations.

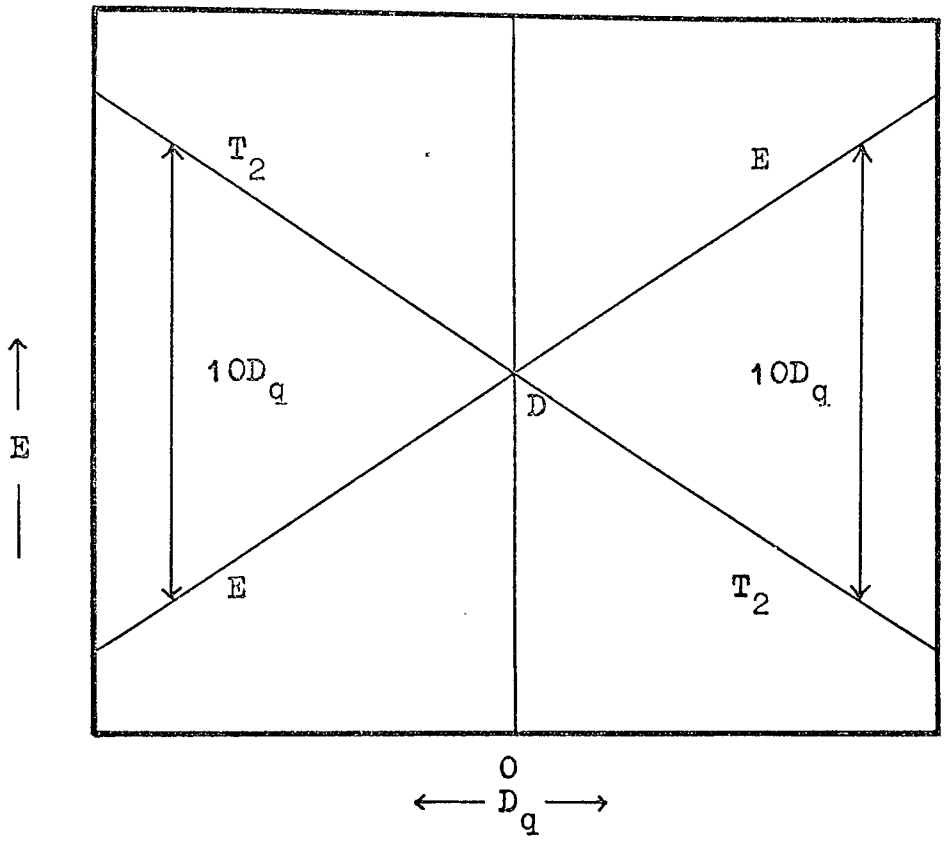
Tanabe and Sugano[58] have calculated the energies of the terms as a function of $10D_q$ and B and their diagrams contain plots of $10D_q/B$ versus E/B. They take as their energy zero the energy of the ground state so that absorption transition energies may be estimated simply by vertical measurement from the base line. In this way experimental spectra may be compared with predicted spectra by fitting the observed bands to the Tanabe-Sugano diagram with an appropriate $10D_q/B$ value.

Accurate values of $10D_q$ and B are however best obtained by solving the simultaneous equations used to construct these diagrams.

The spin-allowed spectral bands of all other d^n configurations may be analysed in a similar way to that given for the above d^2 configuration. Tanabe and Sugano have given diagrams for all d^n configurations and both $10D_q$ and B may be obtained from these diagrams with sufficient accuracy for most purposes.

1.6.2. Tetrahedral Stereochemistry

In a tetrahedral complex, the t_2 orbitals interact more strongly with ligands than the e orbitals and as a result $E(t_2) > E(e)$. Experimentally, the separation between t_2 and e is approximately one-half $[10D_q^* = (4/9)\ 10D_q$ where $10D_q^* = E(t_2) - E(e)]$ as large in a tetrahedral complex as it is in an octahedral complex with similar ligands. The terms for d^1 configuration are ^2E and $^2T_2$ and the term diagram is the inverse of that for an octahedral field. This information is usually presented by means of an 'Orgel diagram'[55] (Fig.12). For a d^1 configuration there is an increasing tetrahedral field to the left of the diagram and an increasing octahedral field to the right. Since the d^9 octahedral term diagram is the inverse of d^1, it is the same as the d^1 tetrahedral term diagram. A similar relationship holds for d^4 and d^6 configurations.



d^1, d^6 tetrahedral d^9, d^4 tetrahedral

d^9, d^4 octahedral d^1, d^6 octahedral

Fig.1.2. Orgel diagram showing the splitting of a field-free ion D term (arising from configurations d^1, d^4, d^6 and d^9) in both octahedral and tetrahedral fields.

Thus, for example, the spectrum of a tetrahedral d^1 complex can be interpreted using a Tanabe-Sugano diagram for the octahedral d^9 case. Because of the absence of a centre of symmetry in tetrahedral complexes the d-d transitions are

usually much more intense than in octahedral species.

1.6.3. Transition Energy Ratio Diagrams

In view of the small scale used by Tanabe and Sugano their graphical method for calculating values of D_q and B is often not very accurate. An alternative approach involves the use of plots of transition energy ratios versus D_q/B and $E(\nu_3)/B$. In general the electronic spectra of high spin complexes of metal ions whose free ion ground term is ^nF consists of three spin-allowed transitions, Fig.1.3, though it is not always possible to observe all three bands.

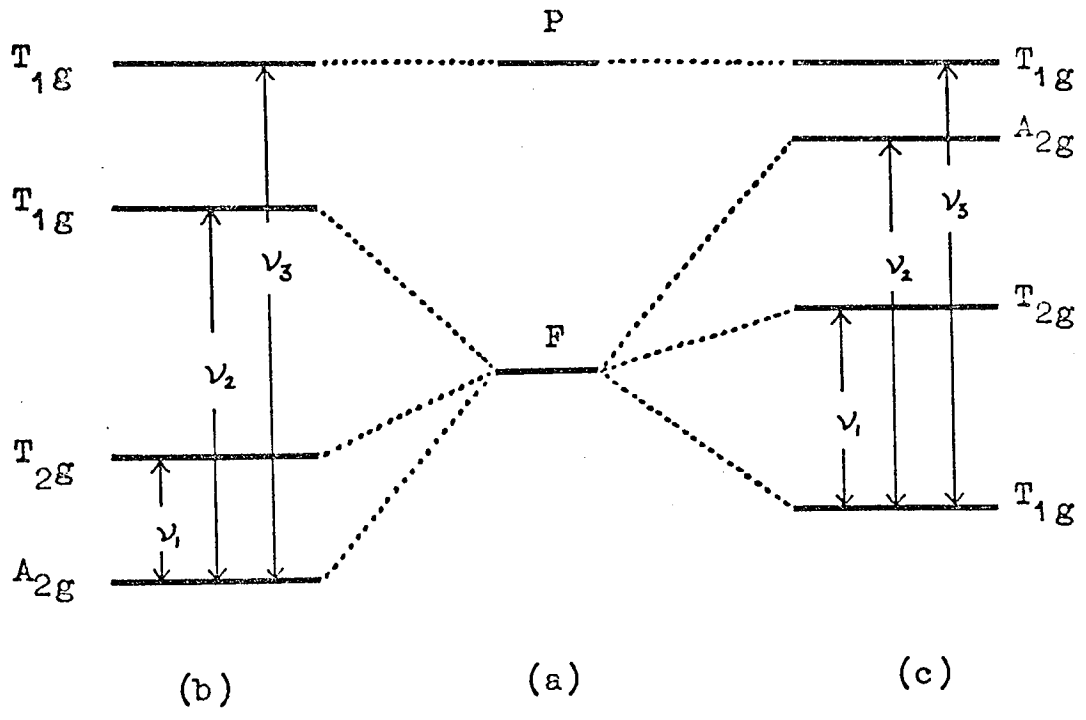


Fig.1.3. Energy level diagram* for high spin ions with an F-free ion ground term.[59]

(a) Free-ion terms.

(b) Splitting for d^3 and d^8 in an octahedral field and for d^2 and d^7 in a tetrahedral field.

(c) Splitting for d^2 and d^7 in an octahedral field and for d^3 and d^8 in a tetrahedral field.

* The g suffix is not applicable for tetrahedral transitions.

The assignments and energies of these bands are summarized as follows:[60]

Octahedral d^3 and d^8, tetrahedral* d^2 and d^7			
ν_1	$T_{2g} \leftarrow A_{2g}$		$10D_q$
ν_2	$T_{1g} \leftarrow A_{2g}$		$7.5B + 15D_q - \frac{1}{2}Q$
ν_3	$T_{1g}(P) \leftarrow A_{2g}$		$7.5B + 15D_q + \frac{1}{2}Q$
	$Q^2 = 225B^2 + 100D_q^2 - 180D_qB$		

Octahedtral d^2 and d^7, tetrahedral* d^3 and d^8			
ν_1	$T_{2g} \leftarrow T_{1g}$		$5D_q - 7.5B + \frac{1}{2}Q^1$
ν_2	$A_{2g} \leftarrow T_{1g}$		$15D_q - 7.5B + \frac{1}{2}Q^1$
ν_3	$T_{1g}(P) \leftarrow T_{1g}$		Q^1
	$(Q^1)^2 = 225B^2 + 100D_q^2 + 180D_qB$		

* The g suffix is not applicable for tetrahedral species because they lack a centre of inversion.

The lowest energy spin-allowed transition in the case

of A_2 ions corresponds directly with $10D_q$. This is generally observed in octahedral complexes but is very rarely observed in tetrahedral complexes; since its estimated position is in a very inaccessible region of the spectrum, namely the 3-5 kK region. It will therefore tend to be obscured by the vibrational spectrum of the ligands. When all three transitions are observed, values of B and D_q are readily calculated since $15B = \nu_1 + \nu_2 + \nu_3$.[61] However it is very rare to observe all three bands.

When ν_1 is not observed then values for $10D_q$ and B must be obtained from the second and third spin-allowed transitions. Lever[57,59,62] has approached this problem by plotting values of the ratios of the transition energies against D_q/B and $E(\nu_3)/B$. Fitting of a spectrum to the curves so obtained is rapid. These graphs together with some examples are given in the Appendix.

1.6.4. Errors Associated with the Measurement of $10D_q$

As already stated (Sect. 1.6.3.) a value of $10D_q$ can, in certain cases, be taken as $E(\nu_1)$. Alternatively it may be calculated from $E(\nu_2)$ and $E(\nu_3)$. The latter procedure is more desirable as the error introduced by vibrational broadening of bands is generally much less for the higher energy transitions than in the case of ν_1.

In using either of these methods for calculating D_q, one

must assume that the energies of the ground state and those of the excited state may be described by the same values of $10D_q$ and B, that is that the parameters are constant.

TABLE1.2

$10D_q$ Values for Octahedral NiL_6^{2+} Complexes

Ligand L	$10D_q(\nu_1)cm^{-1}$	$10D_q(\nu_2,\nu_3)cm^{-1}$
Caprolactam	8320	8030
Tetramethylsulfone	7750	7750
N- Dimethylformamide	8500	8120
N-Methylacetamide	7520	7530
Pyridine-N-oxide	8400	8440
Ammonia	10750	10950
Ethanol	8180	7990
n-Propylamine	9920	10180
N-Dimethylbutamide	7490	7080
N-Methylformamide	8380	8160
N-Diethylformamide	8400	8180
Acetonitrile	10600	11040
Valerolactam	8330	7970
Butyrolactam	8100	7960

In a series of octahedral complexes, Table1.2, Lever[59] has shown that values of D_q calculated from ν_1 and the corresponding values calculated from ν_2 and ν_3 can often show good agreement, but sometimes the agreement is quite poor. Furthermore the fact that $10D_q(\nu_2,\nu_3)$ is sometimes larger and sometimes smaller than $10D_q(\nu_1)$ reflects the random variation

of the parameters in the excited states. However in view of the lack of a complete structural understanding of these complexes Lever has pointed out that some disagreement between the two $10D_q$ values may possibly be attributed to some distortion of the octahedron.

Nevertheless it is clear that calculated values of D_q, when used to interpret chemical results must be regarded with discretion. The correlation of chemical trends based on varying values of D_q such as placing a set of ligands (which have insufficiently different crystal field splitting abilities to produce appreciably separated values of D_q) in a spectrochemical series, must also be treated with caution. The simple aliphatic amines are an example of such a series of ligands and the problem of placing them in an unambiguous spectrochemical series can readily be appreciated.

1.6.5. The Average Ligand Field Approximation

It is reasonable to assume that when a complex contains several kinds of ligands which do not differ sufficiently to produce distinct splitting of spectral bands, it will be possible to treat the complex as though it contained identical ligands whose properties are numerical averages of those of the actual ligands.

This theory has been used and its validity tested by many workers.[63,64,65] Cotton and co-workers[66] have obtained

close agreement between observed values of D_q and B with those calculated for the complexes $Co(Ph_3PO)_2X_2$ (X = Cl, Br, I). Their results can be summarized as follows:-

X	Observed		Calculated	
	$10D_q(cm^{-1})$	B^1	$10D_q(cm^{-1})$	B^1
Cl	3270	760	3405	749
Br	3180	754	3265	741
I	4030	725	4115	739

B^1 = Interelectronic repulsion parameter in the complex.

1.6.6. The Magnitude of $10D_q$

It is well known that the ligand field parameter D_q is primarily a function of the metal ion, the ligand and the stereochemistry. For a given metal and stereochemistry D_q increases with ligand in the following manner:-

$$I^- < Br^- < SCN^- \text{ (S-bonded)} < F^- < OH^- < H_2O < SCN^- \text{(N-bonded)} < NH_3 \simeq py < SO_3^{2-} < dipy < NO_2^{2-} \text{ (N-bonded)} < CN^-$$

A similar series exists for the variation of D_q with metal ion for a given ligand:-

$$Mn(11) < Co(11) \simeq Ni(11) < V(11) < Fe(111) <$$
$$Cr(111) \simeq V(111) < Co(111) < Mn(1V) < Mo(111) <$$
$$Rh(111) < Ir(111) < Pt(1V)$$

Since the number of complexes formed by simple aliphatic amines is relatively small, values of D_q for these ligands, relative to ammonia, are extremely scarce. Hence their position in the spectrochemical series is normally not considered. Drago and co-workers[67] have prepared a series of complexes having the general formula $Ni(RNH_2)_6(ClO_4)_2$ (R = H, Methyl, Ethyl, n - Propyl, i - Propyl) and recorded their spectra in various solvents. Values of D_q were taken directly from the wave numbers of the first (lowest energy) spin-allowed absorption band and are as follows:-

R	Solvent	$^3T_{2g} \leftarrow {}^3A_{2g}$ $(10D_q)$ (kK)
H	10% aq. NH_3	10.52
Methyl	CH_3NO_2	9.93
Ethyl	CH_3NO_2	9.87
n-Propyl	$n\text{-}C_3H_7NH_2$	9.92
i-Propyl	$CH_3NO_2+i\text{-}C_3H_7NH_2$	9.48

The accuracy of the assumption $\nu_1 = 10D_q$ for a complex with A_2 term as ground state has been discussed (Sect. 1.6.5.). For these alkylamines it is difficult to make comparisons of their D_q splitting abilities but it is clear that ammonia

occupies a higher position in the spectrochemical series. Obviously values of D_q calculated from ν_2 and ν_3 would have been useful in this work as a comparison of these values with $10D_q(\nu_1)$ would give some indication of the accuracies of the values obtained for D_q.

In accounting for the observed values of D_q these workers[67] consider charge-dipole interaction to be very important. The higher position of ammonia relative to methylamine is attributed to the slightly larger dipole moment of ammonia. In the same way the similarity in D_q values for CH_3NH_2, $C_2H_5NH_2$ and $n\text{-}C_3H_7NH_2$ correlates with the similarity of the reported dipole moments for these molecules.

1.7. Electronic Spectra of Known Complexes

Octahedral Nickel(11): Regular octahedral nickel(11) complexes with O_h symmetry have a simple spectrum in which the three spin-allowed transitions from the $^3A_{2g}$ ground state to $^3T_{2g}$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ levels are usually observed. These occur in the 7-13, 11-20 and 19-27 kK regions respectively having comparatively low extinction coefficients. In Table1.3 these bands are tabulated for some amine complexes.

TABLE1.3

Absorption Spectra (kK) of Six Coordinate Nickel(11) Derivatives[67]

Complex	$^3T_{2g} \leftarrow {}^3A_{2g}$ ν_1	$^3T_{1g} \leftarrow {}^3A_{2g}$ ν_2	$^3T_{1g(P)} \leftarrow {}^3A_{2g}$ ν_3
$Ni(NH_3)_6^{2+}$	10.53	17.24	28.01
$Ni(CH_3NH_2)_6^{2+}$	9.93	16.23	
$Ni(CH_3NH_2)_6^{2+}$	10.00	16.78	27.32
$Ni(C_2H_5NH_2)_6^{2+}$	9.87	16.31	
$Ni(C_2H_5NH_2)_6^{2+}$	9.66	16.67	27.03
$Ni(n\text{-}C_3H_7NH_2)_6^{2+}$	9.92	16.45	27.17
$Ni(n\text{-}C_3H_7NH_2)_6^{2+}$	9.82	16.50	26.81

Values of D_q vary between 640 and 1270 cm^{-1} depending on the position of the ligand in the spectrochemical series while values of B are always less than the value of 1041 cm^{-1} found in the free ion.

Geometrical distortions and/or the introduction of non-identical ligands in a regular octahedral complex may cause a lowering of symmetry. The study of the energy levels in pseudooctahedral complexes has been carried out by many workers [68,69,70]. The orbital triplets $^3T_{1g}$ and $^3T_{2g}$ (in O_h symmetry undergo further splitting (Fig.1.4), so that a large number of electronic transitions are expected in the spectra. Fig.1.4 illustrates how the terms split when a complex of the type NiX_6 is cis and trans substituted giving complexes of the type cis - NiX_4Y_2 (C_{2v} symmetry) and trans - NiX_4Y_2 (D_{4h} symmetry).

The largest splittings are expected for a trans-distortion. An example of a spectrum with trans distortion is that of $Ni(pyridine)_4Cl_2$.[71] The ν_1 transition is resolved into two components at 8.5 and 10.9 kK, whereas the ν_2 transition gives rise

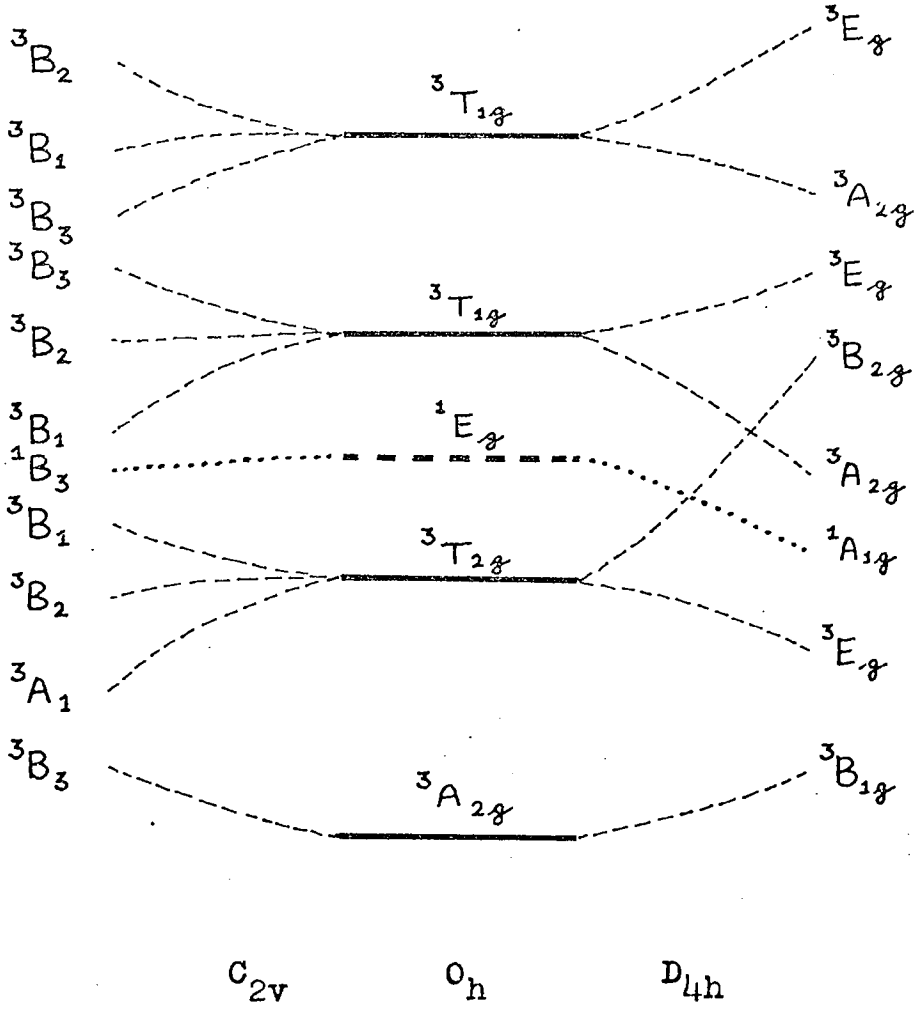


Fig. 1.4 The effects of distortion of the energy levels of octahedral Ni(11) complexes:
cis - octahedral (C_{2v}) and trans- octahedral (D_{4h}).[73]

to a shoulder at 14.3 kK and a peak at 15.8 kK. Very often however, octahedral complexes of nickel (11) having non-identical

ligands retain the simple form in O_h symmetry and this is further evidence for the validity of the rule of average environment (Sect. 1.6.5).

Tetrahedral Nickel (11): The intensity of the spectral transitions in tetrahedral complexes is significantly greater than that in octahedral complexes because the latter have a centre of inversion whereas the former do not. In general, tetrahedral nickel (11) complexes are characterized by a multiple visible band of high intensity in the region 16 kK, assignable to the $^3T_1(P) \leftarrow {}^3T_1$ (ν_3) transition. This band is usually flanked on the high and low energy sides by weaker spin forbidden transitions to components of the ^1D and ^1G levels. The ν_2 ($^3A_2 \leftarrow {}^3T_1$) occurs around 8 kK while ν_1 ($^3T_2 \leftarrow {}^3T_1$) occurs deep in the infrared around 3-5 kK. For the now well known tetrahedral anion $NiCl_4^{2-}$. Smith et al.[72] assigned as follows: D_q, 345 cm^{-1}; B, 734 cm^{-1}; ν_1, 4.08 kK ($\epsilon \simeq 12$); ν_2, 7.46 kK ($\epsilon \simeq 21$); ν_3, 14.16 kK ($\epsilon \simeq 150$).

Steric hindrance seems to be the main factor which imposes a tetrahedral structure in many nickel (11) complexes.[4,73] The presence of the bulky triphenylmethylarsonium cation undoubtedly favours the existence of the regular tetrahedral $NiCl_4^{2-}$ ion in the solid $(Ph_3MeAs)_2NiCl_4$.[74] Spectra of the tetrahedral complexes or cations of nickel (11) (see Sect. 1.2.1.) with simple amines have not been correlated to the stereochemistry.

Octahedral Cobalt(11): While the spectra of octahedral complexes of nickel(11) are relatively easy to interpret, the assignment of transitions in octahedral cobalt(11) complexes can often be quite difficult. The $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ (ν_3) transition occurs in the visible region around 20 kK as a multiple band. Normally this

transition overlaps with spin-forbidden transitions to doublet states derived mainly from ^2G and ^2H terms. A band in the 8 - 10 kK region can also be assigned with certainty as the $^4T_{2g} \leftarrow {}^4T_{1g}$ (ν_1) transition. The $^4A_{2g} \leftarrow {}^4T_{1g}$ (ν_2) is not normally observed but can easily be mistaken as a spin-forbidden component of the visible band.

Ferguson and co-workers[75] have investigated the spectra of cobalt(11) in a number of six coordinate environments. They conclude that the asymmetric visible band, together with spin-forbidden components on the high and low energy sides, is typical of the spectra of octahedral cobalt(11) complexes. They also indicate that the $^4A_{2g} \leftarrow {}^4T_{1g}(\nu_2)$ transition occurs around 12 kK.

As already stated the lowering of symmetry in regular octahedral nickel(11) complexes is often revealed by splitting of bands. In contrast, deviations from O_h symmetry in octahedral cobalt(11) complexes can frequently result in appreciable intensity enhancement. Examples are the cobalt(11) nitrates $CoL_2(NO_3)_2$ where L is a sterically hindered amine,[76] or a phosphine or arsine oxide.[77] Apart from the increased intensity, the visible band does not exhibit any more structure than a regular octahedral cobalt(11) complex (which, incidentally, is further support for the validity of the rule of average environment) but the near infrared band (to $^2T_{2g}$) is split into at least two components.

Tetrahedral Cobalt(11): The spectra of tetrahedral nickel(11) derivatives differ little from their cobalt(11) analogues. The $^4T_1(P) \leftarrow {}^4A_2$ (ν_3) transition appears as multiple absorption in the visible while the $^4T_1 \leftarrow {}^4A_2$ (ν_2) transition appears in the near infrared. In contrast to tetrahedral nickel(11) this band may also display multiple splitting. The first band ν_1 in the 3 -5 kK region, has been rarely observed.

The spectra, as recorded by Hatfield and Yoke,[25] of some ethylamine complexes of cobalt(11) dihalides are shown in Fig. 1.5. Only those portions of the spectra in the visible

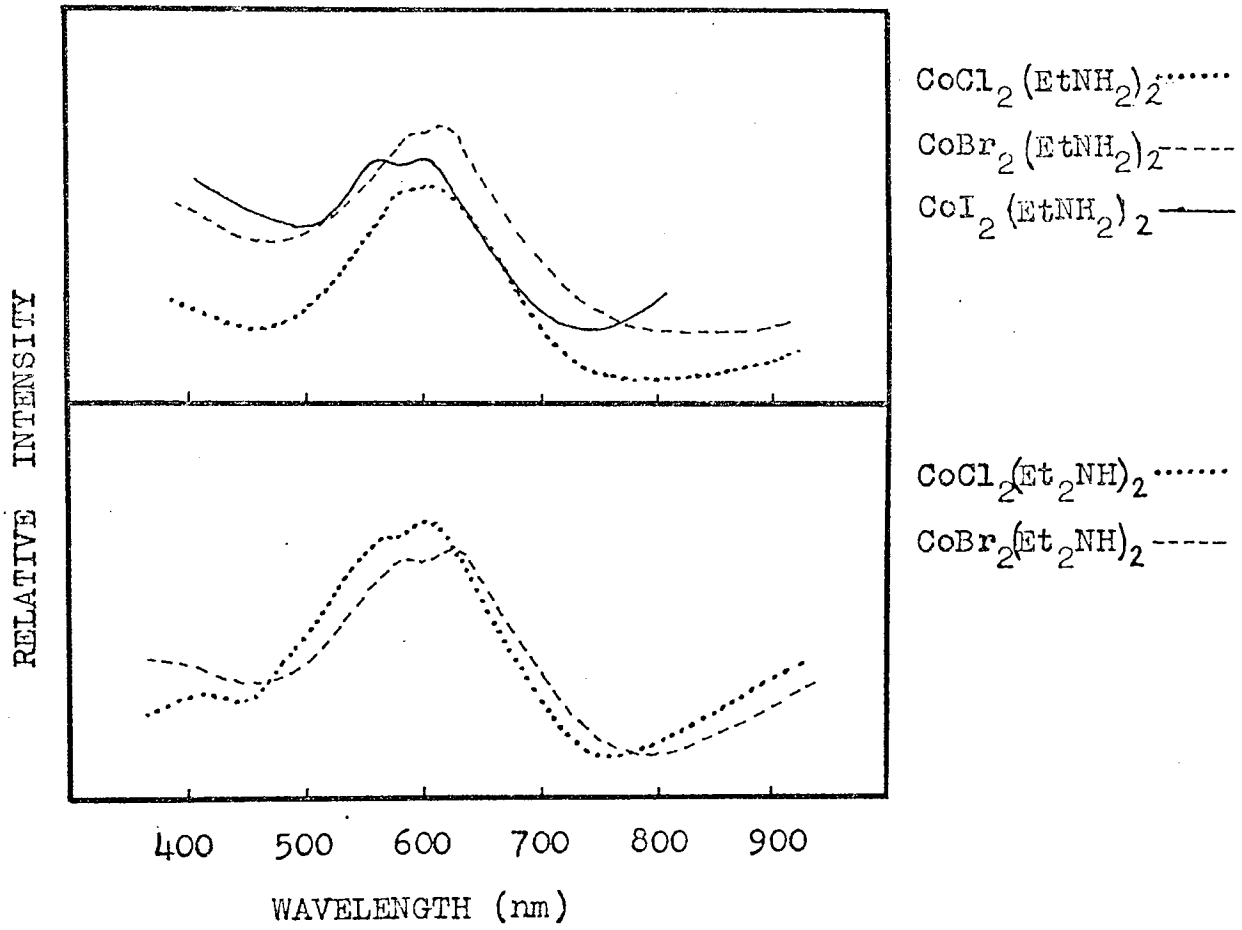


Fig.1.5. Reflectance spectra of the complexes of ethylamines with cobalt(11) halides[25]

region were recorded by these workers. This visible band is probably due to the transition $^4T_1(P) \leftarrow {}^4A_2$ (ν_3), which is characteristic of cobalt(11). It does not, however, display the multiple splitting normally associated with this transition. The near infrared band corresponding to the

transition $^4T_1 \leftarrow {}^4A_2$ (ν_2) was not located. Obviously a knowledge of the position of this band would have been extremely useful and would have helped verify the tetrahedral nature of the complex. In addition it may have yielded some information with respect to the amount of deviation from C_{2v} symmetry.

In view of the structural lability and susceptibility towards hydrolysis of tetrahedral and/or octahedral cobalt(11) and nickel(11) complexes, very often extra care is required when analysing the spectra. Moreover equilibria between tetrahedral and octahedral forms are often set up in solution. Clearly, measurement in the solid state is important to verify if the same species exists in solution.

Octahedral Chromium(111): The highest energy transition, $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ (ν_3) occurs above 30 kK so that it may be obscured if ultraviolet absorbing ligands are used. The intensity of this band is usually less than the intensity of the other two spin-allowed bands. The second highest energy transition, $^4T_{1g} \leftarrow {}^4A_{2g}$ (ν_2) occurs in the region 17 - 24 kK, while the lowest energy transition, $^4T_{2g} \leftarrow {}^4A_{2g}$ (ν_1) usually occurs between 13 and 17 kK. Splitting of ν_1 frequently occurs when there is deviation from O_h symmetry.

The electronic spectra of stereochemistry of nickel(11) and cobalt(11) other than tetrahedral and octahedral are not considered here; but a comprehensive review of all the usual stereochemistry is given by workers

such as Lever,[57] Sacconi[78] and Carlin[79].

2. EXPERIMENTAL

2.1. Measurement and Instrumentation

(A) SPECTRA

(i) Diffuse Reflectance Spectra

Diffuse reflectance spectra (30 - 4 kK) were recorded using a Unicam SP-700 spectrophotometer with an SP-735 diffuse reflectance attachment. Magnesium oxide was used as a reference and also as a diluent whenever necessary.

(ii) Solution Spectra

Solution spectra in the ultra-violet and visible regions were obtained using Unicam SP-700 and SP-1800 instruments with matched 1 mm. and 10 mm. silica cells.

(iii) Infrared Spectra

Infrared spectra were recorded for paraffin oil mulls and liquid films in caesium iodide supports between 4000 cm^{-1} and 250 cm^{-1} and for fluorochemical mulls in similar supports between 4000 cm^{-1} and 1300 cm^{-1} using a Perkin Elmer 457 instrument. In cases where the sample reacted with caesium iodide the 4000 - 250 cm^{-1} region was spanned using a combination of potassium bromide (4000 -400 cm^{-1}) and

polythene (600 - 250 cm^{-1}) supports. In the region 400 - 200 cm^{-1} the Perkin Elmer 225 spectrophotometer was used.

(B) CONDUCTIVITY:

Molar conductivities of freshly prepared solutions (10^{-3}M) in nitromethane were determined with a Mullard conductivity bridge using a standard conductivity cell, type E7591/B, and cell constant 1.36.

The conductivity bridge measures the conductance of the solution within the cell. Conductance is the reciprocal of electrical resistance; thus if R is the resistance of the solution in ohms, the conductance, G, is equal to $^1/R$ mhos or ohms $^{-1}$. The specific conductance, k, i.e. the conductance between opposite faces of 1 cm^3 of solution is calculated from the expression:

$$k = \text{cell constant} \times G$$

The units of k are mho cm^{-1}. Molar conductivity, Λ_M is then obtained from the expression:

$$\Lambda_M = k/C_M$$

when C_M is the concentration of solute expressed in mole. cm^{-3}.

(C) MAGNETISM:

Paramagnetic susceptibilities were measured by the Gouy method at room temperature. A magnet power supply, type D 104 (Newport Instruments), was used to produce the

field while a semi-micro balance, model S.M.12 (Stanton Instruments Ltd.), was used to measure the difference in the force developed in the absence and presence of the magnetic field.

Magnetic susceptibilities were calculated using the equation:

$$10^6\chi_g = (\alpha+\beta F')/W$$

where

α = constant allowing for displaced air and is equal to 0.029 × specimen volume.

β = tube "calibration constant".

W = weight of the sample (in grams).

F' = force on the sample alone (milligrams).

The constants α and β were determined using the calibrant mercury(11) tetrathiocyanato - cobaltate(11), $Hg[Co(NCS)_4]$ which as a susceptibility (χ_g) of 16.44×10^{-6} c.g.s. units at 20°.[80a] The units centimetres and grams are retained in this section for all calculations; standard international units are not used. The tube calibration was checked by measuring the magnetic susceptibility of tris (ethylenediamine)-nickel(11) thiosulphate, $Ni(en)_3S_2O_3$, for which a value of χ_g equal to 10.60×10^{-6} c.g.s. units was obtained. This agrees satisfactorily with the literature value.[81]

The magnetic moments, μ_{eff}, were obtained using the expression:

$$\mu_{eff} = 2.84(T.\chi_M^1)^{\frac{1}{2}} \text{ B.M.}$$

where

T = 273 + room temperature

$\chi_M^1 = \chi_M$ + diamagnetic correction

($\chi_M = \chi_g \times$ molecular weight)

In all cases diamagnetic corrections were made from Pascal's constants as listed by Figgis and Lewis.[80b]

(D) MOLECULAR WEIGHTS

Molecular weights were determined thermoelectrically using a Mechrolab Vapour Pressure Osmometer (Model 301A). The temperature was maintained at 25° and a non-aqueous thermistor probe was used to measure the temperature difference between droplets of pure solvent and solution.

The instrument is designed to read to ± 0.0001° but the sensitivity varies somewhat with solvent and concentration of solute. Benzene, toluene and carbon tetrachloride are excellent solvents while concentrations of solute varying between 0.005M and 0.10M give the best results. Such concentrations are very suitable for organic compounds but the solubility range of complexes is usually much lower. The accuracy of the instrument may often, therefore, be limited by the low solubility of complexes.

(E) ANALYSIS:

Microanalysis for carbon, hydrogen and nitrogen were carried out by Mrs. Taylor, microanalytical laboratory, this department, and by Drs. G. Weiler and F. Strauss, 164 Banbury Road, Oxford.

Chromium was estimated volumetrically [82a] by oxidation of chromium(III) to dichromate using persulphate, adding excess standard ferrous solution, followed by back-titration of the excess of the latter with standard potassium dichromate solutions. The nickel and cobalt content of complexes was determined gravimetrically by the pyridine -ammonium thiocyanate method.[82b,82c] Halides (chloride, bromide, iodide) were determined volumetrically by Volhard's method.[82d]

In all cases, prior to estimation of metal or halogen, the complexes were boiled for 20 - 25 minutes in approx. 25 cm^3 of 0.5N sodium hydroxide solution to remove any interfering amine, followed by neutralization with dilute nitric acid.

(F) AIR-SENSITIVE COMPLEXES:

Air sensitive complexes were manipulated using a combination of Schlenk glassware, syringes, and glove-boxes.[83] Schlenk glassware was used for filtration, purification and isolation of various complexes. The essential feature of most of this type of apparatus is a sidearm fitted with a stopcock. Through the sidearn the equipment is evacuated to eliminate air and an inert gas introduced. A high vacuum is not needed because the purage cycle is repeated several times. A manifold (Fig.2.1) equipped with a series of two-way stopcocks enables the purge cycle to be

repeated efficiently and rapidly.

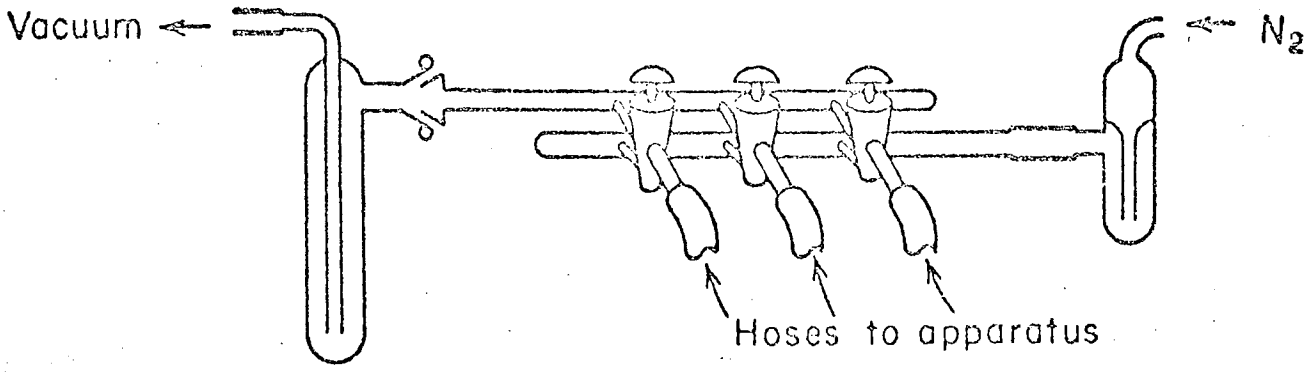


Fig.2.1. Manifold for medium vacuum and inert gas.

A precipitate may be collected and washed using the arrangement shown in Fig.2.2. Suction filtration is accomplished by partial evacuation of the lower Schlenk tube. The precipitate is then washed by the introduction of solvent from the dropping funnel.

There are several possible ways for drying a solid. If the complex has a low dissociation pressure it may be dried under vacuum. Alternatively, solvent may be removed by passing a continuous slow stream of nitrogen through the Schlenk tube. This is a particularly useful method when the complex has a relatively high dissociation pressure. Gentle heating of the Schlenk tube in a water bath may be necessary to compensate for the temperature drop associated

with the latent heat of vaporization of the solvent. A combination of partial vacuum and a slow stream of nitrogen may also be useful for drying certain complexes.

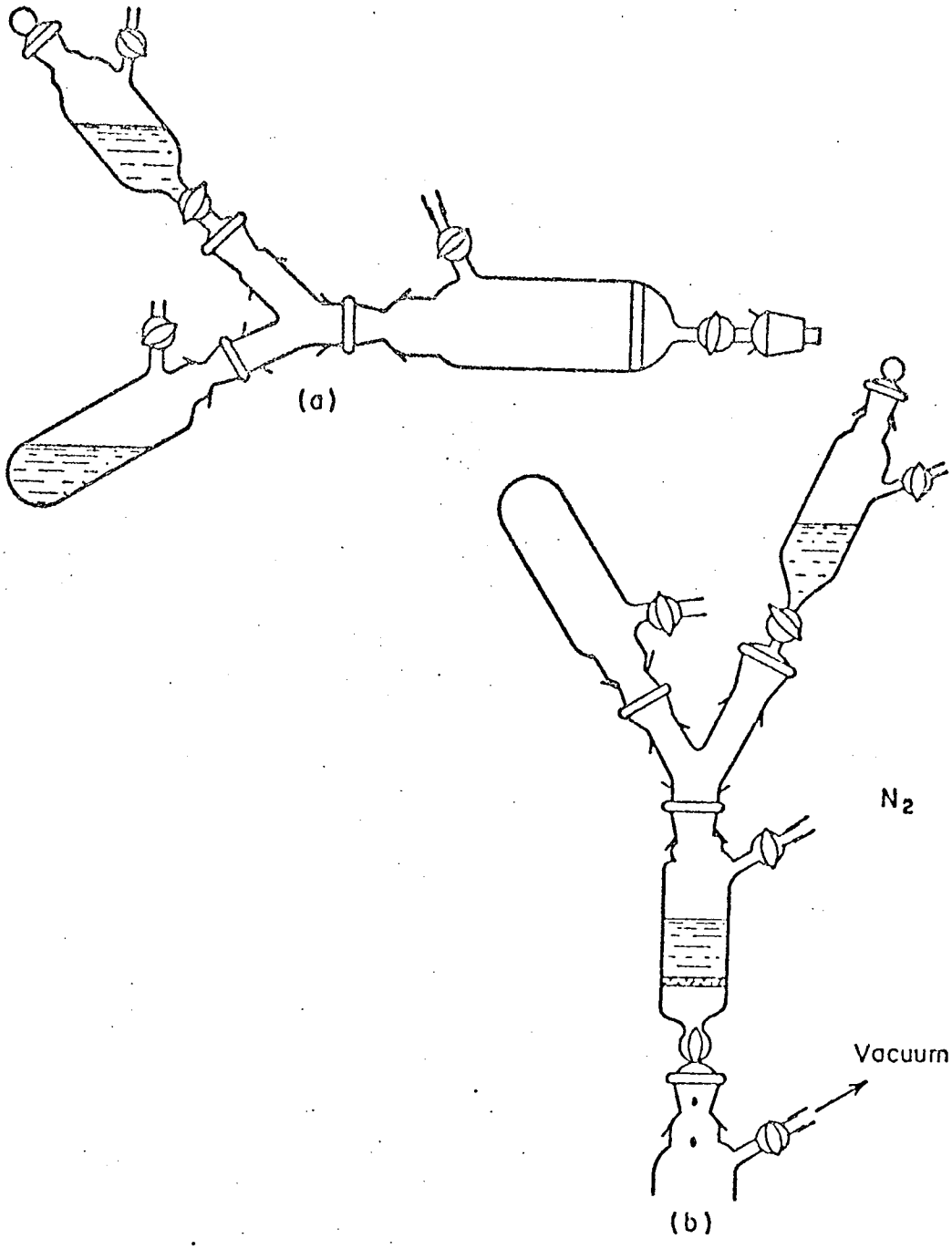


Fig.2.2. (a) Schlenk tube with mother liquor and precipitate and dropping funnel. (b) The filtrate being collected in a previously purged Schlenk tube.

An inert-atmosphere glove bag was used for handling air-sensitive complexes for analysis, infrared spectra, reflectance spectra and magnetic susceptibility measurements. The glove bag was fitted with a nitrogen inlet and an open end which could be closed by rolling and clamping. The bag was purged by several cycles of filling with inert gas and collapsing, followed by continuous flush. Provided that the air-sensitive compounds had not to be manipulated over long periods of time the glove bag was found to provide a completely adequate inert atmosphere. Moreover the simplicity and rapidity of generating the inert-atmosphere made it much more desirable than manipulation using a dry-box, especially in cases where a series of analyses and/or spectra had to be recorded.

2.2. Preparation and Purification of Reagents

2.2.1. Anhydrous Metal Halides

(i) Nickel(11) chloride

Method(a)* A 250 cm^3 r.b.f. was charged with 20g of finely ground nickel(11) chloride hexahydrate and 80 cm^3

* With slight modification this is the method outlined by A.R. Pray in Inorganic Syntheses.[84]

of freshly distilled thionyl chloride was added at room temperature. Evolution of sulphur dioxide and hydrogen chloride began at once .[F] After bubbling had ceased the flask was fitted with a reflux condenser and the slurry was refluxed for 4 hours. Excess thionyl chloride was removed under vacuum at 80° and the product was placed in a slow stream of nitrogen at the same temperature for 5 hours. The final traces of thionyl chloride were removed by placing the nickel(11) chloride over potassium hydroxide in a high vacuum for 24 hours. The nickel(11) chloride is extremely hygroscopic and handling in a dry inert atmosphere is necessary at all times.

Anal. Calcd. for $NiCl_2$: Ni,45.29;Cl,54.71. Found: Ni,45.40; Cl,54.79.

Method(b): The general method for the preparation of nickel(11) halides using triethy lorthformate is outlined by L.G.L. Ward in Inorganic Syntheses.[85]
Finely ground nickel(11) chloride hexahydrate (20g) was spread evenly on a large clockglass and heated in an oven at 80° for 24 hours. The resultant dihydrate was quickly pulverized and transferred to a 250 cm^3 r.b.f. containing 80g of triethlorthoformate. The mixture was refluxed with constant

[F] The preparation must be carried out in an efficient fume hood as large volumes of sulphur dioxide and hydrogen chloride are rapidly liberated immediately following the addition of thionyl chloride.

magnetic stirring for 3 hours and the volatile compounds were then removed under reduced pressure.

Anal. Calcd. for $NiCl_2$: Ni,45.29;Cl,54.71. Found: Ni,45.21; Cl,54.78.

(11) Cobalt(11) chloride

Method(a), as outlined for the preparation of nickel(11) chloride, was used with equal success for the preparation of cobalt(11) chloride. This chloride has a pale blue colour; it is extremely hygroscopic and must be handled at all times in a dry inert atmosphere.

Anal. Calcd. for $CoCl_2$: Co,45.39;Cl,54.61. Found: Co,45.44; Cl,54.75

(111) Chromium(111) chloride

In general chromium(111) chloride may be prepared using a high-temperature method [86,87] (e.g. reaction of the metal with Cl_2 at 960° followed by sublimation in a stream of chlorine) or by dehydrating chromium(111) chloride hexahydrate using thionyl chloride at a low-temperature.[84] In this work a sample of the high-temperature form, of German origin, was used in addition to a low-temperature sample. The low-temperature form was prepared in the usual way using thionyl chloride as outlined for the preparation of nickel(11) chloride in method(a). However, it was

noticeably much more difficult to dehydrate chromium(111) chloride hexahydrate than nickel(11) - or cobalt(11) chloride hexahydrate. Refluxing with thionyl chloride for a minimum of 8 hours was necessary and it was also found desirable to leave the product standing in excess thionyl chloride overnight before removing the volatile contaminants.

The high-temperature form is violet coloured and stable indefinitely in air while the low-temperature form is peach coloured, extremely hygroscopic, and handling in a dry inert atmosphere is necessary at all times.

Anal. Calcd. for $CrCl_3$: Cr,32.84;Cl,67.16. Found: Cr,32.80; Cl,67.32 (high-temperature form); Cr,32.95;Cl,67.31 (low-temperature form).

(1v) Nickel(11) bromide

Method(a): A 250 cm^3 r.b.f. was charged with 20g of finely ground nickel(11) bromide hexahydrate and 60 cm^3 of freshly prepared thionyl bromide was added at room temperature. Evolution of sulphur dioxide and hydrogen bromide began at once. After bubbling had ceased the flask was fitted with a reflux condenser and heated to 80° for 6 hours. If thionyl bromide (boiling point 139.7°) is refluxed or distilled under atmospheric pressure it undergoes decomposition rapidly [88] according to the scheme:

$$4SOBr_2 \longrightarrow 2SO_2 + S_2Br_2 + 3Br_2$$

The product was allowed to stand in excess thionyl bromide overnight at room temperature. Volatile contaminants were removed at reduced pressure at 100° and a slow stream of nitrogen was passed through the nickel(11) bromide at the same temperature for 4 hours. The final traces of thionyl bromide were removed by placing the product over potassium hydroxide in a high vacuum for 24 hours.

Anal. Calcd. for $NiBr_2$: Ni, 26.87; Br, 73.13. Found: Ni, 26.98; Br, 73.32

Thionyl bromide was prepared by the action of hydrogen bromide on thionyl chloride at 0° [88]; hydrogen bromide was prepared by bromination of tetrahydronaphthalene:[89] Tetrahydronapthalene (300 cm^3) was placed in a 500 cm^3 flask, fitted with a dropping funnel (containing 50 cm^3 of bromine) and delivery tube. The tetrahydronaphthalene was stirred magnetically and a steady stream of hydrogen bromide obtained by releasing bromine at a slow rate. This hydrogen bromide was bubbled slowly through thionyl chloride (150 cm^3) contained in a 250 cm^3 flask at 0° for 16 hours. The resultant thionyl bromide solution (heavily contaminated with thionyl chloride and bromine) was purified by fractional distillation at reduced pressure. The fraction 69°-70° at 60 mm. Hg was collected and used for the above dehydration.

Yield: 50%

<u>Caution:</u> Care must be taken when carrying out this fractionation. One fraction exploded violently while

standing at room temperature.

Method(b): Finely ground nickel(11) bromide hexahydrate (20g) was spread evenly on a large clockglass and placed in a vacuum desiccator over P_4O_{10} for 48 hours. The water content of the yellow product was much reduced and varied between 2.1 and 2.8 moles per mole of nickel(11) bromide. Anhydrous nickel(11) bromide was now prepared from this hydrated form using triethylorthoformate as outlined in method(b) for the preparation of nickel(11) chloride.

Anal. Calcd. for $NiBr_2$: Ni,26.87;Br,73.13. Found: Ni,26.81; Br,73.28.

(v) Cobalt(11) bromide

Anhydrous cobalt(11) bromide was readily prepared by dehydrating finely ground cobalt(11) bromide hexahydrate (20g) at 130° in a slow stream of nitrogen at 10 cm. Hg. Cobalt(11) bromide hexahydrate may be prepared by dissolving the carbonate in hydrobromic acid [90] but is more readily obtained from BDH chemicals. The pale green anhydrous form is extremely hygroscopic and handling in a dry inert atmosphere is desirable at all times.

Anal. Calcd. for $CoBr_2$: Co,26.94;Br,73.06. Found: Co,26.99; Br,73.12.

(vi) Nickel(ii) - and Cobalt(ii) iodide

Anhydrous nickel(ii) iodide was prepared by dehydrating nickel(ii) iodide dihydrate (of BDH quality) using triethylorthoformate. The anhydrous nickel(ii) iodide was sometimes used without removing the dehydrating agent; on other occasions the triethylorthoformate was removed under reduced pressure leaving a black residue of nickel(ii) iodide. This method was also used to dehydrate cobalt(ii) iodide dihydrate (of BDH quality) but any attempt to remove the dehydrating agent under reduced pressure resulted in the formation of an intractable gum. However cobalt(ii) iodide was also successfully prepared by heating the dihydrate at 150° in a slow stream of nitrogen under atmospheric pressure.

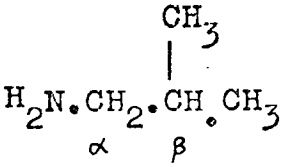
2.2.2. Amines

In general the amines were obtained from two sources: (a) BDH Chemical Ltd., Poole and (b) ICI, Billingham. Tri methylamine, ethylamine and diethylamine of BDH quality were used without further purification. All other amines were purified by refluxing with barium oxide, followed by fractional distillation at atmospheric pressure or under reduced pressure prior to use. They were stored over potassium hydroxide pellets.

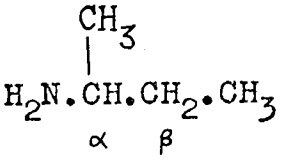
2.3. Preparations

Preliminary Remarks:

Many of the amine complexes considered in this section have been shown to have analogous formulae and composition. For example dibromotetrakis-(iso-butylamine)cobalt(11) and dibromotetrakis(sec-butylamine)cobalt(11) have the same molecular weight and the differences between these two complexes are determined solely by the differences between the two isomeric amines:



iso-butylamine



sec-butylamine

Predominantly these differences are associated with the position of a methyl group relative to the $-NH_2$ group. In sec-butylamine the methyl group on the α-carbon makes the amine very sterically hindered with respect to coordination to a metal cation. In contrast, iso-butylamine is much less sterically hindered as the offending methyl group is on a β-carbon. Because of this there is a pronounced difference with respect to dissociation in the relative stabilities of both the above mentioned complexes. Accordingly the method of preparation and isolation of dichlorotetrakis-(iso-butylamine)cobalt(11) requires a completely different approach to that for dichlorotetrakis-

(sec-butylamine)cobalt(11). Thus in order to maintain maximum clarity and unambiguity the majority of preparations are considered independently.

The format and rules applicable to Inorganic Syntheses are followed throughout. In an attempt to anticipate possible mistakes and misunderstandings by other workers repeating the work, footnotes are included with many of the preparations. Reference is made to these by means of an asterisk or other suitable symbol.

Caution: Many of the amines considered here are highly volatile toxic liquids at room temperature and pressure. For example trimethylamine boils at 3° and forms a gas-air explosive mixture. The preparation of the complexes in the followingsections were at all times carried out in an efficient fume hood, well isolated from a naked flame.

2.3.1. Complexes of Nickel(11)

Table 2.1 contains a list of the complexes whose preparations are considered in this section.

Table 2.1

Complex	Formula
α-Dichlorobis-(tri methylamine)nickel(11)	α-$NiCl_2 \cdot 2NMe_3$
β-Dichlorobis-(trimethylamine)nickel(11)	β-$NiCl_2 \cdot 2NMe_3$
Dibromobis-(trimethylamine)nickel(11)	$NiBr_2 \cdot 2NMe_3$
Diiodobis-(trimethylamine)nickel(11)	$NiI_2 \cdot 2NMe_3$

Table 2.1 contd.

dibromo-(triethylamine)nickel(11)	$NiBr_2.NEt_3$
Dichlorotetrakis-(iso-butylamine)nickel(11)	$Ni(i\text{-}BuNH_2)_4Cl_2$
Dibromotetrakis-(iso-butylamine)nickel(11)	$Ni(i\text{-}BuNH_2)_4Br_2$
Dithiocyanatotetrakis-(iso-butylamine)nickel(11)	$Ni(i\text{-}BuNH_2)_4(CNS)_2$

α-Dichlorobis-(trimethylamine)nickel(11)

Method(a): A spherical three-necked, 50 cm^3 flask fitted with a reflux condenser was charged with 0.75g of anhydrous nickel(11) chloride and 7 cm^3 of 2-2' dimethoxypropane. The mixture was heated to 40° and stirred magnetically under an atmosphere of dry nitrogen, while a continuous stream of trimethylamine* was slowly leaked through the reaction mixture. When all the nickel(11) chloride had reacted the source of heat was removed and simultaneously the flow of trimethylamine gas was stopped. ‖ The solution was set aside and after standing at 0° overnight deep blue hygroscopic crystals were

* Trimethylamine was sealed in a 250 cm^3 flask and the flow of the gas at room temperature regulated through teflon-plug stopcock. It was necessary to seal the stopper into the flask using a plastic metal adhesive.

‖ The source of heat must be removed immediately after the flow of trimethylamine gas has been stopped, otherwise rapid conversion of the complex to a red β-form takes place.

formed. The crystals were collected in a Schlenk frit (see sect.2.1 Fig.2.2.), washed with 5 cm^3 of 2-2' dimethoxypropane and dried in a slow stream of nitrogen at 20° and 20 cm. Hg over a period of two hours. The yield is nearly quantitative.

Anal. Calcd. for $C_6H_{18}N_2Cl_2Ni$: C,29.08;H,7.32;N,11.30; Cl,28.61;Ni,23.69. Found: C,29.01;H,7.28;N,11.26;Cl,28.51; Ni,23.60.

Method(b): Nickel(11) chloride hexahydrate was heated in an oven at 80° for 24 hours. The resultant dihydrate (0.75g) was transferred to a spherical three-necked 50 cm^3 flask containing 5 cm^3 of triethylorthoformate and refluxed under nitrogen for three hours.* The volatile compounds were removed under reduced pressure and 5 cm^3 of dry benzene ¶ added to the residue. After heating to 40° the reaction mixture was stirred magnetically and trimethylamine gas passed slowly through the solution until all the metal halide had reacted. The solution was cooled at 0° for two

* The preparation of anyhdrous nickel(11) halides via the triethylorthoformate dehydration route has been carried out and discussed by Ward[85] (see also sect. 2.2.1).

¶ The complex may be prepared in situ using triethylorthoformate as a solvent but the ease of removal of benzene makes it a much favoured solvent.

hours and the deep blue crystals collected in a Schlenk frit, washed with benzene, and dried in a slow stream of nitrogen at 20° and 20 cm. Hg over a period of one and a half hours.

Anal. Calcd. for $C_6H_{18}N_2Cl_2Ni$: C,29.08;H,7.32;N,11.30; Cl,28.61;Ni,23.69. Found: C,29.0;H,7.22;N,11.24;Cl,28.55; Ni,23.51.

β-Dichlorobis-(trimethylamine)nickel(11)

A spherical three-necked, 50 cm^3 flask, fitted with a reflux condenser, was charged with 0.75g anhydrous nickel(11) chloride* and 8 cm^3 of anhydrous benzene. The mixture was heated to 40° and stirred magnetically under an atmosphere of dry nitrogen. Trimethylamine gas was slowly bubbled through the mixture until all the metal halide had reacted.

At this stage the product was composed completely of the blue α-form in a benzene solution saturated with free ligand. The flow of trimethylamine gas was now stopped and the temperature raised to 45°. No coordinated amine is lost under these condi tions but the free ligand in the benzene solution is gradually expelled. When the benzene was free

* Alternatively nickel(11) chloride hexahydrate may be used as starting material and dehydration effected using triethylorthoformate as in method(b) for the preparation of α-dichlorobis-(trimethylamine)nickel(11).

of excess trimethylamine a red β-form of the complex began to form rapidly. Conversion was complete after half an hour. The product was collected in a Schlenk frit, washed with anhydrous benzene to remove any traces of the blue isomer, and finally dried in a slow stream of nitrogen at 20° and 20 cm. Hg.

Anal. Calcd. for $C_6H_{18}N_2Cl_2Ni$: C,29.08;H,7.32;N,11.30; Cl,28.61;Ni,23.69. Found: C,28.95;H,7.24;N,11.25;Cl,28.50; Ni,23.58.

The Interconvertability of α-$NiCl_2.2NMe_3$ and β-$NiCl_2.2NMe_3$

The red isomer (β-$NiCl_2.2NMe_3$) is rapidly converted to the blue form by donor solvents such as acetone, nitromethane and trimethylamine. Before the red isomer forms in good yield the free trimethylamine must be removed from the benzene solution. The passage of gaseous trimethylamine into a gently refluxing solution of complex will therefore enhance the formation of the α-form and reduce the yield of the β-form. In this way a mixture of both isomeric forms can be obtained in the product. Furthermore the β-isomer can readily be converted back to the α-form by passing trimethylamine gas through a powdered sample. Conversion is quantitative.

Dibromobis-(trimethylamine)nickel(11)

Nickel(11) bromide hexahydrate was spread on a clockglass

($\frac{1}{8}$" thick layer) and placed under high vacuum in a desiccator containing P_4O_{10} over a period of 48 hours. The water content of the yellow product was much reduced and varied between 2.1 and 2.8 moles per mole of nickel(11) bromide.

A spherical three-necked, 50 cm^3 flask, fitted with a reflux condenser, was now charged with 0.80g of the nickel(11) bromide (2.1 - 2.8)hydrate and 5 cm^3 of triethylorthoformate. The reaction mixture was stirred magnetically and refluxed under nitrogen for three hours. On cooling to 40° trimethylamine gas was leaked through the reaction mixture until all the metal halide had reacted. Copious quantities of deep blue crystals began to form in the hot solution and the yield became nearly quantitative on standing the mixture at 0° for two hours. The crystals were collected in a Schlenk frit, washed with benzene and dried in a slow stream of nitrogen at 20° and 20 cm. Hg.

Anal. Calcd. for $C_6H_{18}N_2Br_2Ni$: C,21.40;H,5.39;N,8.32;Br,47.46; Ni,17.43. Found: C,21.32;H,5.33;N,8.21;Br,47.33;Ni,17.29

At this stage triethylorthoformate may be removed under reduced pressure and the preparation continued using benzene as a solvent as in the preparation of α-dichlorobis (trimethylamine)nickel(11), method(b). However, since no isomers are formed with the bromide the triethylorthoformate can safely be removed after the preparation of the complex without any danger of conversion to a β-form.

Diiodobis-(trimethylamine)nickel(11)

A three-necked 50 cm^3 flask, fitted with a reflux condenser, was charged with recently prepared crystalline nickel(11) iodide (1.5 - 2.5)hydrate (0.90g) and 5 cm^3 of triethylorthoformate. The mixture was stirred magnetically at 50° for three hours under an atmosphere of nitrogen. Volatile compounds were removed under reduced pressure and 5 cm^3 of anhydrous benzene added to the black residue of anhydrous nickel(11) iodide.

The mixture was stirred magnetically, heated to 40° and trimethylamine gas slowly bubbled through the solution. Reaction of the nickel(11) iodide with trimethylamine took place immediately and was complete after 45 minutes. The resultant dark green solution was allowed to stand and bright green crystals formed on cooling to 0°. The crystals were collected in a Schlenk frit, washed with 5 cm^3 of benzene, and dried in a slow stream of nitrogen at 20° and 20 cm. Hg.

Anal. Calcd. for $C_6H_{18}N_2I_2Ni$: C,16.73;H,4.21;N,6.50;I,58.92; Ni,13.62. Found: C,16.65;H,4.18;N,6.41;I,58.72;Ni,13,50.

Dibromo-(triethylamine)nickel(11)

Nickel(11) bromide hexahydrate was partially dehydrated by placing it in a vacuum desiccator over P_4O_{10} for a period of 24 hours [see preparation of dibromobis-(trimethylamine) nickel(11)]. A spherical 50 cm^3 flask, fitted with a reflux condenser, was charged with 0.80g of the resultant nickel(11) bromide (2.1 - 2.8)hydrate and 5 cm^3 of triethylorthoformate.

The mixture was refluxed for three hours with constant magnetic stirring under an atmosphere of dry nitrogen.

Excess triethylamine (10 cm^3) was added to the reaction mixture and refluxing continued for one hour. A deep red, highly hygroscopic precipitate formed. When cool, the precipitate was collected in a Schlenk frit, washed with anhydrous benzene, and dried in a slow stream of nitrogen at 30° and 20 cm. Hg over a period of two hours.

Anal. Calcd. for $C_6H_{15}NBr_2Ni$: C,22.54;H,4.73;N,4.38;Br,49.99; Ni,18.36. Found: C,22.61;H.4.84;N,4.28;Br,50.52;Ni,18.44

Dichlorotetrakis-(iso-butylamine)nickel(11)

Method(a): A 50 cm^3 spherical flask, fitted with a reflux condenser, was charged with 0.75g of nickel(11) chloride dihydrate and 5 cm^3 of triethylorthoformate. The mixture was refluxed for three hours with constant magnetic stirring. Excess iso-butylamine (10 cm^3) was now added and refluxing continued until all the metal halide was consumed (about 30 minutes) and a pale blue solution had formed. On cooling to 0° for two hours a copious yield of pale blue crystals was obtained. The crystals were collected by suction filtration, thoroughly washed with six or seven 5 cm^3 volumes of anhydrous ether, air dried, and finally dried in a vacuum desiccator for 20 to 30 minutes. The yield was nearly quantitative.

Anal. Calcd. for $C_{16}H_{44}N_4Cl_2Ni$: C,45.52;H,10.51;N,13.27; Cl,16.79;Ni,13.91. Found: C,45,50;H,10.45;N,13.20;Cl,16.85;

Ni,13.82.

Method(b): Excess iso-butylamine (10 cm^3) was added to 0.75g of anhydrous nickel(11) chloride, dissolved in 15 cm^3 of absolute ethanol. The mixture was refluxed with constant magnetic stirring for half an hour, cooled, and the pale blue crystals collected, washed, and dried as in method(a).

Anal. Calcd. for $C_{16}H_{44}N_4Cl_2Ni$: C,45.52;H,10.51;N,13.27; Cl,16.79;Ni,13.91. Found: C,45.59;H,10.63;N,13.11;Cl,16.61; Ni,14.02.

Dibromotetrakis-(iso-butylamine)nickel(11)

This complex was prepared in a similar way as the analogous chloride, using either method(a) or Method(b). In method(a) nickel(11) bromide (2.1 - 2.8)hydrate was refluxed with triethorthoformate to effect dehydration while in method(b) the anhydrous form of nickel(11) bromide, as prepared via thionyl bromide was used with absolute alcohol as solvent. Both methods gave almost quantitative yields.

Anal. Calcd. for $C_{16}H_{44}N_4Br_2Ni$: C,37.60;H,8.68;N,10.96;Br,31.27; Ni,11.49. Found, method(a): C,37.55;H,8.59;N,10.81;Br,31.30; Ni,11.58; method(b): C,37.58;H,8.55; N,10.88;Br,31.28;Ni,11.52.

Dithiocyanatotetrakis-(iso-butylamine)nickel(11)

Mehtod(a): A 50 cm^3 spherical flask, containing 5 cm^3 of benzene was charged with 0.80g of anhydrous nickel(11) thiocyanate. Excess amine (10 cm^3) was added and the mixture was gently refluxed with constant magnetic stirring for half an hour. On cooling to room temperature 20 cm^3 of dry ether was added to the reaction mixture and the pale blue precipitate collected by suction filtration and washed several times with 2 cm^3 volumes of dry ether. Drying of the product was completed by placing it in a vacuum desiccator for 20 - 30 minutes.

Anal. Calcd. for $C_{18}H_{44}N_6S_2Ni$: C,46.25;H,9.49;N,17.98;S,13.72 Ni,12.56. Found: C,46.20;H,9.55;N,17.81;S,13.58;Ni,12.49.

Method(b): A 50 cm^3 spherical flask was charged with 0.80g of anhydrous nickel(11) thiocyanate. Iso-butylamine was slowly added in small volumes until all the thiocyanate was consumed. The exothermic reaction was controlled so that the temperature did not exceed 40°. Anhydrous benzene (15 cm^3) was added to the product and the mixture was gently refluxed for half an hour with constant magnetic stirring. The mixture was then cooled to room temperature and 20 cm^3 of anhydrous ether added, and the pale blue precipitate collected, washed and dried as in method(a).

Anal. Calcd. for $C_{18}H_{44}N_6S_2Ni$: C,46.25;H,9.49;N,17.98;S,13.72; Ni,12.56. Found: C,46.30;H,9.55;N,18.00;S,13.66;Ni,12.45

2.3.2. Complexes of Cobalt(11)

Table 2.2 contains a list of the complexes whose preparations are considered in this section.

Table 2.2

Complex	Formula
Dichlorobis-(trimethylamine)cobalt(11)	$CoCl_2 \cdot 2NMe_3$
Dibromobis-(trimethylamine)cobalt(11)	$CoBr_2 \cdot 2NMe_3$
Diiodibis-(trimethylamine)cobalt(11)	$CoI_2 \cdot 2NMe_3$
Dithiocyanato$^{bis}_{\Lambda}$-(trimethylamine)cobalt(11)	$Co(CNS)_2 \cdot 2NMe_3$
Dichlorotetrakis-(iso-butylamine)cobalt(11)	$Co(i\text{-}BuNH_2)_4Cl_2$
Dichlorobis-(iso-butylamine)cobalt(11)	$Co(i\text{-}BuNH_2)_2Cl_2$
Dibromotetrakis-(iso-butylamine)cobalt(11)	$Co(i\text{-}BuNH_2)_4Br_2$
Dibromobis-(iso-butylamine)cobalt(11)	$Co(i\text{-}BuNH_2)_2Br_2$
Diiodotetrakis-(iso-butylamine)cobalt(11)	$Co(i\text{-}BuNH_2)_4I_2$
Dithiocyanatotetrakis-(iso-butylamine)cobalt(11)	$Co(i\text{-}BuNH_2)_4(CNS)_2$
Dithiocyanatobis-(iso-butylamine)cobalt(11)	$Co(i\text{-}BuNH_2)_2(CNS)_2$
Dichlorobis-(sec-butylamine)cobalt(11)	$Co(s\text{-}BuNH_2)_2Cl_2$
Dibromotetrakis-(sec-butylamine)cobalt(11)	$Co(s\text{-}BuNH_2)_4Br_2$
Dibromobis-(sec-butylamine)cobalt(11)	$Co(s\text{-}BuNH_2)_2Br_2$
Diiodotetrakis-(sec-butylamine)cobalt(11)	$Co(s\text{-}BuNH_2)_4I_2$
Dithiocyanatobis-(sec-butylamine)cobalt(11)	$Co(s\text{-}BuNH_2)_2(CNS)_2$

Table 2.2. contd.

Dichlorobis-(tert-butylamine)cobalt(11)	$Co(t\text{-}BuNH_2)_2Cl_2$
Dithiocyanatobis-(tert-butylamine)cobalt(11)	$Co(t\text{-}BuNH_2)_2(CNS)_2$
Dichlorotetrakis-(iso-propylamine)cobalt(11)	$Co(i\text{-}PrNH_2)_4Cl_2$
Dichlorobis-(iso-propylamine)cobalt(11)	$Co(i\text{-}PrNH_2)_2Cl_2$
Dibromotetrakis-(iso-propylamine)cobalt(11)	$Co(i\text{-}PrNH_2)_4Br_2$
Dibromobis-(iso-propylamine)cobalt(11)	$Co(i\text{-}PrNH_2)_2Br_2$
Diiodotetrakis-(iso-propylamine)cobalt(11)	$Co(i\text{-}PrNH_2)_4I_2$
Dithiocyanatotetrakis-(iso-propylamine)cobalt(11)	$Co(i\text{-}PrNH_2)_4(CNS)_2$
Dithiocyanatobis-(iso-propylamine)cobalt(11)	$Co(i\text{-}PrNH_2)_2(CNS)_2$
Dichlorobis-(cyclohexylamine)cobalt(11)	$Co(C_6H_{11}NH_2)_2Cl_2$
Dibromotetrakis-(cyclohexylamine)cobalt(11)	$Co(C_6H_{11}NH_2)_4Br_2$
Dibromobis-(cyclohexylamine)cobalt(11)	$Co(C_6H_{11}NH_2)_2Br_2$
Diiodotetrakis-(cyclohexylamine)cobalt(11)	$Co(C_6H_{11}NH_2)_4I_2$
Dithiocyanatotetrakis-(cyclohexylamine)cobalt(11)	$Co(C_6H_{11}NH_2)_4(CNS)_2$
Dithiocyanatobis-(cyclohexlamine)cobalt(11)	$Co(C_6H_{11}NH_2)_2(CNS)_2$

Dichlorobis-(trimethylamine)cobalt(11)

A three-necked spherical 50 cm^3 flask, fitted with a reflux condenser was charged with 0.75g of anhydrous cobalt(11) chloride and 10 cm^3 of dry benzene. The mixture was heated to 55° and stirred magnetically under an atmosphere of nitrogen. Trimethylamine gas was slowly bubbled through the reaction mixture until all the cobaltous halide was consumed. Long blue crystalline needles of the complex began to form in the hot solution. On cooling, the crystals were collected in a Schlenk frit and dried without further purification in a slow stream of nitrogen at 30° and 20 cm Hg.

Anal. Calcd. for $C_6H_{18}N_2Cl_2Co$: C,29.05;H,7.31;N,11.29;Cl,28.58; Co,23.76. Found: C,28.94;H,7.26;N,11.10;Cl,28.51;Co,23.70.

Dibromobis-(trimethylamine)cobalt(11)

The procedure outlined for the preparation and isolation of dichlorobis-(trimethylamine)cobalt(11) was followed.

Anal. Calcd. for $C_6H_{18}N_2Br_2Co$: C,21.39;H,5.38;N,8.32;Br,47.43; Co,17.49. Found: C,21.30;H,5.29;N,8.26;Br,47.40;Co,17.31

Diiodobis-(trimethylamine)cobalt(11)

The procedure outlined for the preparation and isolation of dichlorobis-(trimethylamine)cobalt(11) was followed.

Anal. Calcd. for $C_6H_{18}N_2I_2Co$: C,16.72;H,4.21;N,6.50;I,58.89; Co,13.67: Found: C,16.66;H,4.16;N,6.44;I,58.41;Co,13.58

Dithiocyanatobis-(trimethylamine)cobalt(11)

A three-necked 50 cm^3 spherical flask, fitted with a reflux condenser, was charged with 0.75g of cobalt(11) thiocyanate hemihydrate and 5 cm^3 of triethylorthoformate. The mixture was stirred magnetically and heated under reflux for two hours.* It was then cooled to 60° and trimethylamine gas slowly leaked through the reaction mixture until all the metal thiocyanate was consumed. Sparkling blue crystals of the complex formed in the hot solution and after standing at 0° for 30 minutes the product was collected in a Schlenk frit, washed with 3 cm^3 of benzene and dried in a slow stream of nitrogen at 20° and 20 cm. Hg.

Anal. Calcd. for $C_8H_{18}N_4S_2Co$: C,32.76;H,6.19;N,19.10;S,21.86; Co,20.09. Found: C,32.71;H,6.16;N,19.11;S,21.73;Co,20.15.

* At this stage the triethylorthoformate can be removed successfully under reduced pressure and replaced by anhydrous benzene. Either method was found equally suitable as the thiocyanate showed no tendency towards gum formation in triethylorthoformate. It could also be removed fairly readily after complex formation, though benzene was found to be more desirable in this respect.

Dichlorotetrakis-(iso-butylamine)cobalt(11)

Method(a): A 50 cm^3 r.b.f. was charged with 0.5g anhydrous cobalt(11) chloride and 10 cm^3 of a 50% v/v mixture of benzene and iso-butylamine. The reaction mixture was refluxed with constant magnetic stirring for 15 minutes and the deep blue solution allowed to cool at 0^o overnight. The red crystals (which formed in the blue solution) were collected in a Schlenk frit, washed with 3 cm^3 of a 40% solution of iso-butylamine in anhydrous ether*, and dried in a 10 cm. Hg vacuum over a period of two hours. If more vigorous drying conditions are used or longer drying periods amine is gradually stripped from the tetrakis - complex and formation of a blue bis - complex becomes evident. Should this happen the tetrakis-complex can be reformed by placing it overnight in an atmosphere saturated with amine vapour. Yield: 70% based on metal halide.

Anal. Calcd. for $C_{16}H_{44}N_4Cl_2Co$: C+H+N,69.26;Cl,16.79;Co,13.95; Found: C+H+N,69.10;Cl,16.61;Co,13.90.

* Any attempt to wash the crystals with a solvent containing less than 40% amine results in rapid formation of a blue bis - complex.

Method(b): A 50 cm^3 r.b.f. was purged with nitrogen and charged with 5 cm^3 of iso-butylamine. Anhydrous cobalt(11) chloride was added in small quantities while the reaction mixture was continuously swirled. The exothermic reaction

was controlled so that the temperature did not exceed 30°. Addition of metal halide was continued until a thick red paste had formed and the majority of amine had been consumed. An equal volume (5 cm^3) of ether was added and the red precipitate collected in a Schlenk frit and dried without further purification in a moderate vacuum for 15 minutes.
Yield: Nearly quantitative.

Anal. Calcd. for $C_{16}H_{44}N_4Cl_2Co$: C+H+N,69.26;Cl,16.79;Co,13.95; Found: C+H+N,69.30;Cl,16.68;Co,13.91.

Dichlorobis-(iso-butylamine)cobalt(11)

Method(a): A 50 cm^3 r.b.f., containing 10 cm^3 of anhydrous benzene, was charged with 0.65g (5 m. moles) of cobalt(11) chloride and 1 cm^3 (10 m. moles) of iso-butylamine. The mixture was refluxed with constant magnetic stirring for half an hour. Deep blue crystals formed in the hot solution. On cooling to room temperature the product was collected in a sintered glass crucible at the water pump and washed several times with 1 cm^3 volumes of dry ether, and finally dried in a vacuum desiccator for 30 minutes.
Yield: 75%, based on metal halide.

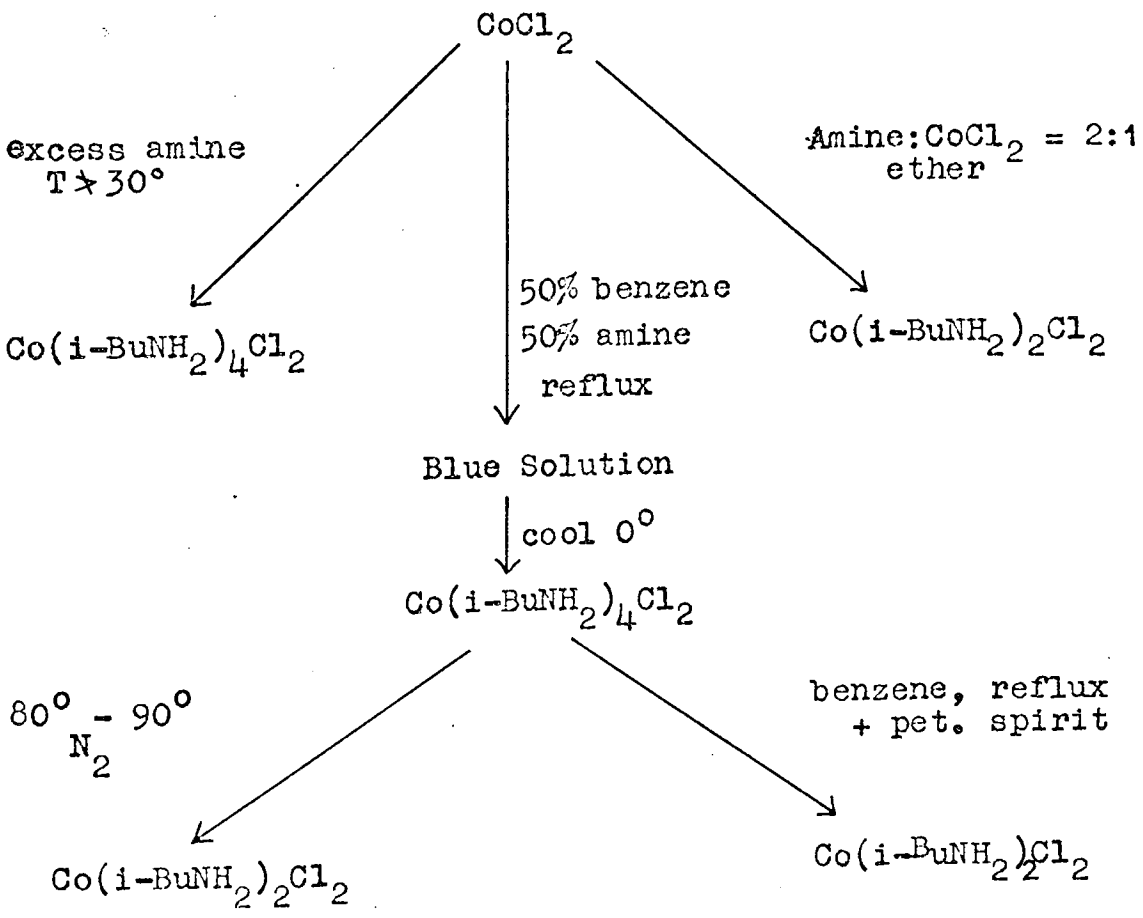
Anal. Calcd. for $C_8H_{22}N_2Cl_2Co$: C,34.80;H,8.03;N,10.15, Cl,25.68;Co,21.34. Found: C,34.71;H,8.10;N,10.11;Cl,25.61; Co,21.41.

Other Methods: The bis-complex was also prepared in high purity by stirring cobalt(11) chloride (0.65g, 5 m. moles) with the amine (1.2 ml., 12 m. moles) in 15 cm^3 of anhydrous ether for 24 hours, collecting and isolating the product as in method(a)

It was further prepared by gently heating the tetrakis at 80° - 90° in a slow stream of nitrogen over a period of one hour.

Finally, it was prepared by refluxing the tetrakis complex in a large volume of benzene and quickly adding petroleum/spirit to the hot solution.

The preparations of both bis and tetrakis - complexes can be summarized as follows:



Dibromotetrakis-(iso-butylamine)cobalt(11)

Method(a): A 50 cm^3 r.b.f. was charged with 0.5g anhydrous cobalt(11) bromide and 10 cm^3 of a 50% v/v mixture of benzene and iso-butylamine. The reaction mixture was refluxed with constant magnetic stirring for 15 minutes and allowed to cool to room temperature. The pink crystals were collected in a sintered glass crucible by suction filtration, quickly washed with several 2 cm^3 volumes of dry ether and finally dried in a vacuum desiccator over a period of twenty minutes. Yield: 90% based on metal halide.

Anal. Calcd. for $C_{16}H_{44}N_4Br_2Co$: C+H+N,57.22;Br,31.27;Co,11.53; Found: C+H+N,57.00;Br,31.21;Co,11.50.

Method(b): This is similar to method(b) for the preparation of dichlorotetrakis-(iso-butylamine)cobalt(11). Anhydrous cobalt(11) bromide was added in small quantities to 5 cm^3 of iso-butylamine contained in a 50 cm^3 r.b.f. The exothermic reaction was controlled so that the temperature did not exceed 30^o. Addition of amine was continued until a thick pink paste had formed and the majority of the amine had been consumed. A large volume (30 cm^3) of ether was added to the reaction mixture and after swirling, the bright pink crystals were quickly collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of dry ether, and finally dried in a vacuum desiccator for twenty minutes. The yield was quantitative.

Anal. Calcd. for $C_{16}H_{44}N_4Br_2Co$: C+H+N,57.22;Br,31.27;Co,11.53;

Found: C+H+N,57.20;Br,31.10;Co,11.50.

Dibromobis-(iso-butylamine)cobalt(11)

Method(a): The procedure described in method(a) for the preparation of dichlorobis-(iso-butylamine)cobalt(11) was followed. A 50 cm^3 r.b.f. containing 10 cm^3 of benzene was charged with 1.09g (5 m. moles) of cobalt(11) bromide and 1.0 cm^3 (10 m. moles) of iso-butylamine and refluxed with constant magnetic stirring for half an hour. The solution was cooled to room temperature for two hours and the deep blue precipitate was then collected in a sintered glass crucible, washed with 2 - 5 cm^3 of ether and finally dried in a desiccator for twenty minutes.
Yield: 60%, based on metal halide.

Anal. Calcd. for $C_8H_{22}N_2Br_2Co$: C,26.32;H,6.08;N,7.67;Br,43.78; Co,16.14. Found: C,26.21;H,6.02;N,7.61;Br,43.67;Co,16.28

Other Methods: When the tetrakis-complex was gently heated to 130° - 140° in a slow stream of nitrogen over a period of 1 hour two molecules of amine were eliminated:

$$Co(i\text{-}BuNH_2)_4Br_2 \xrightarrow[N_2]{130^\circ - 140^\circ} Co(i\text{-}BuNH_2)_2Br_2 + 2i\text{-}BuNH_2$$

It was also prepared by refluxing the tetrakis in toluene and quickly adding petroleum/spirit to the hot solution. Whereas benzene was used in the corresponding preparation of dichlorobis-(iso-butylamine)cobalt(11), toluene (because of its higher boiling point) was necessary in this preparation.

Diiodotetrakis-(iso-butylamine)cobalt(11)

A 50 cm^3 r.b.f. was purged with nitrogen and charged with 5 cm^3 of iso-butylamine. Cobalt(11) iodide dihydrate was added in small quantities and the mixture was continuously swirled. The vigorous exothermic reaction was controlled so that the temperature did not exceed 30°. Addition of cobalt(11) iodide dihydrate was continued until the majority of amine had been consumed and a thick pink paste had formed. The reaction mixture was gently heated to 50° for 15 minutes and on cooling a large volume (20 cm^3) of ether was added. The bright pink crystals were collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of ether and dried in a desiccator for 20 - 30 minutes.
The yield was quantitative.

Anal. Calcd. for $C_{16}H_{44}N_4I_2Co$: C+H+N,48.34;I,41.93;Co,9.74;
Found: C+H+N,48.29;I,41.76;Co,9.79.

Dithiocyanatotetrakis-(iso-butylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 0.5g of cobalt(11) thiocyanate hemihydrate and 10 cm^3 of a 50% v/v mixture of benzene and iso-butylamine. A deep red solution formed after refluxing for 45 minutes and on cooling to room temperature for 1 hour a copious yield of pale pink crystals was obtained. The crystals were collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of a dilute solution of the ligand in dry ether (6 drops/25 cm^3 ether). Washing the crystals with dry ether not containing a few drops of ligand, tends to decompose the complex slightly

with the formation of a bis-species. The crystals were dried in a vacuum desiccator over a period of 30 minutes. Yield: 75%

Anal. Calcd. for $C_{18}H_{44}N_6S_2Co$: C,46.23;H,9.48;N,17.97;S,13.71; Co,12.60. Found: C,46.21;H,9.51;N,17.88;S,13.76;Co,12.66.

Dithiocyantobis-(iso-butylamine)cobalt(11)

Method(a): A 50 cm^3 r.b.f. containing 10 cm^3 of dry benzene was charged with 0.88g (5 m. moles) of cobalt(11) thiocyanate hemihydrate and 1.0 cm^3 (10 m. moles) of iso-butylamine. The mixture was gently refluxed with constant magnetic stirring. After 10 minutes a deep blue solution formed but on further refluxing dark violet crystals began to form in the hot solution. Refluxing was continued until all the cobalt(11) thiocyanate was consumed. The solution was then cooled to room temperature and the dark violet crystals were collected in a sintered glass crucible and washed several times with a very dilute solution of ligand in ether (5 drops/25 cm^3 ether). The crystals were dried in a vacuum desiccator for 30 minutes. Yield: 50%

Anal. Calcd. for $C_{10}H_{22}N_4S_2Co$: C,37.37;H,6.90;N,17.43;S,19.95; Co,18.34. Found: C,37.35;H,6.94;N,17.41;S,19.90;Co,18.26.

Method(b): A 50 cm^3 r.b.f. was charged with 10 cm^3 of absolute alcohol, 0.88g (5 m. moles) of cobalt(11) thiocyanate hemihydrate and 1.0 cm^3 (1o m. moles) of iso-butylamine.

The mixture was refluxed with constant magnetic stirring for 30 minutes and then cooled to 0^{o}. After 1 hour dark violet crystals began to form and crystallization was complete after five hours. The product was collected in a sintered glass crucible and washed several times with a dilute solution of ligand in ether (5 drops/25 cm^3 ether). The crystals were dried in a vacuum desiccator for 30 minutes.
Yield: 70%, based on metal thiocyanate.

Anal. Calcd. for $C_{10}H_{22}N_4S_2Co$: C,37.37;H,6.90;N,17.43;S,19.95; Co,18.34. Found: C,37.10;H,6.93;N,17.45;S,19.84;Co,18.33.

Dichlorobis-(sec-butylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 0.5g of anhydrous cobalt(11) chloride and 10 cm^3 of a 50% v/v mixture of benzene and sec-butylamine.[P] The exothermic reaction was controlled so that the temperature did not exceed 30^{o}. The mixture was gently refluxed for 15 minutes with constant magnetic stirring and allowed to cool to room temperature. Ether was cautiously added until deep blue crystals of the complex separated out. The crystals were collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of a dilute etheral solution (5 drops/25 cm^3 ether) and finally dried in a

[P] Since no tetrakis-complex forms the ratio of metal halide to ligand is not critical. The bis-complex can be prepared when the ratio of $CoCl_2$:ligand is 1:2 but equally well when the ratio is 1:20.

vacuum desiccator over a period of 30 minutes.

Yield: 80%

Anal. Calcd. for $C_8H_{22}N_2Cl_2Co$: C,34.80;H,8.03;N,10.15;Cl,25.68; Co,21.34. Found: C,34.85;H,8.01;N,10.19;Cl,25.74;Co,21.38.

Dibromotetrakis-(sec-butylamine)cobalt(11)

Method(a): A 50 cm^3 r.b.f. was charged with 0.80g of cobalt(11) dibromide and 10 cm^3 of a 50% v/v mixture of benzene and sec-butylamine. The reaction mixture was refluxed with constant magnetic stirring until a deep blue solution had formed. After cooling overnight at 0° pink crystals separated out of the blue solution. The crystals were collected in a Schlenk frit and slowly washed with a 40% solution of ligand in ether and stored in a similar solution at 0°.

All attempts to dry the complex resulted in rapid loss of amine and formation of the bis-complex. While under such conditions no reliable analytical data could be obtained for the complex, a comparison of its reflectance spectrum with that of $Co(i\text{-}BuNH_2)_4Br_2$ clearly suggested that the pink product was $Co(s\text{-}BuNH_2)_4Br_2$.

Method(b): Anhydrous cobalt(11) bromide was added in small quantities to 5 cm^3 of sec-butylamine contained in a 50 cm^3 r.b.f. The exothermic reaction was controlled so that the temperature did not exceed 30°. When the majority of amine had been consumed 10 cm^3 of a 40% solution of ligand in ether was added to the pink paste. The pink crystals were collected

in a Schlenk frit and stored in a 40% solution of ligand in ether.

Dibromobis-(sec-butylamine)cobalt(11)

The procedure outlined for the preparation of dibromobis-(iso-butylamine)cobalt(11) was followed. In this case the precipitate was collected in a sintered glass crucible, washed several times with 1 cm^3 volumes of a dilute solution of ligand in ether (2 drops/25 cm^3) and finally dried in a vacuum desiccator for 30 minutes.

Anal. Calcd. for $C_8H_{22}N_2Br_2Co$: C,26.32;H,6.08;N,7.67;Br,43.78; Co,16.14. Found: C,26.28;H,6.01;N,7.68;Br,43.89;Co,16.19.

Diiodotetrakis-(sec-butylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 1.0g cobalt(11) iodide dihydrate and 5 cm^3 of triethylorthoformate. The mixture was gently refluxed for 1 hour and the resultant viscous green solution allowed to cool at room temperature. Sec-butylamine (5 cm^3) was added in small volumes and the vigorous exothermic reaction controlled so that the temperature did not exceed 30°. The deep blue solution, so formed, was gently refluxed with constant magnetic stirring for 30 minutes and allowed to cool at 0° for 1 hour. After vigorous agitation of the solution with a glass rod deep red crystals formed rapidly in the blue solution. A volume (20cm^3) of dry ether was added to complete crystallization. The product was collected in a glass crucible, washed several times with

1 cm^3 volumes of a dilute solution of ligand in ether (2 drops /25 cm^3 ether) and finally dried in a vacuum desiccator for 30 minutes.

Yield: 70%, based on metal iodide dihydrate.

Anal. Calcd. for $C_{16}H_{44}N_4I_2Co$: C+H+N,48.34;I,41.93;Co,9.74.
Found: C+H+N,48.59;I,41.99;Co,9.79.

Dithiocyanatobis-(sec-butylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 5 cm^3 of sec-butylamine. Cobalt(11) thiocyanate hemihydrate was added in small quantities while the reaction mixture was continuously swirled. The exothermic reaction was controlled so that the temperature did not exceed 30°. When the majority of amine had been consumed* the deep blue viscous solution was gently refluxed for 15 minutes. On cooling,ether was added cautiously while the deep blue viscous solution was stirred rapidly until crystallization was complete. A large volume (20 cm^3) of ether was added and the crystals were collected in a sintered glass crucible and washed with several small volumes of an amine/etheral solution (2 drops/25 cm^3 ether). The crystals were finally dried in a vacuum desiccator over a

* No tetrakis-complex is formed irrespective of the molar excess of sec-butylamine.

period of 30 minutes.

Yield: 80%

Anal. Calcd. for $C_{10}H_{22}N_4S_2Co$: C,37.37;H,6.90;N,17.43;S,19.95; Co,18.34; Found: C,37.39;H,6.94;N,17.41;S,19.99;Co,18.30.

Dichlorobis-(tert-butylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 0.65g cobalt(11) dichloride and 10 cm^3 of a 50% v/v mixture of sec-butylamine and benzene.* The mixture was gently refluxed for 30 minutes with constant magnetic stirring. After cooling to room temperature the pale blue precipitate was collected in a glass crucible, washed with dilute amine/etheral solution (2 drops/25 cm^3 ether) and dried in a vacuum desiccator for 30 minutes.

Yield: Quantitative.

Anal. Calcd. for $C_8H_{22}N_2Cl_2Co$: C,34.80;H,8.03;N,10.15;Cl,25.68; Co,21.34. Found: C,34.89;H,8.12;N,10.17;Cl,25.61;Co,21.38.

* No tetrakis-complex is formed, irrespective of the molar excess of tert-butylamine.

Dithiocyanatobis-(tert-butylamine)

A 50 cm^3 r.b.f. was charged with 5 cm^3 of tert-butylamine. Cobalt(11) thiocyanate hemihydrate was added in small quantities with constant swirling and the exothermic reaction was controlled so that the temperature did not exceed 20°. When the majority of amine had been consumed the mixture was gently refluxed for 15 minutes. A deep blue precipitate formed in the hot solution. On cooling, a volume (20 cm^3) of anhydrous ether was added to the reaction mixture and after stirring for 1 hour at room temperature the product was collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of a dilute amine/etheral solution (2 drops/25 cm^3 ether). The precipitate was dried in a vacuum desiccator for 30 minutes.

Yield: 90%.

Anal. Calcd. for $C_{10}H_{22}N_4S_2Co$: C,37.37;H,6.90;N,17.43;S,19.95; Co,18.34. Found: C,37.40;H,6.95;N,17.41;S,19.88;Co,18.36.

Dichlorotetrakis-(iso-propylamine)cobalt(11)

A 50 cm^3 r.b.f. was purged with nitrogen, charged with 10 cm^3 of iso-propylamine and placed in an ice/salt bath at 0°. Anhydrous cobalt(11) chloride was added in small portions with constant stirring and the exothermic reaction controlled so that the temperature did not exceed 10°. Addition of metal halide was continued until the majority of amine had been consumed with the formation of a deep pink precipitate. The flask was then allowed to gradually attain room temperature

and most of the excess amine was removed by standing the product at this temperature for 30 minutes. The pink precipitate was stored in a 40% solution of amine in ether at room temperature.

Similar to dibromotetrakis-(sec-butylamine)cobalt(11) this complex has a relatively high dissociation pressure at room temperature. Any attempt to completely dry the complex results in rapid dissociation and formation of a blue bis-species. However, from the approximate analytical values and from a comparison of its reflectance spectrum with that of dichlorotetrakis-(iso-butylamine)cobalt(11) there can be no doubt that the pink product is the tetrakis-complex $Co(i\text{-}PrNH_2)_4Cl_2$.

Anal Calcd. for $C_{12}H_{36}N_4Cl_2Co$: C+H+N,64.55;Cl,19.35;Co,16.09; Found: C+H+N,68;Cl,18;Co,15.

Dichlorobis-(iso-propylamine)cobalt(11)

A 50 cm^3 r.b.f. was purged with nitrogen and placed in an ice/salt bath at 0°. It was charged with 0.65g (5 m. moles) of cobalt(11) chloride, 5 cm^3 of anhydrous benzene and 0.86 cm^3 (10 m. moles) of iso-propylamine taking care that the temperature did not exceed 10° during these additions. The reaction mixture was stirred magnetically and gently heated under reflux for 30 minutes. Deep blue crystals began to form in the hot solution and after cooling at 0° for 2 hours the product was collected in a sintered glass crucible and washed liberally with a solution of amine in ether (4 drops/25 cm^3 ether) and finally dried in a vacuum

desiccator for 30 minutes.

Anal. Calcd. for $C_6H_{18}N_2Cl_2Co$: C,29.05;H,7.31;N,11.29;Cl,28.58; Co,23.76; Found: C,29.08;H,7.29;N,11.29;Cl,28.64;Co,23.81.

Dibromotetrakis-(iso-propylamine)cobalt(11)

The procedure outlined for the preparation of dichlorotetrakis-(iso-propylamine)cobalt(11) was followed. The pink crystals were collected in a sintered glass crucible washed with a solution of amine in ether (2drops/25 cm^3 ether). The product was dried in a vacuum desiccator for 30 minutes.
Yield: Quantitative.

Anal. Calcd. for $C_{12}H_{36}N_4Br_2Co$: C+H+N,31.66;Br,35.12;Co,12.95.
Found: C+H+N,31.78,Br,35.01;Co,12.98

Dibromobis-(iso-propylamine)cobalt(11)

A 50 cm^3 r.b.f. was placed in an ice/salt bath at 0° and charged with 1.09g (5 m. moles) anhydrous cobalt(11) bromide, 5 cm^3 of benzene and 0.86 cm^3 (10 m. moles) of iso-propylamine, taking care that the temperature did not exceed 10° during these additions. The mixture was gently refluxed with constant magnetic stirring for 30 minutes. Deep blue crystals formed in the hot solution. On cooling to room temperature 20 cm^3 of anhydrous ether was added to the reaction mixture and the product was immediately collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of anhydrous ether. It was dried in a desiccator

for 30 minutes.

Yield: 70%

Anal. Calcd. for $C_6H_{18}N_2Br_2Co$: C,21.39;H,5.83;N,8.31;Br,47.43; Co,17.49. Found: C,21.42;H,5.33;N,8.29;Br,47.49;Co,17.34.

Diiodotetrakis-(iso-propylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 1.0g cobalt(11) iodide dihydrate and 5 cm^3 of triethylorthoformate. The mixture was refluxed for 1 hour with constant magnetic stirring. The resultant green viscous solution was cooled to 0^o and iso-propylamine (5 cm^3) added in small volumes, taking care that the temperature did not exceed 20^o. The resultant blue solution was stirred magnetically at room temperature for 30 minutes and cooled at 0^o for 15 minutes. Ether was added cautiously with vigorous agitation and a copious quantity of red crystals quickly formed in the blue solution. These were collected in a sintered glass crucible and washed thoroughly with 2 cm^3 volumes of an amine/etheral solution (2 drops/25 cm^3 ether). The product was dried in a vacuum desiccator over a period of 30 minutes.

Yield: 80%

Anal. Calcd. for $C_{12}H_{36}N_4I_2Co$: C+H+N,43.06;I,46.22;Co,10.73; Found: C+H+N,43.21;I,46.05;Co,10.71.

Dithiocyanatotetrakis-(iso-propylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 10 cm^3 iso-propylamine and 2 cm^3 anhydrous benzene. The mixture was cooled to 0^o and cobalt(11) thiocyanate hemihydrate added in small quantities until the majority of amine had been consumed. The exothermic reaction was controlled so that the temperature did not exceed 10^o. After gently refluxing for 15 minutes the solution was allowed to cool at 0^o overnight. The deep red crystals which formed in the blue solution, were collected in a Schlenk frit and washed slowly with a 40% solution of iso-propylamine in ether, and stored in a similar solution at room temperature.

Similar to the complexes dibromotetrakis-(sec-butylamine) cobalt(11) and dichlorotetrakis-(iso-propylamine)cobalt(11) this complex has a relatively high dissociation pressure at room temperature. However, approximate analytical values and the similarity of its reflectance spectrum with that of dithiocyanatotetrakis-(iso-butylamine)cobalt(11) strongly suggest that the product is the tetrakis-complex $Co(i\text{-}PrNH_2)_4(CNS)_2$.

Anal. Calcd. for $C_{14}H_{36}N_6S_2Co$: total amine,57.46;Co,14.32. Found: total amine,60.0;Co,13.5.

Dithiocyanatobis-(iso-propylamine)cobalt(11)

A 50 cm^3 r.b.f. containing 10 cm^3 of anhydrous benzene, was charged with 0.88g (5 m. moles) of cobalt(11) thiocyanate hemihydrate and 0.86 cm^3 (10 m. moles) of iso-propylamine.

The temperature was controlled so that it did not exceed 10° during these additions. The reaction mixture was gently refluxed for 15 minutes. On cooling to 0° for 1 hour a copious yield of deep blue crystals was obtained. A volume (20 cm^3) of dry ether was added and after swirling, the crystals were collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of dry ether. The product was dried under vacuum for 30 minutes.
Yield: 85%, based on metal thiocyanate.

Anal. Calcd. for $C_8H_{18}N_4S_2Co$: C,32.76;H,6.19;N,19.10;S,21.86; Co,20.09. Found: C,32,79;H,6.24;N,19.11;S,21.76;Co,20.15.

Dichlorobis-(cyclohexylamine)cobalt(11)

A 50 cm^3 r.b.f., containing 10 cm^3 of anhydrous benzene, was charged with 0.65g (5 m. moles) cobalt(11) chloride and 1.14 cm^3 (10 m. moles) of cyclohexylamine. The mixture was refluxed with constant magnetic stirring for 30 minutes, and on cooling at 0° for 3 hours deep blue crystals formed in the blue solution. A volume (20 cm^3) of dry ether was added to the reaction mixture and the product was collected in a sintered glass crucible and washed liberally with small volumes of dry ether. The crystals were dried in a desiccator for 30 minutes.
Yield: 75% based on metal dichloride.

Anal. Calcd. for $C_{12}H_{26}N_2Cl_2Co$: C,43.92;H,7.99;N,8.54;Cl,21.60
Found: C,43.98;H,8.04;N,8.58;Cl,21.52;Co,17.92.

Dibromotetrakis-(cyclohexylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 0.5g anhydrous cobalt(11) bromide and 10 cm^3 of a 50% v/v mixture of benzene and amine. The reaction mixture was gently refluxed with constant magnetic stirring for 30 minutes. A deep blue solution formed and deep red crystals collected in this solution. After cooling to room temperature anhydrous ether (20 cm^3) was added and the product was collected in a sintered glass crucible and washed five times with 3 cm^3 volumes of anhydrous ether. The crystals were dried in a vacuum desiccator for 30 minutes. The tetrakis-complex is reasonably stable and can be washed with ether-free amine. This is desirable as it is rather difficult to remove free cyclohexylamine under vacuum. However, it is advisable not to agitate the crystals too vigorously during the washing procedure as sudden transformation of some of the crystals to a bis-complex may take place. If this happens washing with a 25% solution of cyclohexylamine in ether is necessary to restore the tetrakis-complex. The complex can be exposed to the air for periods up to 10 minutes without any serious decomposition.
Yield: 80%, based on metal bromide.

Anal. Calcd. for $C_{24}H_{52}N_4Br_2Co$: C+H+N,64.45;Br,25.97;Co,9.57
Found: C+H+N,64.59;Br,25.92;Co,9.51;

Dibromobis-(cyclohexylamine)cobalt(11)

The procedure for the preparation of dichlorobis-(cyclohexylamine)cobalt(11) was followed. A 50 cm^3 r.b.f.,

containing 10 cm^3 of anhydrous benzene, was charged with 1.09g (5 m. moles) cobalt(11) bromide and 1.14 cm^3 (10 m. moles) of cyclohexylamine. The mixture was refluxed with constant magnetic stirring for 30 minutes and on cooling to 0^o for 3 hours deep blue crystals collected in the blue solution. A volume (20 cm^3) of dry ether was added to the reaction mixture and the product was collected in a sintered glass crucible and washed several times with small volumes of dry ether. The crystals were dried in a vacuum desiccator for 30 minutes.

Yield: 70%

Anal. Calcd. for $C_{12}H_{26}N_2Br_2Co$: C,34.55;H,6.28;N,6.72;Cl,38.31; Co,14.13. Found: C,34.61;H,6.31;N,6.68;Cl,38.35;Co,14.10.

Diiodotetrakis-(cyclohexylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 1.0g cobalt(11) diiodide dihydrate and 5 cm^3 of triethylorthoformate. The mixture was refluxed for 1 hour and the resultant viscous green solution allowed to cool to 0^o. Cyclohexylamine (5 cm^3) was added in small volumes and the vigorous exothermic reaction controlled so that the temperature did not exceed 50^o. At first the reaction mixture assumed a deep blue colour but slowly bright red crystals began to form in the hot solution. After the addition of amine was complete a copious yield of red crystals had collected in the reaction mixture. On cooling to room temperature ether (20 cm^3) was added and the product was collected in a sintered glass crucible and washed several times with 2 cm^3 volumes of

dry ether. The crystals were dried in a vacuum desiccator for 30 minutes.

Yield: 90%

Anal. Calcd. for $C_{24}H_{52}N_4I_2Co$: C+N+H,55.92;I,35.77;Co,8.31. Found: C+H+N,55.86;I,35.62;Co,8.36.

Dithiocyanatotetrakis-(cyclohexylamine)cobalt(11)

A 50 cm^3 r.b.f. was charged with 0.5g cobalt(11) thiocyanate hemihydrate and 10 cm^3 of a 50% v/v mixture of benzene and cyclohexylamine. The reaction mixture was refluxed with constant magnetic stirring for 1 hour. Deep red crystals began to form in the hot solution and the yield was greatly enhanced by standing the solution at 0^o for 2 hours, followed by the addition of 20 cm^3 of dry ether. The product was collected in a sintered glass crucible, washed with five 3 cm^3 volumes of dry ether and dried in a desiccator for 30 minutes.

Yield: 65%

Anal. Calcd. for $C_{26}H_{52}N_6S_2Co$: C,54.61;H,9.17;N,14.70;S,11.21; Co,10.31. Found: C,54.66;H,9.19;N,14.62;S,11.18;Co,10.35.

Dithiocyanatobis-(cyclohexylamine)cobalt(11)

A 50 cm^3 r.b.f., containing 10 cm^3 of anhydrous benzene, was charged with 0.88g (5 m. moles) of cobalt(11) thiocyanate hemihydrate and 1.14 cm^3 (10 m. moles) of cyclohexylamine. After refluxing for 10 minutes a deep blue solution formed

but on further refluxing a pale pink precipitate collected in the hot solution. The product was collected in a sintered glass crucible, washed with small volumes of anhydrous ether and dried in a desiccator for 30 minutes. Yield: 65%

Anal. Calcd. for $C_{14}H_{26}N_4S_2Co$: C,45.02;H,7.02;N,15.00;S,17.17; Co.15.78. Found: C,45.08;H,7.04;N,15.06;S,17.19;Co,15.83.

2.3.3. Complexes of Chromium(111) chloride

Table 2.3 contains a list of the complexes whose preparations are considered in this section.

Table 2.3

Complex *	Formula
Chloropentakis-(ethylamine)chromium(111) chloride	$[Cr(C_2H_5NH_2)_5Cl]Cl_2$
Chloropentakis-(n-propylamine)chromium(111) chloride	$[Cr(C_3H_7NH_2)_5Cl]Cl_2$
Chloropentakis-(methylamine)chromium(111) chloride	$[Cr(CH_3NH_2)_5Cl]Cl_2$

Table 2.3. contd.

Chloromono-(tribenzylamine)chromium(III).Acetone	$CrCl_3.N(Bz)_3.Acetone$
Chloromono-(tribenzylamine)chromium(111)	$CrCl_3.N(Bz)_3.$
Chlorotris-(acetone)chromium(111)	$CrCl_3.3Me_2CO$
Chlorotris-(diethylketone)chromium(111)	$CrCl_3 3Et_2CO$
Chlorobis-(3-methylbutanone)chromium(111)	$CrCl_3.2Me_2CHCOMe$

* All the complexes were prepared using both high-temperature and low-temperature forms of chromium(111) chloride (see sect. 2.2.1).

P These complexes have been prepared and characterized previously.

Chloropentakis-(ethylamine)chromium(111) chloride

A 50 cm^3 r.b.f. was charged with 10 cm^3 of anhydrous ethylamine and cooled to 0^o in an ice/salt bath. Chromium(111) chloride was added in small quantities and the vigorous exothermic reaction controlled so that the temperature did not exceed 10^o. After each addition the reaction mixture was stirred rapidly with a glass rod. Addition of metal chloride was continued until the majority of amine was consumed and a viscous red gum had formed.

Excess amine (2 cm^3) was added and the reaction mixture allowed to stand at room temperature for two hours. The gum was dissolved in the minimum volume of methanol and precipitated by slow addition of ether. The product was collected in a sintered glass crucible, washed liberally with several 2 cm^3 volumes of ether and dried in a vacuum desiccator for two hours.

Yield: 50%, based on chromium(111) chloride.

Anal. Calcd. for $C_{10}H_{35}N_5Cl_3Cr$: total amine,58.6;total Cl,27.8; Cr,13.6. Found: total amine,58.1;total Cl,27.2;Cr,13.8(high-temperature form); total amine 58.2;total Cl,27.5;Cr,13.8 (low-temperature form).

While the analysis of this complex was always satisfactory the infrared spectrum showed an unexpected peak of moderate intensity situated at 2300 cm^{-1}. This observation and its implications is fully discussed in sect.3.3. The corresponding complexes with n-propylamine and methylamine were prepared to investigate if any related behaviour occured.

Chloropentakis-(n-propylamine(chromium(111) chloride

The procedure outlined for the preparation of chloropentakis-(ethylamine)chromium(111) chloride in method(a) was followed:

Anal. Calcd. for $C_{15}H_{45}N_5Cl_3Cr$: total amine,64.8;total Cl,23.7. Found: total amine 65.4;total Cl,23.0;Cr,11.6(high-temperature

form); total amine,65.6;total Cl,23.2;Cr,11.2(low temperature form).

Chloropentakis-(methylamine)chromium(111) chloride.

Methylamine was generated from methylamine hydrochloride and soda-lime and condensed in a nitrogen trap containing 1g of chromium(111) chloride. When the reaction appeared complete the trap was allowed to attain room temperature. The product was dissolved in 20 cm^3 of dilute hydrochloric acid, filtered, and gently evaporated to a smaller volume (10 cm^3). On cooling to 0^o overnight deep red crystals separated; they were collected in a sintered glass crucible, washed with distilled water and dried in a vacuum desiccator over P_4O_{10} for 24 hours.

Anal. Calcd. for $C_5H_{25}N_5Cl_3Cr$: total amine,49.5;total Cl,33.9; Cr,16.6. Found: total amine 49.6,total Cl 33.6; Cr,16.4 (high-temperature form); total amine,49.3;total Cl,40.1; Cr,16.4(low-temperature form).

Chloromono-(tribenzylamine)chromium(111).acetone

A 50 cm^3 r.b.f. was charged with 0.78g (5 m. moles) of chromium(111) chloride dissolved in 8 cm^3 of acetone and 1.44g (5 m. moles) of tribenzylamine dissolved in an equal

volume of acetone. The high-temperature form of chromium(111) chloride must be refluxed before it dissolves. The reaction mixture was gently refluxed and a deep red viscous gum formed in the hot solution after 30 minutes. The supernatant liquid was decanted and replaced with 20 cm^3 of anhydrous ether. After standing at room temperature overnight the gum solidified. The product was crushed under ether, quickly collected in a sintered glass crucible and washed liberally with ether to remove unreacted amine. The complex was dried in a vacuum desiccator for 30 minutes.

Anal. Calcd. for $C_{24}H_{27}NOCl_3Cr$: C,57.21;H,5.40;Cl,21.11; Cr,10.32. Found: C,56.89;H,5.61;Cl,21.01;Cr,10.41 (high-temperature form); C,56.82;H,5.49;Cl,20.89;Cr,10.48 (low-temperature form).

Chloromono-(tribenzylamine)chromium(111)

The infrared spectrum of chloromono-(tribenzylamine)chromium(111). acetone indicates that the acetone is present as a lattice component and is not coordinated to the metal. The carbonyl stretching frequency for acetone occurs at 1712 cm^{-1}, When coordinated to a metal cation this frequency is reduced by approximately 50 wavenumbers. In this complex $\nu(C{=}O)$ is situated at 1700 cm^{-1}, thus strongly suggesting the presence of uncoordinated acetone.

The acetone is rapidly expelled when the complex is heated in a slow stream of nitrogen over the temperature range 90° - 110°. Infrared analysis was used as a probe to determine when all the acetone had been removed.

Anal. Calcd. for $C_{21}H_{21}NCl_3Cr$: C,56.58;H,4.75;Cl,23.86; Cr,11.67; Found: C,56.63;H,4.87;Cl,23.95;Cr,11.60 (high-temperature form); C,56.43;H,4.78;Cl,23.59;Cr,11.61 (low-temperature form).

Chlorotris-(acetone)chromium(111)

A 50 cm^3 r.b.f., containing 10 cm^3 of acetone was charged with 1.0g of chromium(111) chloride. The reaction mixture was refluxed under an atmosphere of nitrogen until all the chromium(111) chloride has dissolved. The volume of the deep purple coloured solution was reduced by half and allowed to stand at 0^o. After 5 hours a copious quantity of purple coloured crystals was obtained. These were collected in a Schlenk frit and dried in a slow stream of nitrogen at room temperature over a period of two hours. The crystals are extremely hygroscopic and handling in an inert atmosphere is necessary at all times.

Anal. Calcd. for $C_9H_{18}O_3Cl_3Cr$: C,32.50;H,5.46;Cl,31.98;Cr,15.36; Found: C,32.80;H,5.61;Cl,32.10;Cr,15.31 (high-temperature form) C,32.71;H,5.63;Cl,31.81;Cr,15.40 (low temperature form).

Chlorotris-(diethylketone)chromium(111)

A 50 cm^3 r.b.f., containing 10 cm^3 of diethylketone, was charged with 1.0g of chromium(111) chloride. The mixture was refluxed with constant magnetic stirring under an atmosphere of nitrogen until all the chromium(111) chloride had dissolved. A trace of zinc dust noticeably accelerated

the reaction when the high-temperature form of chromium(111) chloride was used. The deep purple solution was allowed to stand at 0^{o} and after one week deep purple coloured crystals were deposited in the solution.. The crystals were collected in a Schlenk frit and washed 4 times with 1 cm^3 volumes of dry benzene. If benzene is liberally used the crystals rapidly break down to give an intractable gum. Drying was completed by heating the product to 40^{o} in a slow stream of nitrogen over a period of 1 hour.

Anal. Calcd. for $C_{15}H_{30}O_3Cl_3Cr$: C,43.23;H,7.26;Cl,25.52; Cr,12.48; Found: C,43.76;H,7.10;Cl,25.41;Cr,12.62 (high-temperature form); C,43.80;H,7.01;Cl,25.15;Cr,12.71 (low-temperature form).

Chlorobis-(3-methylbutanone)chromium(111)

The procedure outlined for the preparation of chlorotris-(diethylketone)chromium(111) was followed. In this case crystallization of the complex was complete after two weeks.

Anal. Calcd. for $C_{10}H_{20}O_2Cl_3Cr$: C,43.23;H,7.26;Cl,32.17; Cr,15.73; Found: C,43.62;H,7.33;Cl,32.42;Cr,15.68 (high-temperature form); C,43.61;H,7.21;Cl,32.33;Cr,15.79 (low-temperature form).

The Reaction of Cyclohexanone, 3-Methylcyclohexanone and Diphenylketone with Chromium(111) chloride

Solutions of chromium(111) chloride in cyclohexanone and

3-methylcyclohexanone were readily prepared by refluxing the ketone with the metal chloride. All attempts to crystallize complexes from these solutions failed. The solutions were stood at 0° for three months but no crystals were obtained. Ether was also used unsuccessfully.

A solution of diphenylketone in benzene was refluxed with chromium(111) chloride over a period of three days but no reaction took place. The addition of zinc dust was of no avail.

3. RESULTS AND DISCUSSION

3.1. Complexes of Nickel(11)

3.1.1. Monomeric Tetrahedral Complexes $NiX_2 \cdot 2NMe_3$, X = Cl,Br,I, and the Polymeric Octahedral Complex $NiCl_2 \cdot 2NMe_3$.

Nickel(11) complexes are known with a six-coordinate octahedral configuration, with five-coordinate square pyramidal or trigonal bipyramidal structures, and with four-coordinate square-planar or tetrahedral structures; these configurations are often only approximately regular. Magnetic susceptibility measurements used in conjunction with electronic and infrared spectra data usually enable such structures to be determined with fair certainty and often permit a study of deviations from regular geometry. In this section and in the following sections structural analysis is based mainly on this type of evidence. For simplicity the 'g' subscript, used to denote a centre of symmetry in octahedral complexes, is dropped throughout the discussion.

Diffuse reflectance spectra for the isomers α-$NiCl_2 \cdot 2NMe_3$ and β-$NiCl_2 \cdot 2NMe_3$ are shown in Fig.3.1. The α-isomer is characterized by a multiple visible absorption band having a pronounced shoulder on the high energy side and a band of weaker intensity on the low-energy side. This spectrum is typical of tetrahedral stereochemistry and the

positions of the two principal bands at 16.4 kK and 9.0 kK are consistent with electronic transitions between the states $^3T_1(P) \leftarrow {}^3T_1$ and $^3A_2 \leftarrow {}^3T_1$ respectively. The first

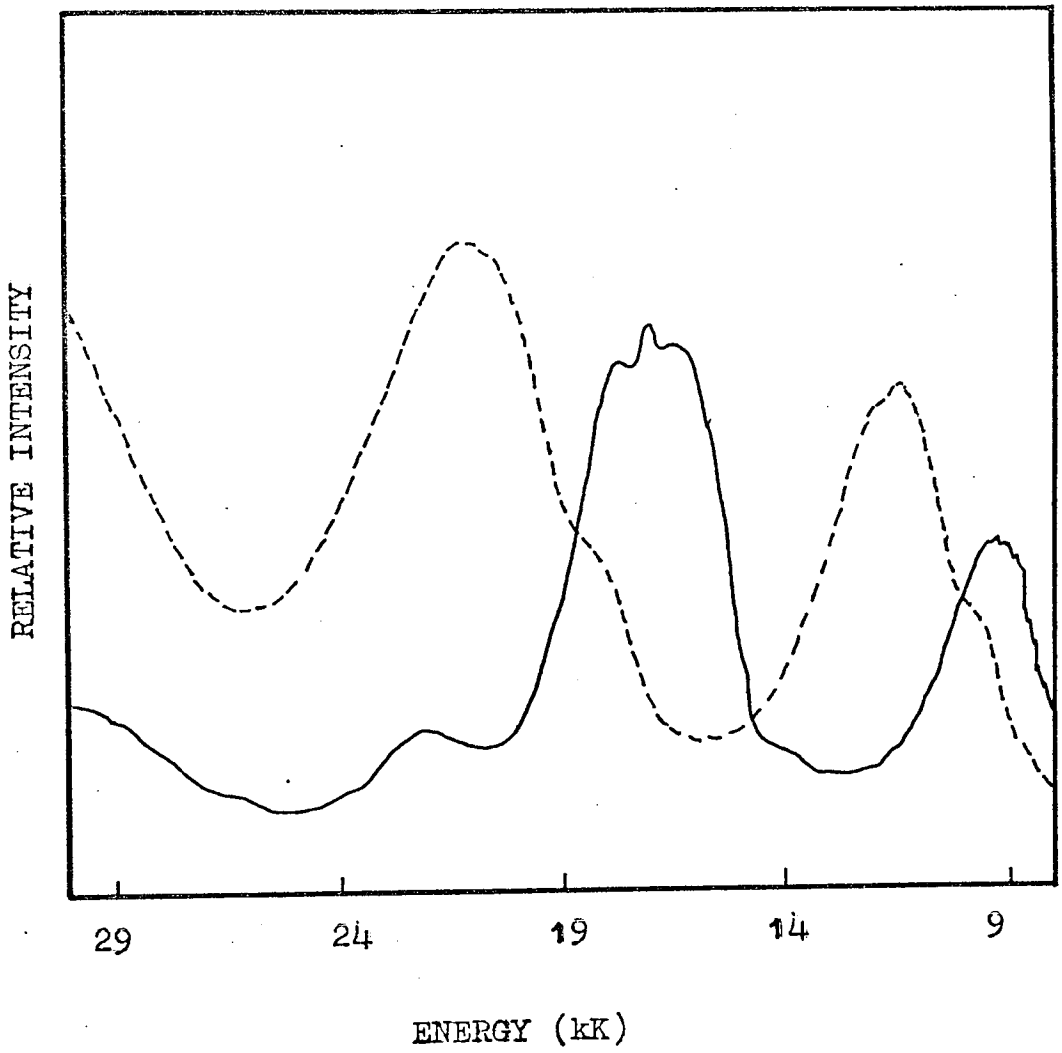


Fig 3.1 Reflectance spectrum of α-$NiCl_2.2NMe_3$ (——) and of β-$NiCl_2.2NMe_3$ (----).

spin-allowed transition i.e. $^3T_2 \leftarrow {}^3T_1$ is expected to be in the 3 - 5 kK region and therefore is not observed. Reflectance

spectra of the complexes $NiBr_2.2NMe_3$ and $NiI_2.2NMe_3$ have a similar profile and their band assignments are tabulated in Table 3.1. While the multiplicity of the visible band is retained in $NiI_2,2NMe_3$ the $^3A_2 \leftarrow {}^3T_1$ transition is resolved into a doublet.

TABLE 3.1

Reflectance spectra of the complexes of nickel(11) with trimethylamine having tetrahedral stereochemistry.

(Abs.Max.kK)

Complex		$^3T_1(P) \leftarrow {}^3T_1$	$^3A_2 \leftarrow {}^3T_1$
		ν_3	ν_2
α-$NiCl_2.2NMe_3$	22.3 sh	16.4	9.0
$NiBr_2.2NMe_3$	22.8 sh	16.5	10.8
$NiI_2.2NMe_3$	19.2 sh	15.2	9.8,6.9

sh, shoulder

The spectrum of the β-isomer, Fig.3.1 has two principal bands with absorption maxima at 21.0 kK and 11.5 kK. Slight shoulders are present on the low energy sides of both bands. The position of these bands is suggestive of an octahedral environment about the nickel atom and in this context it is instructive to compare the spectrum with the spectra of some known and relevant complexes.

The compounds $Nipy_2Cl_2$ and $Nipy_2Br_2$ (py = pyridine) have

polymeric structures containing six-coordinate nickel atoms and bridging halide atoms.[91,92] Bands with max. at 24.1 kK and 13.99 kK in the spectrum of $Nipy_2Cl_2$ have been assigned to transitions $^3T_1(P) \leftarrow {}^3A_2$ (ν_3) and $^3T_1 \leftarrow {}^3A_2$ (ν_2) respectively. The corresponding transitions in the spectrum of $Nipy_2Br_2$ occur at 23.53 kK and 13.85 kK. Each transition has a shoulder on the low energy side, and thus closely resembles the spectrum of β-$NiCl_2 \cdot 2NMe_3$

In addition the spectrum of β-$NiCl_2 \cdot 2NMe_3$ is also very similar (see Table 3.2) to that of $NiCl_2$ and $NiBr_2$ which are known to have halogen bridged octahedral structures.[63] On the basis of these similarities the high energy peak in the spectrum of β-$NiCl_2 \cdot 2NMe_3$ is attributed to the transition $^3T_1(P) \leftarrow {}^3A_2$ while the low energy peak is considered to arise from the transition $^3T_1 \leftarrow {}^3A_2$. The first spin-allowed band is expected to be in the 5 kK region and is not observed.

TABLE 3.2

Diffuse Reflectance Spectra for $NiCl_2$, $NiBr_2$[63] and β-$NiCl_2 \cdot 2NMe_3$ (Abs. Max. kK)

Compound	$^3T_1(P) \leftarrow {}^3A_2$		$^3T_1 \leftarrow {}^3A_2$	
	ν_3		ν_2	
$NiCl_2$	22.1	19.4 sh	12.9	11.6 sh
$NiBr_2$	20.7	17.5 sh	12.1	10.3 sh
β-$NiCl_2$,$2NMe_3$	21.0	18.0 sh	11.5	9.8 sh

sh, shoulder

Infrared spectra for α-$NiCl_2 \cdot 2NMe_3$, β-$NiCl_2 \cdot 2NMe_3$ and $NiBr_2 \cdot 2NMe_3$ are shown in Figs. 3.2, 3.3 and 3.4.

TABLE 3.3a

M-Hal Stretching Frequencies of complexes of Trimethylamine with Ni(11) (cm^{-1})

Complex	ν(Ni - Hal)	
α-$NiCl_2 \cdot 2NMe_3$	310	
$NiBr_2 \cdot 2NMe_3$	270	290 sh
$NiI_2 \cdot 2NMe_3$	245	255 sh

sh, shoulder

The two methyl stretches, the two methyl deformations and the methyl torsion of gaseous trimethylamine have been assigned as 825 cm^{-1} (sym) and 1043 cm^{-1} (asym), 366 cm^{-1} (sym) and 423 cm^{-1} (asym), and 269 cm^{-1} respectively. These vibrations are not significantly changed upon coordination of the amine to a metal cation,[93] although the methyl asymmetric stretching vibration of α-$NiCl_2 \cdot 2NMe_3$ is clearly visible as a doublet at 960 cm^{-1} and 1000 cm^{-1}. Tetrahedral complexes of the type NiL_2X_2 having C_{2v} symmetry are expected to show two Ni - X stretching vibrations in the infrared. Nakamoto[94] has assigned the two bands at 341.2 cm^{-1} and 305.0 cm^{-1} in the infrared spectrum of the tetrahedral complex $NiCl_2(PPh_3)_2$

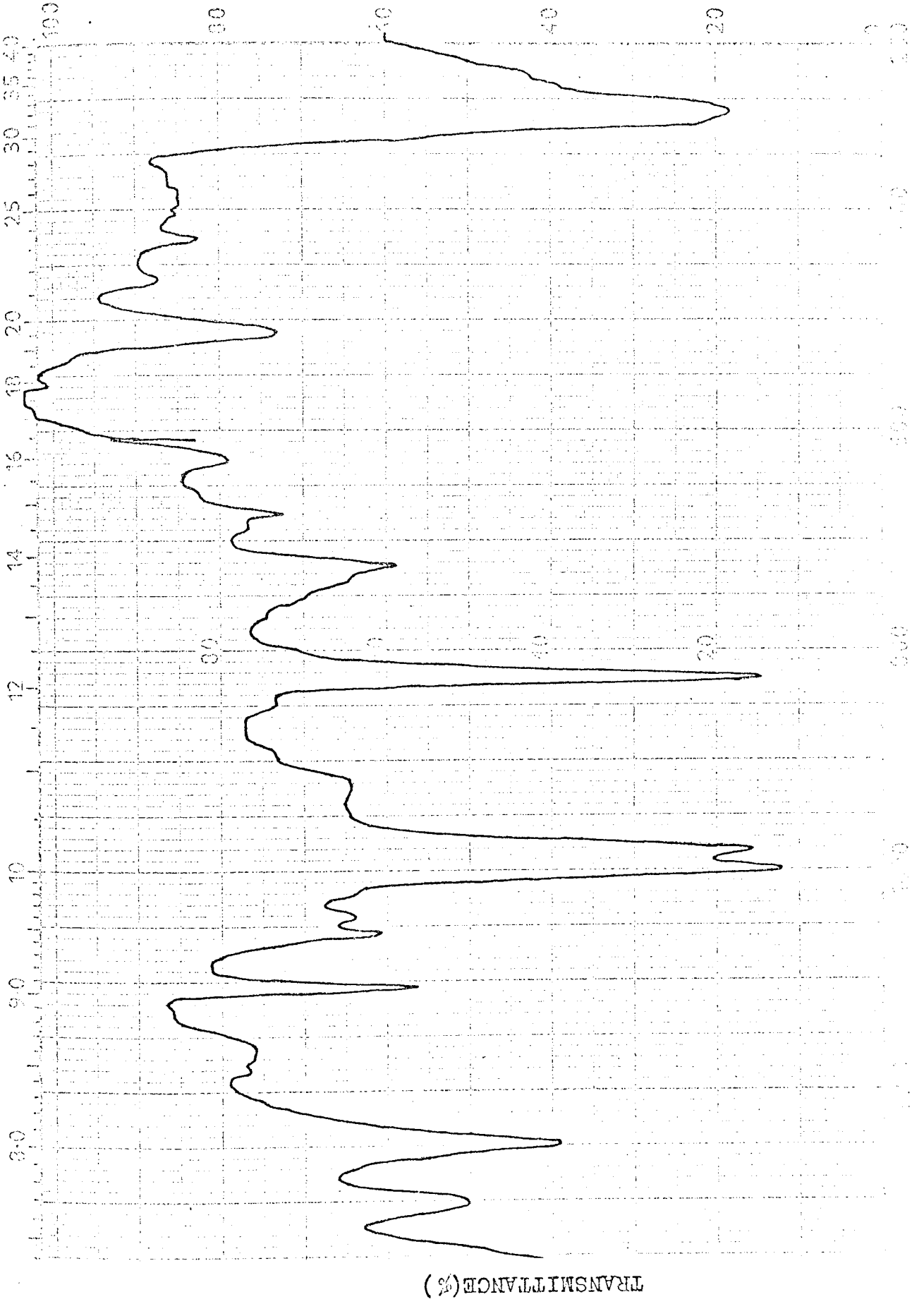


Fig.3.2 Infrared spectrum of α-$NiCl_2 \cdot 2NMe_3$

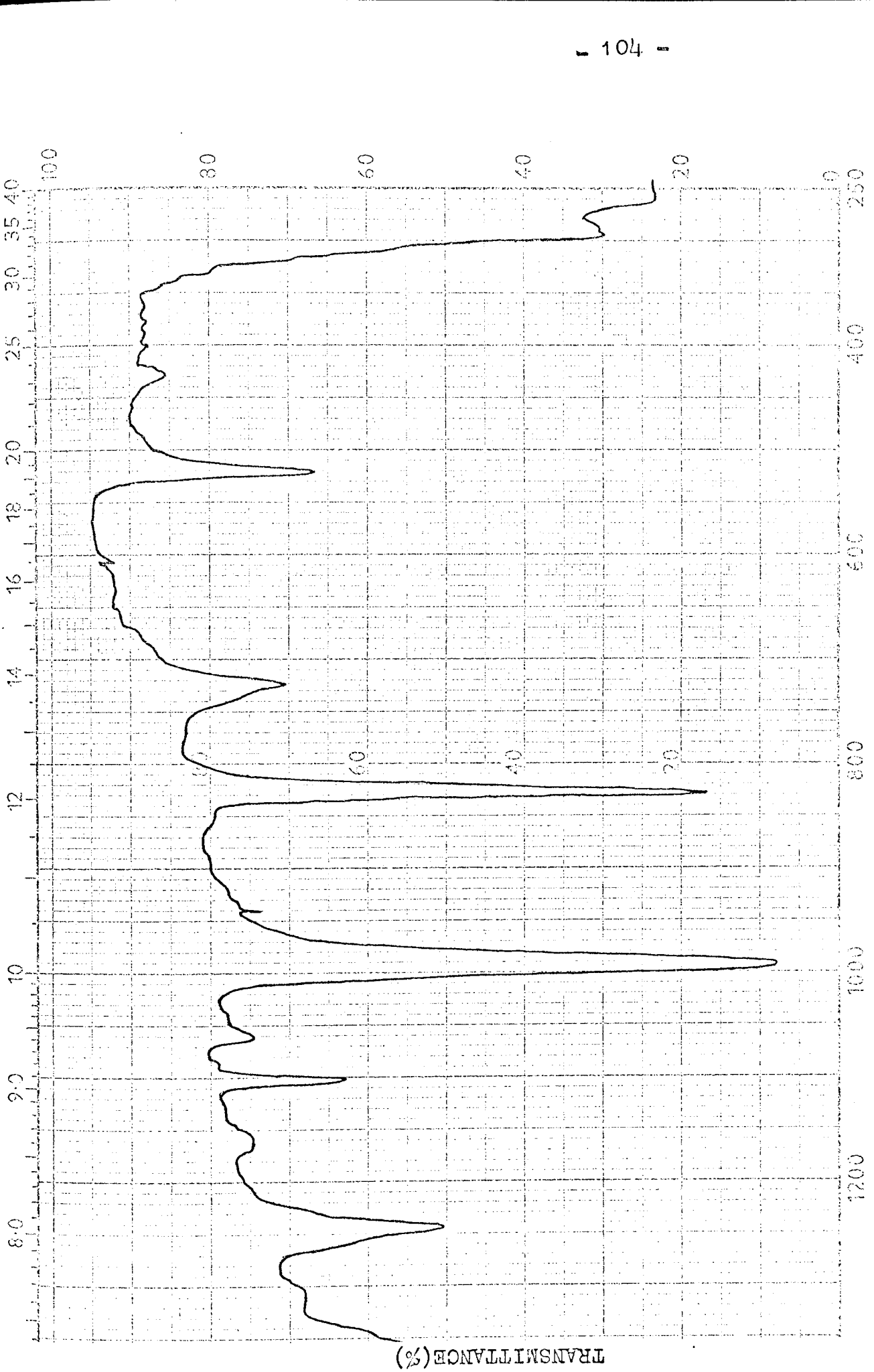


Fig.3.3 Infrared spectrum of β-$NiCl_2 \cdot 2NMe_3$

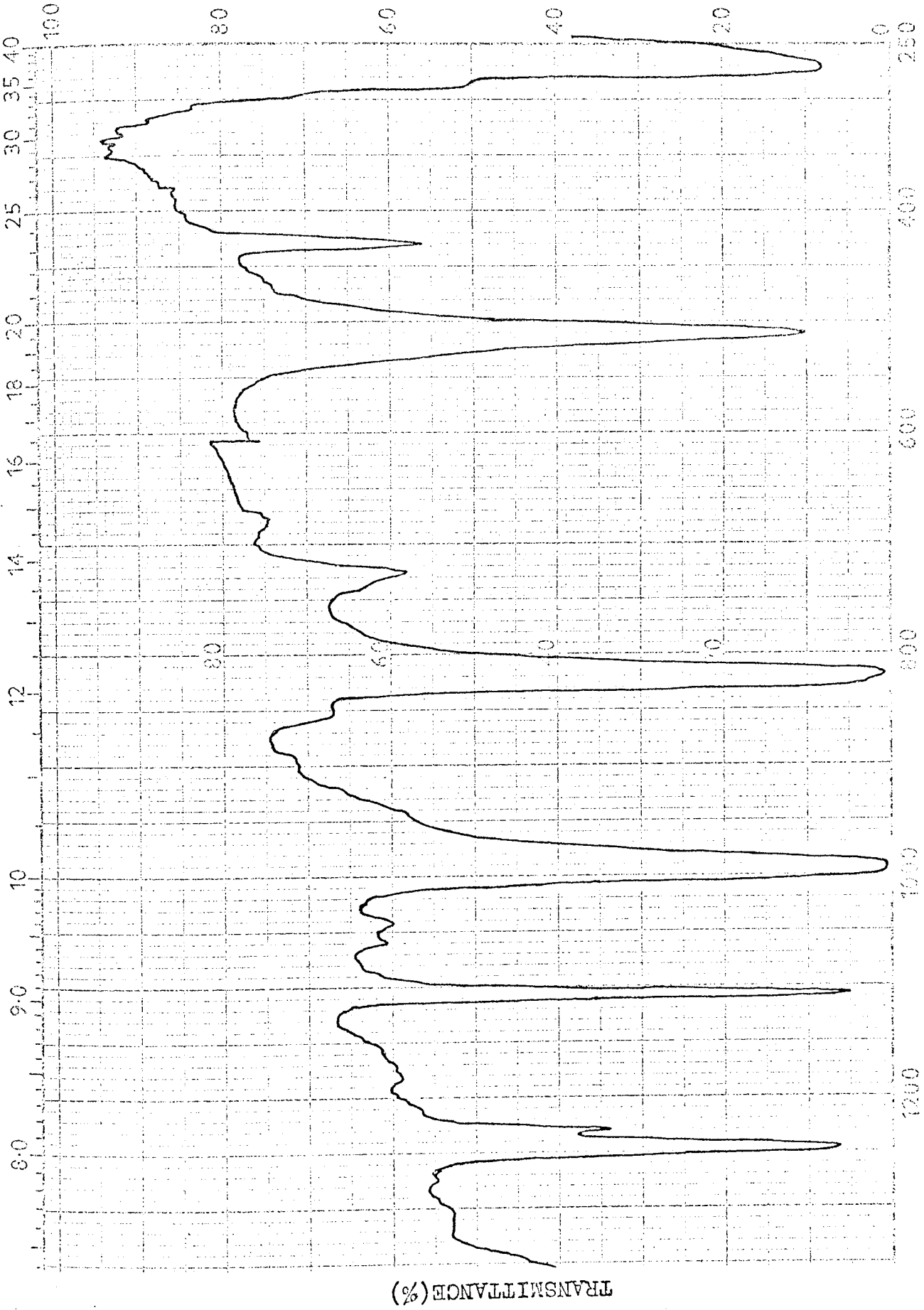


Fig.3.4 Infrared spectrum, $NiBr_2 \cdot 2NMe_3$

to Ni - Cl stretches.

In α-$NiCl_2 \cdot 2NMe_3$ the band at 310 cm^{-1} is assigned to a metal-chlorine stretching frequency while in $NiBr_2 \cdot 2NMe_3$ and $NiI_2 \cdot 2NMe_3$, ν(Ni-Hal) occurs at 270 cm^{-1} and 245 cm^{-1} respectively. The latter two frequencies contain shoulders but the Ni-Cl frequency is unsplit (Table 3.3a). In the β-isomer ν(Ni-Cl) is replaced by broad ill-defined absorption in the 300 - 200 cm^{-1} region.

TABLE 3.3b

Infrared Spectra of the complexes $NiX_2 \cdot 2NMe_3$, X = Cl,Br,I (1300 - 200 cm^{-1})

X = Cl(α):	1300, 1250, 1105, 1055vw, 1040vw, 1000, 980, 825, 722, 675w, 628w, 510, 465vw, 428vw, 310
X = Cl(β):	1245, 1102, 1060vw, 990, 725, 520.
X = Br:	1246, 1230sh, 1108, 1060vw, 995, 820, 725, 675vw, 510, 430, 290sh, 270
X = I:	1240, 1102, 1055vw, 990, 820, 725w, 510, 430, 255sh, 245.

w,weak; vw, very weak; sh, shoulder

This broad absorption has been inferred to indicate the absence of terminal halogen. Similar behaviour has been observed with the two isomers of $Copy_2Cl_2$.[94] The

tetrahedral form has two ν(M-Cl) frequencies at 347 cm^{-1} and 306 cm^{-1} while the octahedral halogen-bridged form shows only broad absorption in this region.

As stated above only one stretching frequency is observed for α-$NiCl_2 \cdot 2NMe_3$ at 310 cm^{-1} although two stretching frequencies are expected. However, this band is strong and broad which suggests that the two ν(Ni-Cl) absorptions coincide. A similar observation has been made for the two ν(M-NCS) absorptions for the complex $Zn(NCS)_2 \cdot 2\alpha$-picoline.[110]

The magnetic moments of spin-free nickel(11) complexes usually lie in the range 2.80 - 4.00 BM. Those for tetrahedral species are usually higher (3.3 - 4.0 BM) than those of octahedral species (2.9 - 3.3 BM), the orbital angular momentum being higher in tetrahedral complexes. The expected μ_{eff} in octahedral complexes is increased above the spin-only value of 2.83 by a factor $(1 + 4\lambda^1)/\Delta E$ owing to spin-orbit coupling.[80] Here λ^1 is the effective spin-orbit coupling constant and ΔE is the d - d separation. The value of λ^1 is very much dependent upon the nature of the attached ligands.

Magnetic Moments for the trimethylamine complexes of nickel(11) are listed in Table 3.4. The large value of 3.38 BM for α-$NiCl_2 \cdot 2NMe_3$ suggests a large orbital contribution and is consistent with the tetrahedral structure postulated for the complex. On the other hand the high value of 3.37 BM obtained for β-$NiCl_2 \cdot 2NMe_3$ is initially surprising in view of the postulated octahedral structure where complete quenching of orbital angular momentum is expected and thus giving a

value much less than 3.37 BM.

TABLE 3.4

Magnetic Moments of Nickel(11) Trimethylamine Complexes

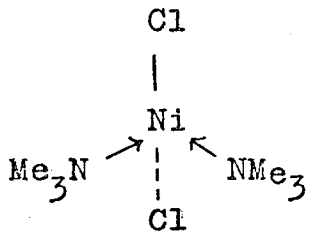
Complex	χ^{1}_{M} * (10^{-6})	μ_{eff}, (BM at 18° - 20°)
α-$NiCl_2 \cdot 2NMe_3$	4837	3.38
β-$NiCl_2 \cdot 2NMe_3$	4820	3.37
$NiBr_2 \cdot 2NMe_3$	4577	3.29
$NiI_2 \cdot 2NMe_3$	4862	3.39

* Corrected molar susceptibility in c.g.s. units.

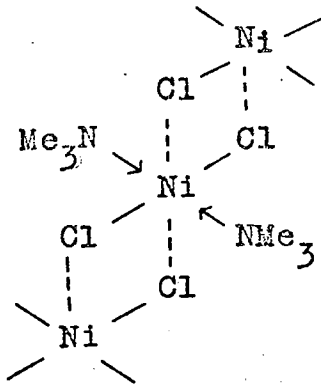
Gill and Nyholm[95] have calculated magnetic moment values expected for the nickel ion in a variety of different circumstances (e.g. zero or infinite spin-orbit coupling, very weak or very strong crystal fields etc.). Although the moment can rise as high as 5.59 BM in the absence of an electrical field, they conclude that in an octahedral environment the magnetic moment should be 3.1 - 3.2 BM. Thus the moment of 3.37 BM obtained for β-$NiCl_2 \cdot 2NMe_3$ is not only outside the range generally associated with octahedral nickel derivatives, but is in fact higher than the theoretical maximum obtainable from simple theory.

However, Lever[96] has pointed out that six-coordinate

halogen-bridged nickel complexes of the type $(NiL_2X_2)_n$ (X = halogen, L = amine) commonly have moments between 3.3 and 3.5 BM, e.g. $Nipy_2Cl_2$ (3.37 BM), $Ni(NH_3)_2Cl_2$ (3.35BM) and Ni(aniline $)_2Cl_2$ (3.36 BM). The value of 3.37 BM obtained for β-$NiCl_2.2NMe_3$ is therefore strongly suggestive of a polymeric halogen-bridged octahedral structure.



α-Isomer



β-Isomer

On the basis of the above evidence the author believes that the chloro-complexes represent an unusual example of octahedral-tetrahedral isomerism for nickel(11). Although a similar type of isomerism has been reported for $NiCl_2L_2$ (L = Quinoline)[97] one would not expect the steric requirements of trimethylamine to be comparable with those of quinoline. Furthermore the nitrogen of trimethylamine is not capable of forming part of a π-electron system, a property which is

considered important in the formation of the structural isomers with quinoline.[97]

The α-form of $NiCl_2 \cdot 2NMe_3$, $NiBr_2 \cdot 2NMe_3$ and $NiI_2 \cdot 2NMe_3$ are only slightly soluble in polar solvents like nitromethane and acetone (giving a blue colour with immediate decomposition) and are completely insoluble in non-polar solvents. The β-form of $NiCl_2 \cdot 2NMe_3$ is immediately decomposed in similar polar solvents and gives a transient blue colour, followed by decomposition, which probably represents a breakdown of octahedral polymer to the tetrahedral form.

In the solid state the β-isomer can be completely converted to the α-isomer by passing trimethylamine gas through a powdered sample at room temperature (see sect.2.3.1). This structural lability implies that the free energy difference between the two isomeric forms is very small, suggesting weak M-Cl-M bridges and high steric compression in the square planar $(NiCl_2 \cdot 2NMe_3)_n$ units of the octahedral species. All efforts to prepare analogous isomers with trimethylamine and nickel(11) bromide failed; presumably the steric repulsion between bromo ligands and trimethylamine ligands is too large to allow the formation of similar square planar units of the type $(NiBr_2 \cdot 2NMe_3)_n$ in an octahedral species.

3.1.2 Monomeric Complexes ML_4X_2, L = iso-butylamine; X = Cl, Br, CNS.

Diffuse reflectance spectra of the complexes $Ni(i\text{-}BuNH_2)_4Cl_2$, $Ni(i\text{-}BuNH_2)_4Br_2$ and $Ni(i\text{-}BuNH_2)_4(CNS)_2$, Fig.3.5, clearly indicate an octahedral environment for the nickel atom. Band assignments are given in Table 3.5.

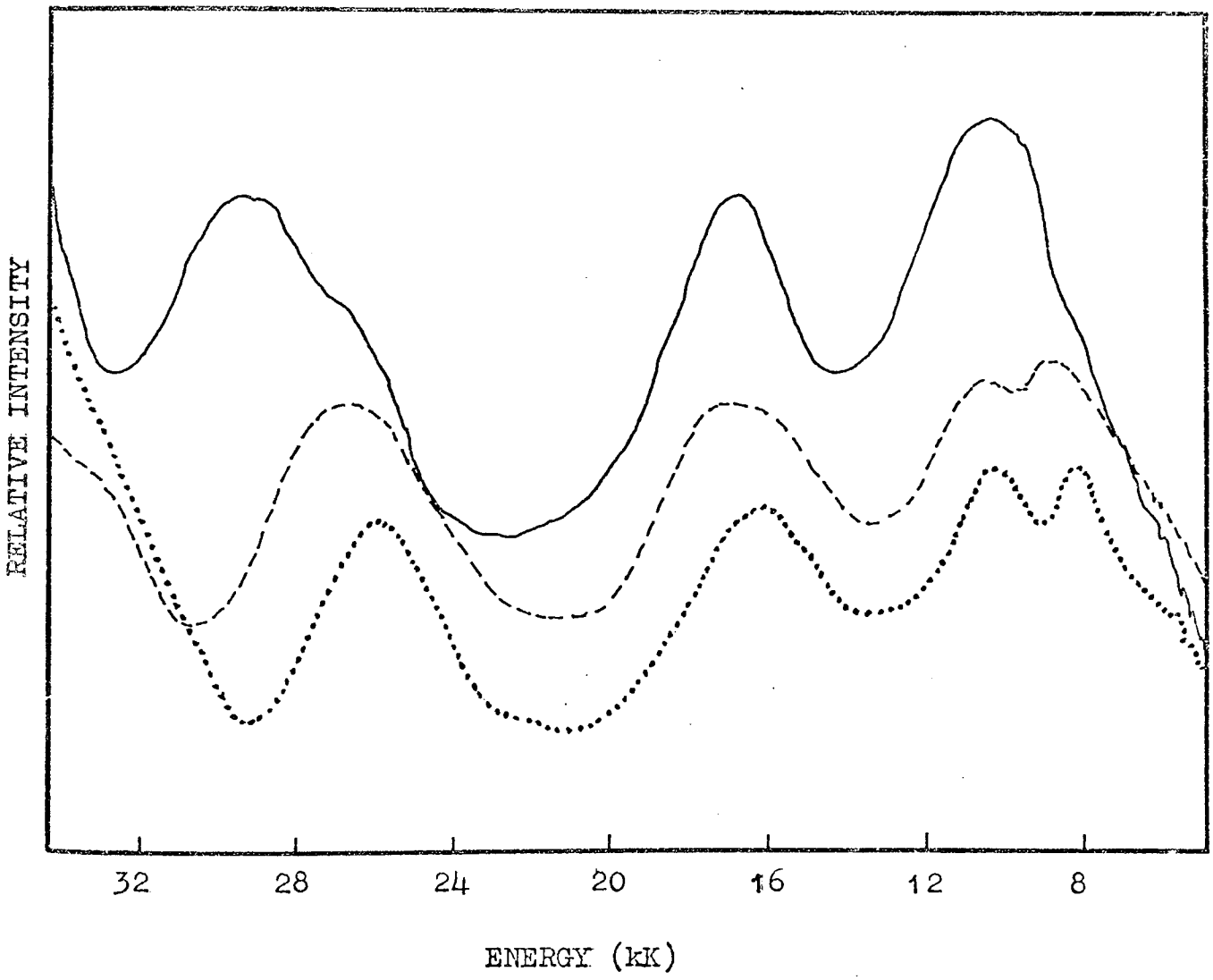


Fig.3.5 Reflectance Spectra of $Ni(i\text{-}BuNH_2)_4X_2$, (X = CNS ——), (X = Br - - - - -), (X = Cl .....).

It is interesting to note that the first spin-allowed transition, i.e. $^3T_2 \leftarrow {}^3A_2$, is unsplit in the thiocyanate complex, slightly split in the bromo complex and significantly split in the chloro complex. Similar behaviour has been observed with the three mononuclear complexes $Nipy_4Cl_2$, $Nipy_4Br_2$ and $Nipy_4(CNS)_2$.[71] Bostrup and Jørgensen[63] have shown from x-ray analysis that these complexes are six-coordinated structures in which the anionic ligands are in trans positions.

TABLE 3.5

Reflectance Spectra of the complexes of nickel(11) with iso-butylamine having octahedral stereochemistry.

(Abs. Max. kK)

Complex	$^3T_1(P) \leftarrow {}^3A_2$ ν_3	$^3T_1 \leftarrow {}^3A_2$ ν_2	$^3T_2 \leftarrow {}^3A_2$ ν_1
$Ni(i\text{-}BuNH_2)_4(CNS)_2$	29.3, 26.5 sh	17.0	10.43
$Ni(i\text{-}BuNH_2)_4Br_2$	26.9	16.7	8.7 10.6
$Ni(i\text{-}BuNH_2)_4Cl_2$	25.8	15.9	8.0 10.8

sh, shoulder

They have assigned the 10.9 and 8.5 kK bands in $Nipy_4Cl_2$ as components of the ν_1 transition which is split due to tetragonal distortion. A similar explanation is offered for the splitting of the ν_1 transition in the bromo complex.

The magnitude of the splitting is taken as an indication of the extent of tetragonal distortion.

The corresponding transition in $Nipy_4(CNS)_2$ is unsplit which indicates the absence of severe tetragonal distortion in this complex. This is attributed to a more symmetrical ligand field since nitrogen coordinated NCS and pyridine occupy fairly close positions in the spectrochemical series.

Thus there seems little doubt that the splitting of the $^3T_2 \leftarrow {}^3A_2$ transition in $Ni(i\text{-}BuNH_2)_4Cl_2$ and $Ni(i\text{-}BuNH_2)_4Br_2$ is due to severe tetragonal distortion and that the complexes are trans-octahedral (see also sect.1.6.6.). Similar to $Nipy_4(CNS)_2$ this tetragonal distortion is absent in $Ni(i\text{-}BuNH_2)_4(CNS)_2$ indicating similar symmetrical ligand fields in both complexes. These rather surprising results suggest that the bonding and stereochemical requirements of pyridine and iso-butylamine are very similar when coordinated to NiX_2 (X = Cl,Br,CNS), even though back-donation of electron density from nickel to the ligand is not possible with iso-butylamine.

Nelson and Shepherd[71] believe that this back-donation of electron density is an important factor stabilizing the mononuclear pyridine complexes. Accordingly they postulate that the apparent inability of complexes $Ni(NH_3)_4(Hal)_2$ to form[98] is due to the inability of NH_3 to form a π-bond thus causing an excessive accumulation of negative charge on the metal ion. Instead ionic complexes $[Ni(NH_3)_6](Hal)_2$ are formed in which the halide ions are not coordinated.[63,98]

However the complexes $Ni(i\text{-}BuNH_2)_4Cl_2$ and $Ni(i\text{-}BuNH_2)_4Br_2$ are quite stable at room temperature and pressure, and in these

complexes no back-donation of electron density from metal to amine is possible. Thus it appears that the π-bonding ability of pyridine in complexes $Nipy_4(Hal)_2$ plays a very passive role in their overall stability.

Mean values of 10.4 - 10.5 kK and 10.2 kK have been reported [71,63] for $10D_q$ ($= \nu_1$) for the complex $Nipy_4(CNS)_2$. The mean value of $10D_q$ (calculated from ν_1) for the complex $Ni(i\text{-}BuNH_2)_4(CNS)_2$ is 10.43 kK while the value of 10.47 kK is obtained using transitions ν_2 and ν_3 (see appendix and sect.1.6.3). This indicates that pyridine and iso-butylamine occupy similar positions in the spectrochemical series. Because of the splitting of ν_1 in $Ni(i\text{-}BuNH_2)_4Cl_2$ and $Ni(i\text{-}BuNH_2)_4Br_2$ mean values of $10D_q$ cannot be estimated using this transition. However, values of 10.05 kK and 10.57 are obtained for these complexes using transitions ν_2 and ν_3. These values are summarized in Table 3.6

TABLE 3.6

The Mean crystal Field Strength ($10D_q$) and Racah Parameter (B) for complexes of nickel(11) with iso-butylamine (kK).

Complex	$10D_q(\nu_1)$	$10D_q(\nu_2\nu_3)$	B
$Ni(i\text{-}BuNH_2)_4(CNS)_2$	10.43	10.47	10.17
$Ni(i\text{-}BuNH_2)_4Br_2$	-	10.57	0.801
$Ni(i\text{-}BuNH_2)_4Cl_2$	-	10.05	0.791

From Table 3.6 it is evident that there is little variation in the apparent crystal field splitting energies of the thiocyanate and bromo complexes which is in good agreement with the rule of average ligand field approximation (sect.1.6.5). The distortion of the chloro-complex may be the cause of its rather low $10D_q$ value.

The spectra of the complexes in dimethylformamide are shown in Fig. 3.6 and all three peaks of each complex are

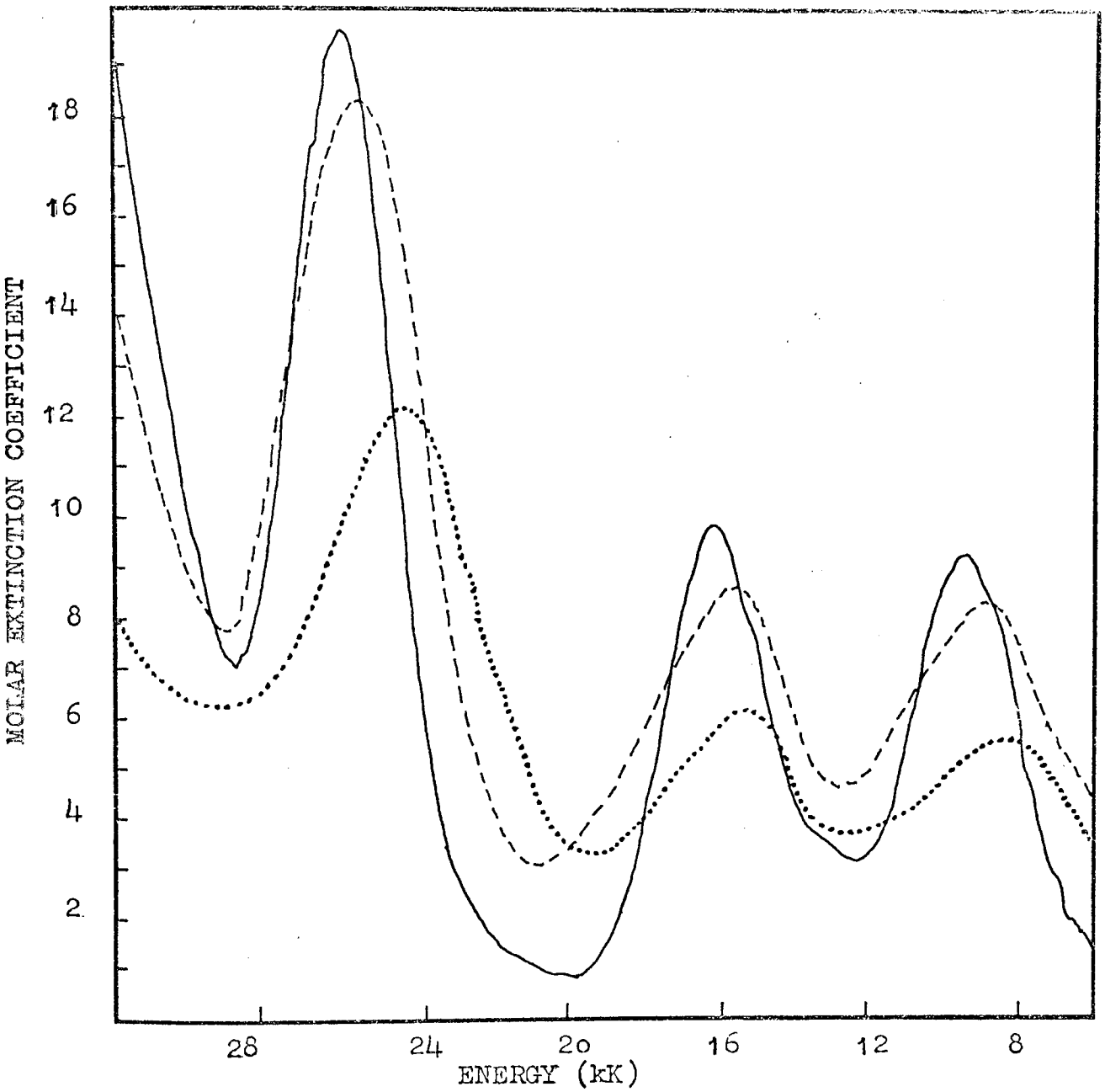


Fig. 3.6 Solution Spectra of the complexes $Ni(i\text{-}BuNH_2)_4X_2$ in dimethylformamide, (X = CNS ——), (X = Br - - -), (X = Cl .....)

slightly shifted to lower energy from those in the solid state (see Tables 3.5 and 3.7). However a more pronounced and important difference is the absence of any splitting in the $^3T_2 \leftarrow {}^3A_2$ transition of $Ni(i\text{-}BuNH_2)_4Cl_2$ and $Ni(i\text{-}BuNH_2)_4Br_2$. This may indicate that the complexes do not suffer severe tetragonal distortion in solution. On the other hand the complex $Ni(i\text{-}BuNH_2)_4(CNS)_2$ has the same undistorted structure in solution and in the solid state since ν_1 is not split in either case.

These observations seem to indicate that the tetragonal distortion of the chloro and bromo complexes in the solid state is a result of lattice requirements in the crystal structure. In solution these requirements are removed and hence the distortion of the complexes is greatly reduced. Apparently the thiocyanate group is capable of fulfilling these lattice requirements in the solid state and hence does not suffer distortion.

Although no similar observations have been recorded for the complexes $Nipy_4X_2$ (X = Cl,Br,CNS) it is reasonable to assume that the tetragonal distortions of $Nipy_4Cl_2$ and $Nipy_4Br_2$ are due to lattice requirements of the crystal structures. Furthermore it is also reasonable to assume that the absence of tetragonal distortion in $Nipy_4(CNS)_2$ is not a consequence of the close positions of CNS (N-bonded) and pyridine in the spectrochemical series[63] but is due to the fact that CNS fulfills the lattice requirements of the complex in the solid state.

TABLE 3.7

Electronic Spectra of $Ni(i\text{-}BuNH_2)_4X_2$ in dimethylformamide

X	Absorption Maxima kK , (ϵ molar)		
Chloride	24.4 (12.3),	15.3 (6.1),	8.2 (5.5)
Bromide	25.5 (18.3),	15.3 (8.8),	8.9 (8.3)
Thiocyanate	26.2 (19.6),	16.8 (10.0),	9.2 (9.2)

Bands listed in the first, second and third columns are assigned to the $^3T_1(P) \leftarrow {}^3A_2$, $^3T_1 \leftarrow {}^3A_2$ $^3T_2 \leftarrow {}^3A_2$ transitions respectively.

The infrared spectrum of $Ni(i\text{-}BuNH_2)_4(CNS)_2$, Fig. 3.7, Table 3.8 provides significant information concerning the bonding of the thiocyanate group in the complex. It is now well known that the thiocyanate group may coordinate to a metal ion through the nitrogen (M-NCS), through the sulphur (M-SCN), or through both (M-NCS-M^1). In general M-N bonds are formed with metals from the first transition series while M-S bonds are formed with metals from the latter half of the second and third transition series.[99]

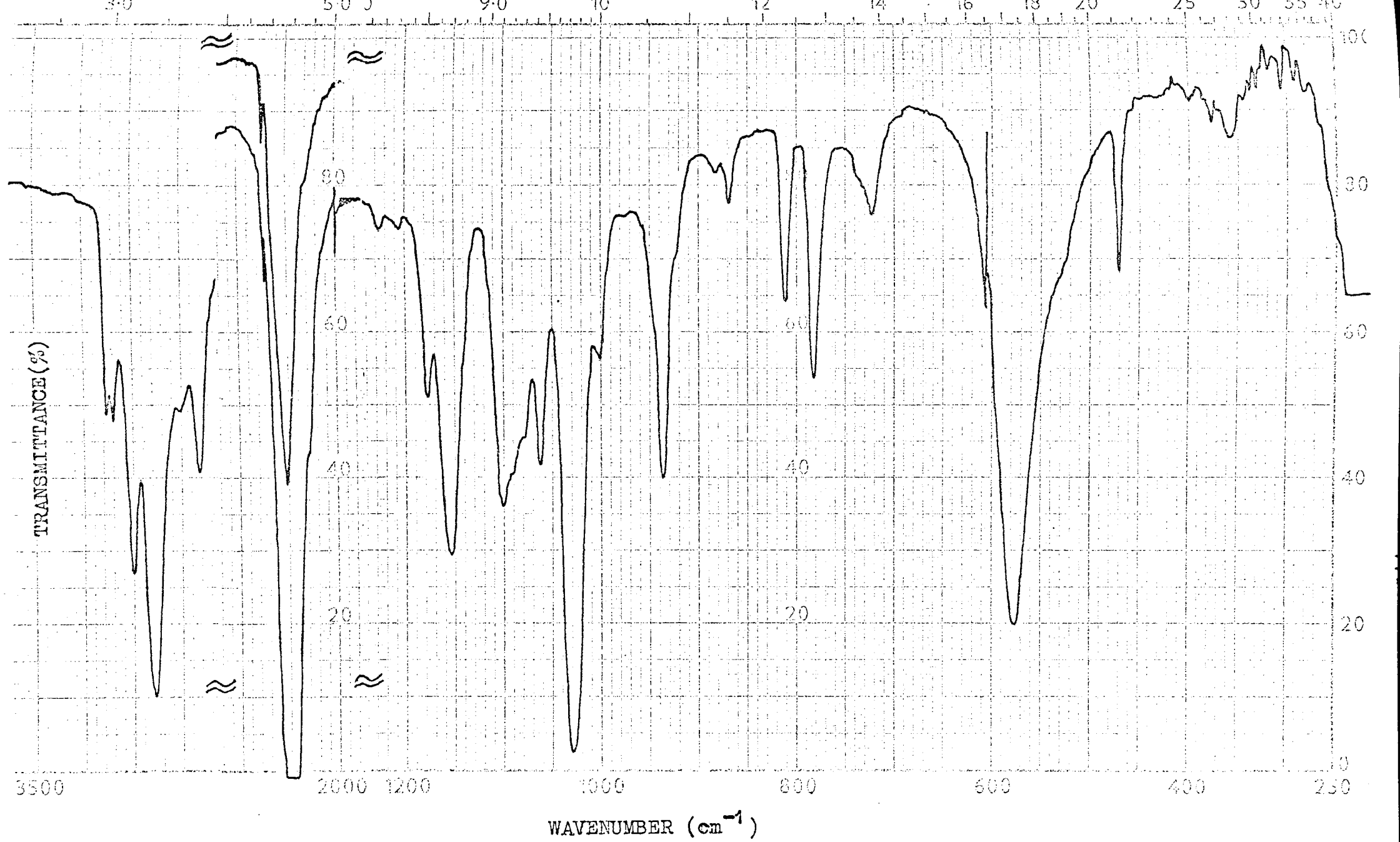


Fig.3.7 Infrared spectrum of $Ni(i\text{-}BuNH_2)_4(CNS)_2$

TABLE 3.8

Infrared Spectra of Complexes $Ni(i\text{-}BuNH_2)_4X_2$, X = Cl, Br, CNS (cm^{-1})

X = Cl:	3328 w, 3240 b, 3170 sh, 2950, 2862, 1670 w, 1588, 1466, 1388, 1368, 1309, 1200, 1180 sh, 1155, 1100, 1030, 939, 885 w, 870, 820, 810 sh, 725, 585 b, 520 sh, 435 vw, 380 vw, 360 w, 330 vw.
X = Br:	3219 b, 3180 sh, 2950, 2862, 1650, 1582, 1470, 1388, 1366, 1311, 1195, 1182 sh, 1162, 1100, 1030, 939, 886 w, 872 w, 820, 810 sh, 720, 580 b, 520 w, 475 w, 380 w, 360 w, 330 w.
X = CNS:	3388 vw, 3320 vw, 3300, 3260, 3161, 2958, 2930 sh, 2870 sh, 2100, 1588, 1470, 1388, 1368 1305, 1178 w, 1150, 1100, 1060, 1030, 1000 sh, 936, 870 w, 810, 780, 720 w, 578 b, 470, 360 w.

w, weak; vw, very weak; b, broad; sh, shoulder

The CN and CS stretching frequencies in the free thiocyante ion occur at 2053 cm^{-1} and 748 cm^{-1} respectively while NCS bending vibrations occur at 486 cm^{-1} and 471 cm^{-1}.[100] In M-NCS complexes the CN stretching frequencies are generally

lower than those in M-SCN complexes.[101] However the CS stretching frequency (780 - 860 cm^{-1} for M-NSC and 690 - 720 cm^{-1} for M-SCN [100,102,103]) and the NCS bending frequency (450 - 490 cm^{-1} for M-NCS and 400 - 440 cm^{-1} for M-SCN[100,103]) are generally more useful for distinguishing between the two types of linkage.

By comparing the spectrum of $Ni(i\text{-}BuNH_2)_4(CNS)_2$ with that of $Ni(i\text{-}BuNH_2)_4Cl_2$ or $Ni(i\text{-}BuNH_2)_4Br_2$ the bands at 2100 cm^{-1}, 780 cm^{-1}, and 470 cm^{-1} are readily identified as $\nu(C{\equiv}N)$, $\nu(C\text{-}S)$ and $\delta(NCS)$ respectively. From the above discussion there can be little doubt that the position of these frequencies clearly indicate that the CNS group is N-bonded in the complex $Ni(i\text{-}BuNH_2)_4(CNS)_2$.

The magnetic moments of the complexes fall within the range 3.0 - 3.2 BM, Table 3.9. These values are within the range expected for mononuclear octahedral complexes[80] and suggest that the orbital angular momentum is quenched to a large extent. The increase in the values above the spin-only value of 2.83 BM for nickel(11) must be attributed to a large degree of spin-orbit coupling.

TABLE 3.9

Magnetic Moments of the Complexes NiL_4X_2, X = Cl, Br, CNS; L = pyridine, iso-butylamine.

	L = pyridine		L = iso-butylamine		
X	μ_{eff} (BM)*	Temp°C	$\chi^1_M(10^{-6})$**	μ_{eff}(BM)	Temp°C
Cl	3.11	15.8	4008	3.08	18.5
Br	3.22	17.2	4262	3.17	19.0
CNS	3.13	15.0	4095	3.11	18.5

* Values taken from refs. 71, 104

** Corrected molar susceptibility in c.g.s. units.

For comparison, magnetic moments of the corresponding complexes with pyridine are also included in Table 3.9. Similar to other comparisons made for these two sets of complexes, the magnetic moments have closely related values and show the same increasing trend from Cl → CNS → Br. Thus on the basis of magnetic data for the complexes $Ni(i\text{-}BuNH_2)_4X_2$, X = Cl, Br, CNS, and on the close similarity of their electronic spectra to those of $Nipy_4X_2$, X= Cl, Br, CNS, there can be little doubt that the complexes described here have mononuclear trans-octahedral structures.

The only other complex of nickel(11) prepared during the present work was the mono-triethylamine complex $NiBr_2 \cdot NEt_3$, which was very unstable at ambient temperature and pressure. Furthermore handling in a dry inert atmosphere was necessary at all times due to the hygroscopic nature of the complex. No bis-complex similar to $NiBr_2 \cdot 2NMe_3$ was isolated. This is reasonable in view of the high steric requirements of triethylamine compared with those of the relatively unhindered trimethylamine molecule (see sect.1.4.3). All attempts to prepare the corresponding chloro-complex of $NiBr_2 \cdot NEt_3$ failed (see sect.2.3.1).

It is therefore surprising to note that Kartopolova et al.[22] report the preparation of complexes $NiCl_2 \cdot 2NEt_3 \cdot \frac{1}{2}H_2O$, $NiBr_2 \cdot 2NEt_3 \cdot 2H_2O$ and $NiI_2 \cdot 2NEt_3 \cdot 2H_2O$. Even more surprising is their method of preparation i.e. the addition of triethylamine to a saturated aqueous alcoholic (96% C_2H_5OH) solution of the nickel salt. Complex formation took place vigorously with the liberation of much heat.

Though the complexes of $Ni(Hal)_2$ with trimethylamine prepared during the course of the present work were stable at room temperature and pressure, they were extremely hygroscopic. Contact with moisture resulted in immediate displacement of amine with the formation of a hydrate $Ni(Hal)_2 \cdot nH_2O$. This seemed to indicate that in the complexes $Ni(Hal)_2 \cdot 2NMe_3$ the trimethylamine molecules were suffering a high degree of steric compression. Consequently no complexes of the type $Ni(Hal)_2 \cdot 2NMe_3 \cdot nH_2O$ were obtained and preparations had to be carried out in absolutely dry benzene. Attempted preparations in 96% ethanol were completely unsuccessful as expected. In view of these results it is difficult to see

how complexes of the type $Ni(Hal)_2 \cdot 2NEt_3 \cdot nH_2O$, having the very highly sterically hindered triethylamine molecule could be prepared in aqueous alcoholic solution.

Kartopolova et al.[22] have also indicated that in the thermal decomposition of the complexes $Ni(Hal)_2 \cdot 2NEt_3 \cdot nH_2O$ the water molecules are first to be eliminated at 40° - 50°, then the first amine molecules at 101° - 144° and finally the second amine molecules at 217° - 256°. These results are difficult to reconcile with the behaviour of trimethylamine complexes prepared during this work.

3.2. Complexes of Cobalt(II)

3.2.1. Monomeric Complexes $CoX_2 \cdot 2NMe_3$ X = Cl, Br, I, CNS.

All the complexes have a deep blue colour and the electronic spectra indicate a tetrahedral environment for the cobalt atom. Diffuse reflectance spectra for the complexes $CoCl_2 \cdot 2NMe_3$ and $Co(CNS)_2 \cdot 2NMe_3$ are shown in Fig.3.8. Band assignments are given in Table 3.10.

The band on the low energy side is assigned to the $^4T_1 \leftarrow {}^4A_2$ transition while the band in the visible region is attributed to the $^4T_1(P) \leftarrow {}^4A_2$ transition. The near infrared absorption is clearly split into three well defined components, Fig. 3.8, Table 3.10, for the complexes $Co(Hal)_2 \cdot 2NMe_3$ but is unsplit for the thiocyanate complex..

In this respect the spectra closely resemble those of the complexes CoL_2X_2 (which belong formally to the point group C_{2v} but have spectra which are, in general, typical of regular tetrahedral (T_d) cobalt complexes) where L is pyridine or

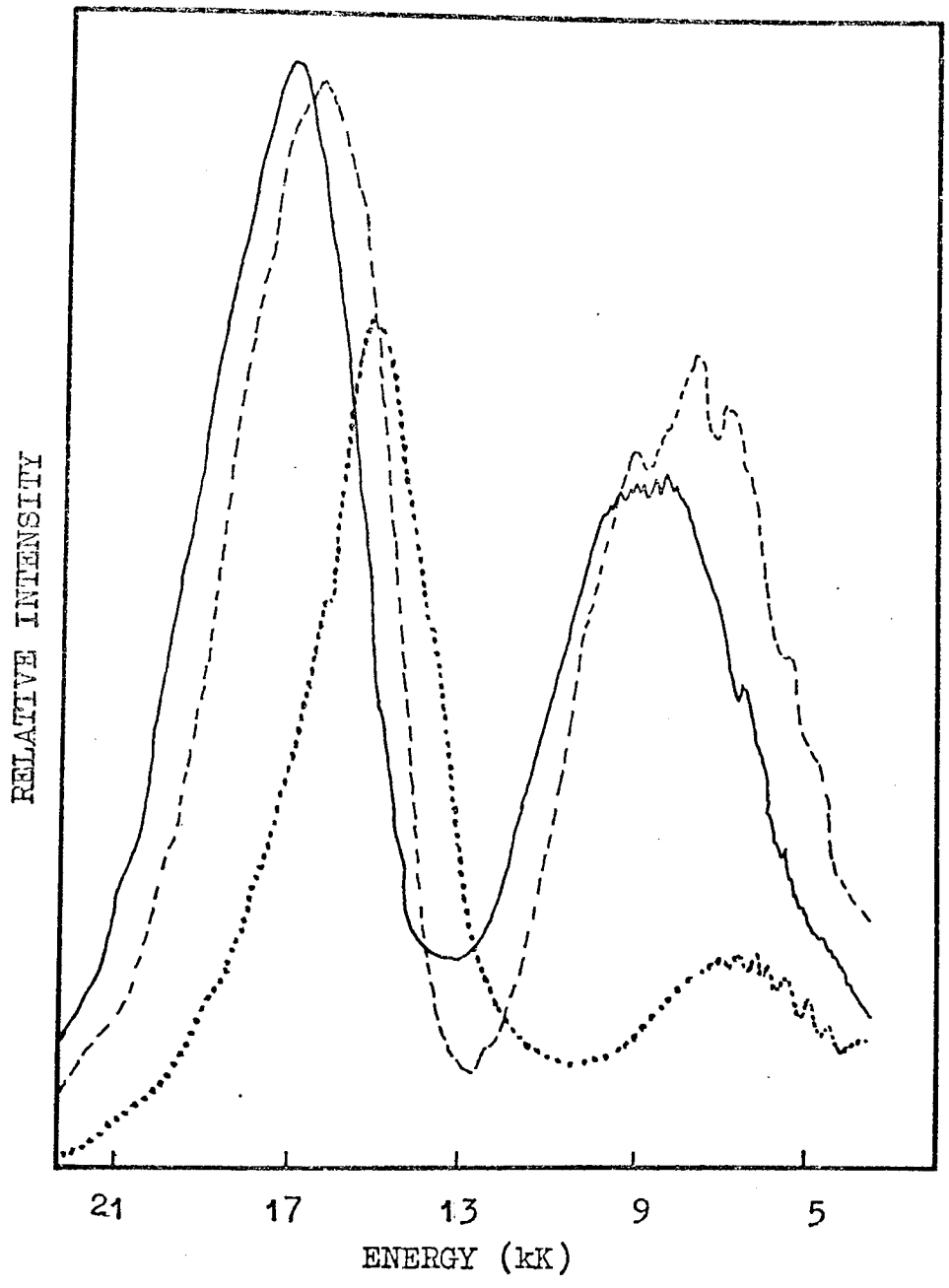


Fig. 3.8 Reflectance spectra of $Co(CNS)_2 \cdot 2NMe_3$ (———), $CoCl_2 \cdot 2NMe_3$ (-----), solution spectrum of $CoCl_2 \cdot 2NMe_3$ (·····) in benzene.

a similar aromatic amine and X is a halogen or pseudo-halogen.[105,106] Lever and Nelson have shown[105] that the ν_2 transi tion $^4T_1 \leftarrow {}^4A_2$ occurs as fairly strong multiple absorption in the 5 - 10 kK region. The overall bandwidths

TABLE 3.10

Electronic spectra of the complexes $CoX_2 \cdot 2NMe_3$, X = Cl, Br, I, CNS. Abs. Max, kK.

	SOLID		BENZENE	
	$^4T_1(P) \leftarrow {}^4A_2$	$^4T_1 \leftarrow {}^4A_2$	$^4T_1(P) \leftarrow {}^4A_2$	$^4T_1 \leftarrow {}^4A_2$
X	ν_3	Components of ν_2	ν_3	ν_2
Cl	16.2	8.8, 7.3, 6.8	15.1	7.2
Br	16.0	8.6, 7.5, 6.8	15.2	7.2
I	15.2	7.9, 6.8, 5.8	14.9	6.8
CNS	16.8	8.8	16.2	9.0

vary from 2.5 kK to 3.5 kK and are composed of three principal absorptions. The two low energy components are almost independent of the amine ligand for a given halogen, but the high energy component shifts by as much as 1 kK to lower energy when an unhindered amine is replaced by a sterically hindered amine. They concluded that the splitting of the ν_2 band is probably due to a lowering of C_{2v} symmetry in these complexes.

Ferguson[106] has discussed the spectra of some solid compounds containing the $CoCl_4^{2-}$ ion and concluded that band width and splitting of the ν_2 transition can best be explained in terms of lower symmetry.

It seems likely therefore that splitting of the ν_2 band

in the complexes $Co(Hal)_2 \cdot 2NMe_3$ indicates a departure from true tetrahedral stereochemistry. On the basis of this argument the absence of splitting in the ν_2 absorption of $Co(CNS)_2 \cdot 2NMe_3$ must be taken to indicate that the complex is free from severe distortion and resembles true tetrahedral stereochemistry more closely than its halo analogues.

Distortion from regular tetrahedral stereochemistry would be expected to be most noticeable in the ν_1 transition $^4T_2 \leftarrow {}^4A_2$ (as was the case with distortion from octahedral symmetry for the complexes $Ni(i\text{-}BuNH_2)_4X_2$, X = Cl, Br, CNS, sect.3.1.2). However this transition is rarely observed as it occurs in a very inaccessable low energy region of the spectrum namely the 3 - 5 kK region. It appears as a very weak feature in the spectra of cobalt ions in tetrahedral lattice sites.[107]

Fairly strong bands observed near 4.6 kK in the diffuse reflectance spectra of complexes CoL_2X_2, L = aromatic amine, X = halogen, pseudo-halogen have been assigned[108,109] as components of the ν_1 band. However such bands are not observed for the same compounds in mull or in solution.[105] The ν_1 transition was not observed in the spectrum of any of the complexes $CoX_2 \cdot 2L$.

The close similarity of the solid and solution spectra, Fig.3.8, Table 3.10, implies that the tetrahedral stereochemistry is retained in solution. However the multiple nature of the ν_2 transition of the halo-complexes disappears in solution and an absorption band similar to that for the thiocyanate complex is obtained. Thus it may be concluded that the halo-complexes in solution do not suffer the same degree of distortion as they do in the solid state.

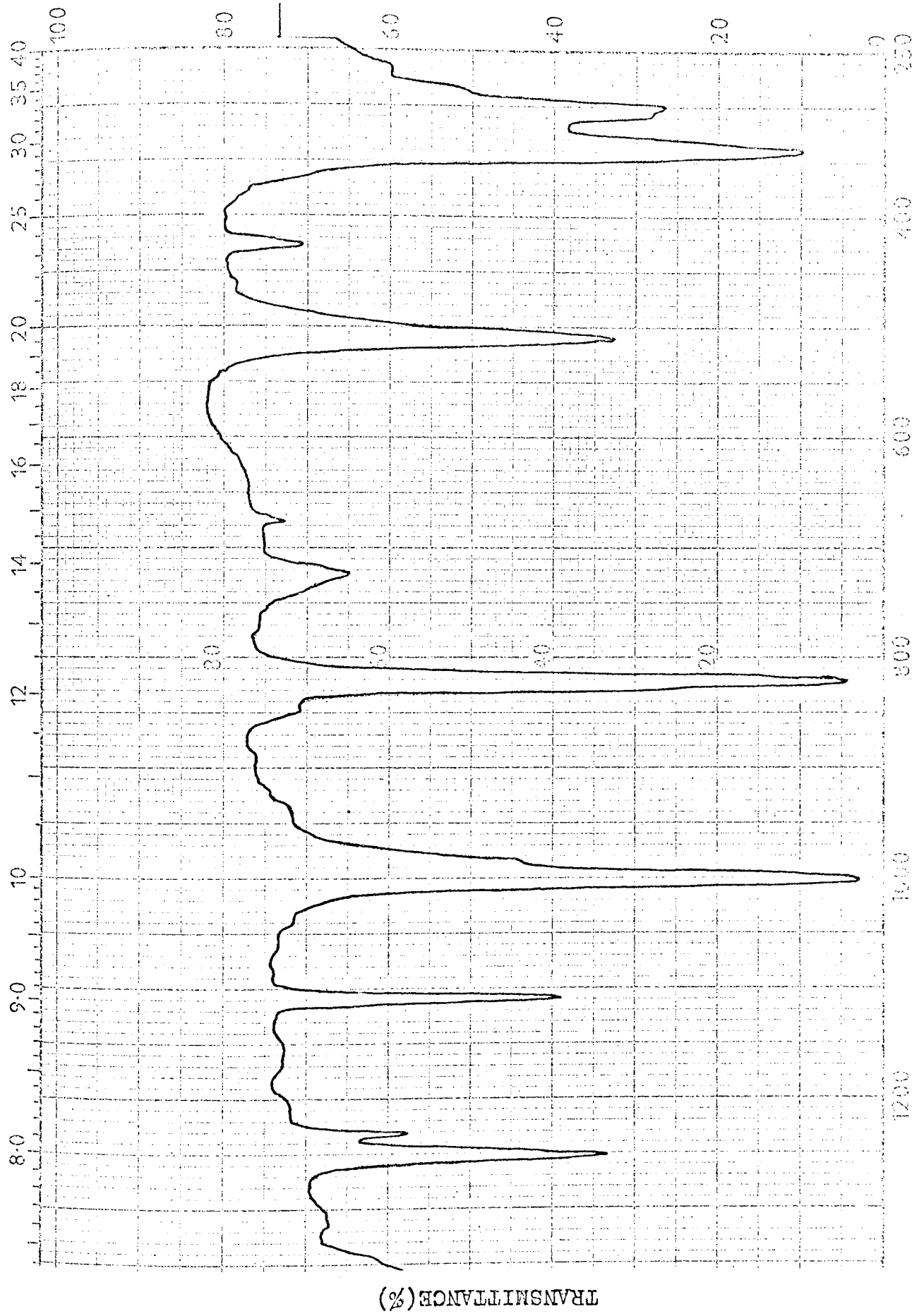


Fig.3.9 Infrared spectrum of $CoCl_2 \cdot 2NMe_3$

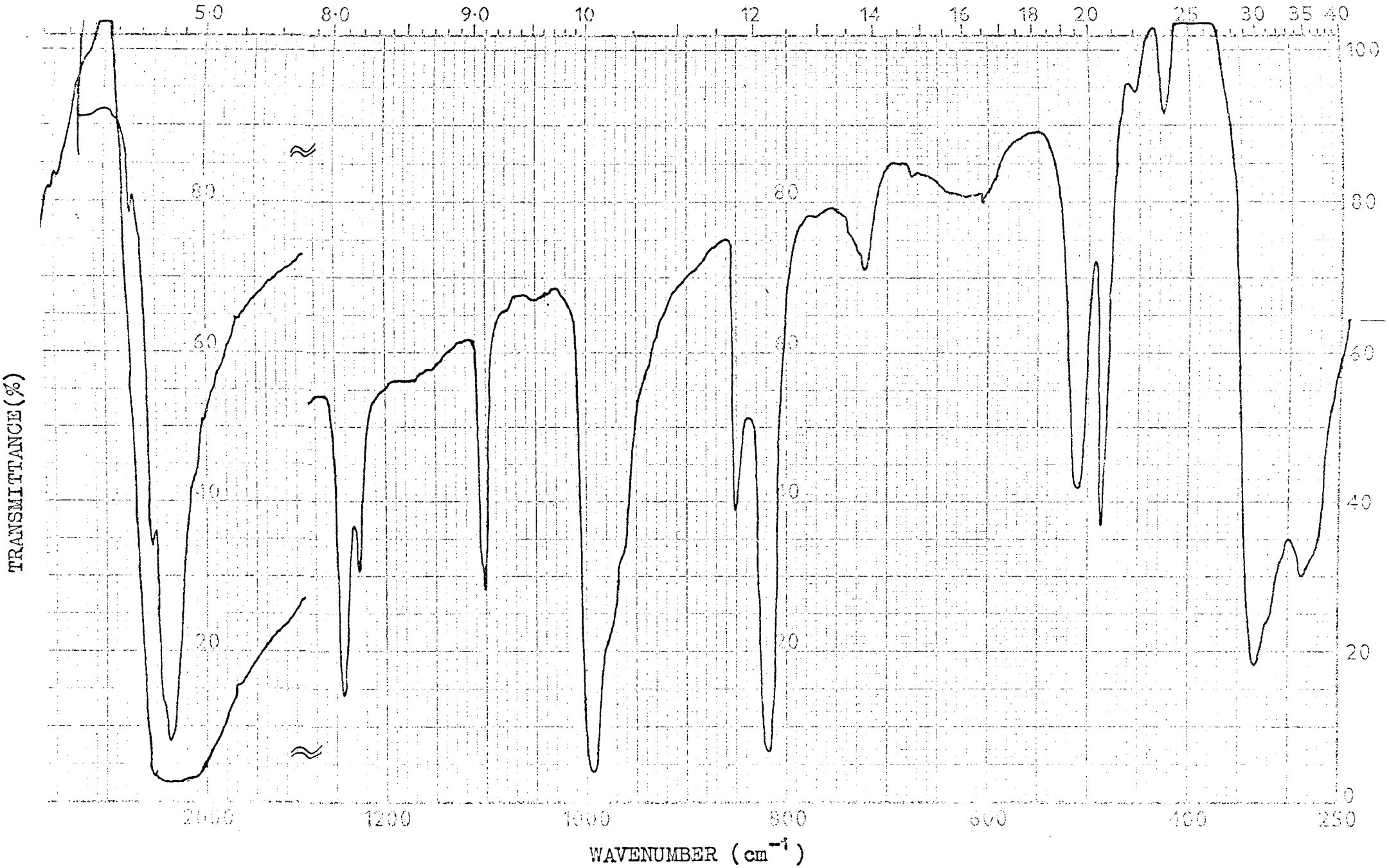


Fig.3.10. Infrared spectrum of $Co(CNS)_2 \cdot 2NMe_3$

Furthermore the similarity of the spectra in solution and in the solid state suggest that no new species, such as $[Co(NMe_3)_4][Co(Hal)_4]$, are formed in solution. This is supported by the fact that the complexes gives practically non-conducting solutions in nitromethane.

The infrared spectra of the complexes, Figs.3.9,3.10, Tables 3.11,3.12, provide further evidence for the proposed tetrahedral structures in addition to evidence for M-N linkage in the thiocyanate complex. In contrast to the complex α-$NiCl_2 \cdot 2NMe_3$ the two M-Cl stretching frequencies are clearly visible in $CoCl_2 \cdot 2NMe_3$. These occur at 338 cm^{-1} and 300 cm^{-1} and can be contrasted with the two Co-Cl stretching frequencies of tetrahedral $Copy_2Cl_2$ which occur at 347 cm^{-1} and 306 cm^{-1}.[94]

TABLE 3.11

Stretching Frequencies M-X for the complexes $CoX_2 \cdot 2NMe_3$, X = Cl, Br, I, CNS. (cm^{-1})

X	ν(M-X)		
Cl	338	300	309 sh
Br	273		
I	247		
CNS	334	288	

sh, shoulder

By comparing the spectrum of $CoCl_2 \cdot 2NMe_3$ with that of $Co(CNS)_2 \cdot 2NMe_3$ (Figs. 3.9,3.10) the thiocyanate stretching vibrations $\nu(C\equiv N)$ and $\nu(C-S)$ can readily be identified at 2078 cm^{-1} and 850 cm^{-1} respectively while the bending vibration $\delta(NCS)$ occurs at 487 cm^{-1}. From previous considerations (sect. 3.2.2.) the positions of these bands leave little doubt but that the CNS group is N-bonded to the metal. The M-NCS stretching vibrations are broad and intense absorptions at 334 cm^{-1} and 288 cm^{-1}. The expected range for these stretching vibrations in tetrahedral complexes CoL_2X_2 is 254 - 327 cm^{-1}.[110]

TABLE 3.12

Infrared Spectra for the complexes $CoX_2 \cdot 2NMe_3$, X = Cl, Br, I, CNS (1300 - 200 cm^{-1})

X = Cl:	1250, 1230 w, 1109, 1002, 975 sh, 722 w, 675 vw, 510, 428 w, 338, 309 sh, 300.
X = Br:	1248, 1230 w, 1108, 1058 vw, 1040 vw, 996, 816, 723, 675 vw, 503, 426, 273.
X = I:	1240, 1228 w, 1105, 1052 vw, 990, 815, 722 w, 515, 505 sh, 430 w, 247.
X = CNS:	1242, 1228 w, 1100, 993, 975 sh, 965 sh, 850, 818 722 w, 510, 487, 425 w, 334, 288.

w, weak; vw, very weak; sh, shoulder.

Magnetic moments for the complexes, Table 3.13, are within the range 4.50 - 4.61 BM and thus exhibit values considerably in excess of the spin-only value (3.89 BM) despite the fact that cobalt(11) has a ground state $^4A_2$ which has no inherent orbital angular momentum. However these values compare very well with magnetic moments obtained for other cobalt(11) complexes: CoI_4^{2-}, 4.77 BM; $CoBr_2^{2-}$, 4.69 BM; $CoCl_4^{2-}$, 4.59 BM; $Co(CNS)_4^{2-}$, 4.90 BM.[52]

TABLE 3.13

Magnetic Moments and Molar Conductivities of the complexes $CoX_2 \cdot 2NMe_3$, X = Cl, Br, I, CNS

X	χ^1_M* (10^{-6})	μ_{eff} (BM at 18° - 20°)	Λ_M**
Cl	8887	4.58	14
Br	8814	4.56	22
I	8992	4.61	26
CNS	8553	4.50	28

* Corrected molar susceptibility in c.g.s. units

** Λ_M = Molar Conductivity, $ohm^{-1} \cdot mol^{-1} \cdot cm^2$.

3.2.2. Monomeric Complexes ML_4X_2, L = iso-butylamine, sec-butylamine, iso-propylamine, cyclohexylamine; X = Cl, Br, I, CNS.

Electronic spectra of six-coordinate cobalt(11) complexes are much more difficult to interpret than those for six-coordinate nickel(11) complexes. The three spin-allowed transitions for NiL_4X_2 species are well separated and readily identified (see sect. 2.3.3). In CoL_4X_2 species the band at 8 - 10 kK can be assigned with certainty to the $^4T_2 \leftarrow {}^4T_1$ (ν_1) transition. In addition to this band a multiple band is always observed in the visible near 20 kK. This band is assigned to the $^4T_1(P) \leftarrow {}^4T_1$ (ν_3) transition and may appear mixed with some spin-forbidden transitions.. The $^4A_2 \leftarrow {}^4T_1$ (ν_2) transition is not normally observed[57] although Ferguson and co-workers have shown[75] that it occurs as a weak feature at 12 kK in the spectrum of $CoCl_2$ at room temperature and at -250°C.

Diffuse reflectance spectra for $Co(i\text{-}BuNH_2)_4Cl_2$ and $Co(i\text{-}BuNH_2)_4(CNS)_2$ are shown in Fig. 3.11. These are typical spectra for all the complexes CoL_4X_2. For purposes of comparison the spectrum of $Copy_4(CNS)_2$ is also shown in Fig3.11. The two principal peaks in the spectra are assigned to transitions $^4T_1(P) \leftarrow {}^4T_1$ (visible) and $^4T_2 \leftarrow {}^4T_1$ (near infrared). The spectrum of $Co(i\text{-}BuNH_2)_4(CNS)_2$ shows a remarkable similarity with that of $Copy_4(CNS)_2$. Both spectra have visible bands with maxima around 20.0 kK and both have a slight shoulder on the low energy side around 18.6 kK.

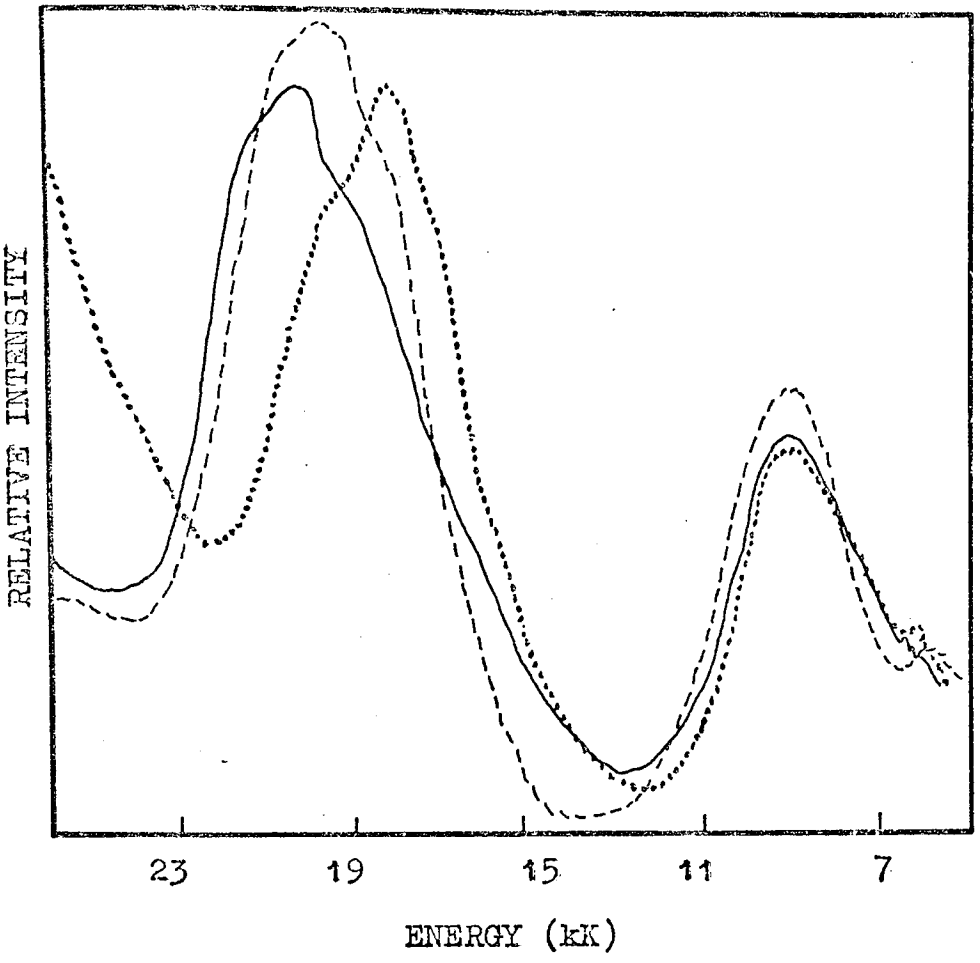


Fig. 3.11 Diffuse reflectance spectra for $Co(i\text{-}BuNH_2)_4(CNS)_2$ (———), $Copy_4(CNS)_2$(- - - -) and $Co(i\text{-}BuNH_2)_4Cl_2$(.....)

Lever has shown[57] that the transition energy ratio ν_2/ν_1 is almost invariant at 2.1 - 2.2 within the range of D_q/B values found for octahedral cobalt(11). The position of the ν_2 band can therefore be readily predicted from the position of ν_1. Since ν_1 for the complex $Co(i\text{-}BuNH_2)_4(CNS)_2$ occurs at 9.3 kK it is quite conceivable that the shoulder at 18 kK may therefore be a component of ν_2. Similar reasoning

holds for the shoulder in the spectrum of $Copy_4(CNS)_2$. However it is also conceivable that the asymmetry of the visible band may arise through low-symmetry components to the ligand field or from the presence of spin-forbidden transitions which have 'stolen intensity' from the very close spin-allowed transition.

From the close similarity of the spectra for complexes $CoL_4(CNS)_2$, L = iso-butylamine, pyridine, it is reasonable to assume that the spectra of $Copy_4X_2$ and $Co(i\text{-}BuNH_2)_4X_2$ would also show characteristics common to both. The complexes $Copy_4X_2$ were not prepared during the course of this work but Allan and co-workers[111] report the presence of three bands in the spectrum of $Copy_4Cl_2$ at 11.11 kK, 16.3 kK and 19.23 kK which have been assigned to transitions $^2E \leftarrow {}^4T_1$, $^4A_2 \leftarrow {}^4T_1$, $^4T_1(P) \leftarrow {}^4T_1$ respectively.

No band in the 11 kK region is observed in the spectrum of $Co(i\text{-}BuNH_2)_4Cl_2$, Fig. 3.11, and no two distinct bands are observed in the visible at 19 kK and 16 kK. Thus similar to the spectrum for $Co(i\text{-}BuNH_2)_4(CNS)_2$ the two principal bands in the spectrum of $Co(i\text{-}BuNH_2)_4Cl_2$ are assigned to transitions $^4T_1(P) \leftarrow {}^4T_1$ (visible) and $^4T_2 \leftarrow {}^4T_1$ (near infrared). The shoulder on the high energy side of the transition $^4T_1(P) \leftarrow {}^4T_1$ is probably due to a spin-forbidden transition which has 'stolen intensity'. A similar explanation has been given by Ferguson[75] for the shoulder on the high energy side of the corresponding transition in the spectrum of $CoCl_2$.

TABLE 3.14

Reflectance Spectra for the complexes CoL_4X_2,* L = Aliphatic Amine; X = Cl, Br, I, CNS; Abs.Max kK.

L	X	$^4T_1(P) \leftarrow {}^4T_1$ ν_3		$^4T_2 \leftarrow {}^4T_1$ ν_1
** Iso-butylamine	Cl	18.2,	19.3 sh	9.2
Iso-butylamine	Br	17.8,	18.9 sh	8.9
Iso-butylamine	I	17.8,	18.8 sh	8.6
Iso-butylamine	CNS	20.1,	18.8 sh	9.3
** Sec-butylamine	Br	17.3,	19.4 sh	8.4
Sec-butylamine	I	17.4,	18.5 sh	8.5
** Iso-propylamine	Cl	17.5,	19.2 sh	8.7
** Iso-propylamine	Br	17.5,	18.9 sh	9.0
Iso-propylamine	I	17.6,	18.9 sh	8.6
** Iso-propylamine	CNS	16.8,	18.8 sh	8.6
Cyclohexylamine	Br	17.6,	19.4 sh	8.8
Cyclohexylamine	I	17.5,	19.0 sh	8.4
Cyclohexylamine	CNS	18.9,	17.0 sh	8.5

* All the complexes are pink to red in colour

** These complexes were saturated with free ligand during spectral measurements.

On the basis of the above discussion the assignments given in Table 3.14 are those for ν_3 and ν_2 transitions only. Shoulders in the visible band are included but have not been assigned as components of the second spin-allowed transition. Some of the complexes, e.g. $Co(i\text{-}BuNH_2)_4Cl_2$ and $Co(s\text{-}BuNH_2)_4Br_2$, were very unstable at ambient room temperature and pressure and readily dissociated to give blue tetrahedral complexes of the type CoL_2X_2. In these cases spectral measurements were made on each complex saturated with free ligand as the octahedral species was relatively stable in excess amine.

The ligand field parameters $10D_q$ and B (Racah parameter), Table 3.15, have been calculated from the observed positions of ν_3 and ν_1 (see appendix). Slight variations of $10D_q$ in all the complexes CoL_4Br_2 and CoL_4I_2 suggest that there is no simple relationship between metal ion - ligand interaction and instability of a particular complex. The complex $Co(i\text{-}PrNH_2)_4Br_2$, which can only be stabilized at ambient room temperature and pressure by saturating the complex with free ligand , has a value 10.11 kK. On the other hand the complex $Co(i\text{-}BuNH_2)_4Br_2$, which is stable indefinitely at room temperature and pressure , has a value 9.95 kK. From the closeness of these two values, and indeed the closeness of all other values , it can be inferred that sterically hindered primary aliphatic amines and sterically unhindered primary aliphatic amines have similar crystal field perturbing abilities, or that the magnitude of $10D_q$ is independent of the steric nature of the amine in their octahedral complexes with cobalt(11).

TABLE 3.15

Approximate Mean Crystal Strength ($10D_q$) and Racah Parameter(B) for the complexes CoL_4X_2 (kK)

L	X	$10D_q$	B
Iso-butylamine	Cl	10.43	0.673
Iso-butylamine	Br	9.95	0.663
Iso-butylamine	I	9.70	0.683
Iso-butylamine	CNS	10.61	0.798
Sec-butylamine	Br	9.50	0.660
Sec-butylamine	I	9.60	0.662
Iso-propylamine	Cl	9.64	0.610
Iso-propylamine	Br	10.11	0.632
Iso-propylamine	I	9.70	0.669
Iso-propylamine	CNS	9.64	0.610
Cyclohexylamine	Br	9.84	0.656
Cyclohexylamine	I	9.48	0.677
Cyclohexylamine	CNS	9.47	0.770

Since the mean crystal field strength is essentially independent of the ligand it would not be meaningful to place the amines in an order of their $10D_q$ splitting abilities. However in the series $Co(i\text{-}BuNH_2)_4X_2$ $10D_q$ values indicate the sequence I < Br < Cl < NCS, which is the normal sequence associated with these ions.

From the close similarity of the $10D_q$ values with that

of ammonia (10.1 kK) it might further be inferred that in the series RNH_2, R = H, i-Butyl, s-Butyl, i-Propyl, cyclohexyl, the crystal field perturbing power is practically independent of the nature of R. It is likely that similar behaviour would be observed with other primary amines. Furthermore these results indicate that the σ lone pairs of the ligands RHN_2 do not differ significantly in their contribution to the magnitude of $10D_q$.

Infrared spectra of the complexes CoL_4X_2 were of little value in helping to distinguish between cis and trans configurations as only broad absorption with no defined band was obtained in the far infrared. The spectrum of $Co(i\text{-}BuNH_2)_4Cl_2$ could not be obtained as the complex immediately dissociated in the mull to form a blue tetrahedral species $Co(i\text{-}BuNH_2)_2Cl_2$. However bromo complexes having trans configurations would be expected to show one M - X stretching vibration while two M - X stretching vibrations would be expected from cis configurations.

In the spectrum of the complex $Co(\text{-}iBuNH_2)_4(CNS)_2$ a fairly well defined band is visible at 233 cm^{-1} which may be due to a ν(M - NCS) vibration. Evidence for M - N bonding in this complex is afforded by the positions of $\nu(C{\equiv}N)$, ν(C-S) δ(NCS) at 2898 cm^{-1}, 780 cm^{-1} and 470 cm^{-1} respectively (see sect. 3.2.2).

The absence of terminal metal-halogen vibrations in the spectra of CoL_4X_2 could result from intramolecular or intermolecular hydrogen bonds of the type NH·····X. This bonding may be capable of completely dampening out M - X vibrations since they occur at very low energy. Primary amines are known to have a strong tendency to associate with

halogen atoms in this manner.[112,113]

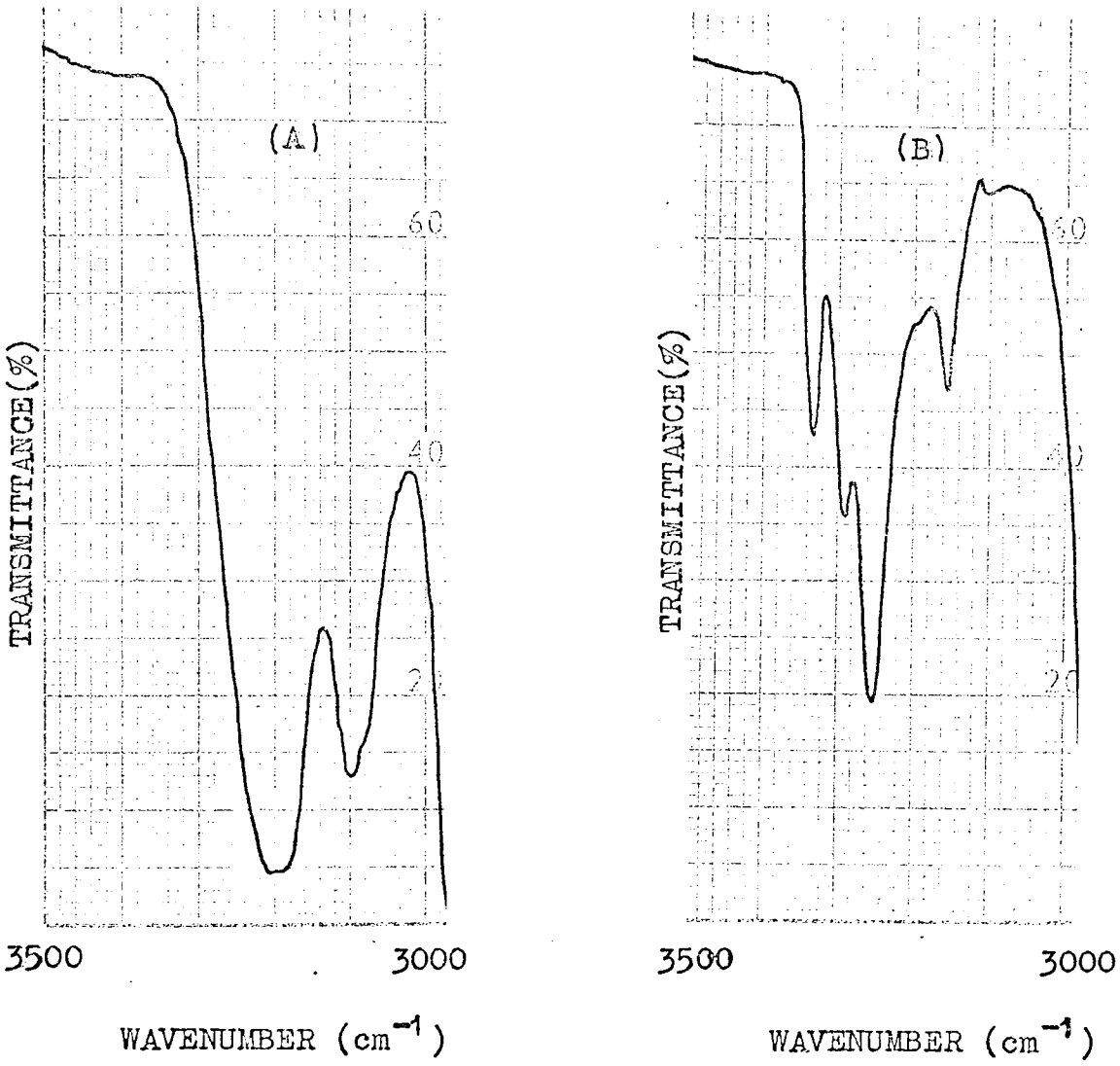


Fig. 3.12 Infrared Spectra of $Co(i\text{-}BuNH_2)_4Br_2$ (A) and $Co(i\text{-}BuNH_2)_4(CNS)_2$ (B)

Evidence that similar hydrogen bonding occurs in the complexes CoL_4X_2 is found by comparing the spectrum of $Co(i\text{-}BuNH_2)_4(CNS)_2$ (where hydrogen bonding is not possible) with that of $Co(i\text{-}BuNH_2)_4Br_2$ (where hydrogen bonding is possible) in the

3000 - 3500 cm^{-1} region, Fig. 3.12.

The N-H stretching vibrations occur as two broad bands at 3100 cm^{-1} and 3200 cm^{-1} in the spectrum of $Co(i\text{-}BuNH_2)_4Br_2$ whereas sharp peaks are clearly visible in the spectrum $Co(i\text{-}BuNH_2)_4(CNS)_2$. Furthermore the bands in the bromo complex are shifted to lower frequencies than those in the isothiocyanato complex. These observations seem to indicate that in complexes of the type CoL_4X_2, X = Cl, Br, I, severe dampening of the N-H vibrations occurs as a result of NH....Hal association.

TABLE 3.16

Infrared Spectra for the complexes CoL_4Br_2, L = isobutylamine, cyclohexylamine (cm^{-1}).

L = Iso-butylamine:	3200, 3100, 2955, 2940 sh, 2873, 1580 1500 w, 1468, 1450 sh, 1392, 1372, 1338 w, 1310 w, 1220 vw, 1163, 1110, 1027, 997 w, 948, 877, 815, 725 vw, 665 b, 550 vw, 393 vw.
L = Cyclohexylamine:	3160, 3077, 2930, 2858, 1570, 1448, 1398 w, 1362 w, 1319 vw, 1280 w, 1265, 1230, 1195, 1185, 1090, 1078, 1052, 965, 923 w, 895, 885sh, 865 vw, 846, 790, 720 vw, 677 b, 628 sh, 574, 510 vw, 449, 428 w, 400 vw, 338, 330, 305 vw.

w, weak; vw, very weak; b, broad; sh, shoulder

Since this type of association has such a pronounced effect on the ν(N-H) vibrations, which occur at relatively high energy, the effect on ν(M-X) vibrations, which occur at very low energy, would be expected to be much more dramatic. The absence of ν(M-X) vibrations in these complexes is therefore not unexpected. A similar behaviour was observed with the complexes $Ni(i\text{-}BuNH_2)_4X_2$, X = Cl, Br, CNS (sect. 3.1.2, Table 3.8). The N-H stretching vibrations of the isothiocyanate complex were sharp and in the region expected for free amine. However those of the chloro and bromo complexes were broad and shifted to lower frequencies.

Apart from the stretching and bending vibrations of CNS, infrared spectra of the complexes CoL_4X_2 do not vary significantly with X for a particular L. Complexes CoL_4X_2, L = iso-butylamine, X = Cl; L = iso-propylamine, X = Br, I, CNS; L = sec-butylamine, X = Br, I were too unstable to record meaningful spectra and decomposed immediately in mulling agents to give blue tetrahedral species. Absorption frequencies for the complexes CoL_4Br_2, L = iso-butylamine, cyclohexylamine, are tabulated in Table 3.16. Absorption frequencies for the complexes CoL_4I_2, L = iso-butylamine, cyclohexylamine, show no significant difference and are not tabulated.

TABLE 3.17

Magnetic Moments for Complexes CoL_4X_2, L = aliphatic amine; X = Br, I, CNS.

L		χ^1_M* (10^{-6})	μ_{eff} (BM, 18° - 20°)
Iso-butylamine	Br	10874	5.06
Iso-butylamine	I	10357	4.94
Iso-butylamine	CNS	10659	5.01
Iso-propylamine	I	10197	4.90
Cyclohexylamine	Br	10538	4.98
Cyclohexylamine	I	10401	4.96

* Corrected molar susceptibility in c.g.s. units.

Only six of the complexes were sufficiently stable to allow accurate calculation of magnetic moments. However these values, Table 3.17, fall within the range expected for spin-free octahedral complexes. They compare very well with values obtained by other workers[114,115] for high-spin octahedral complexes.

All the complexes (pink to red in the solid state) are soluble in a wide range of solvents, e.g. chloroform, nitromethane, acetone, and give deep blue coloured solutions, thus indicating a structural change. Spectra of $Co(i\text{-}BuNH_2)_4Br_2$, in the solid state and when dissolved in nitromethane are shown in Fig. 3.13 and may be compared

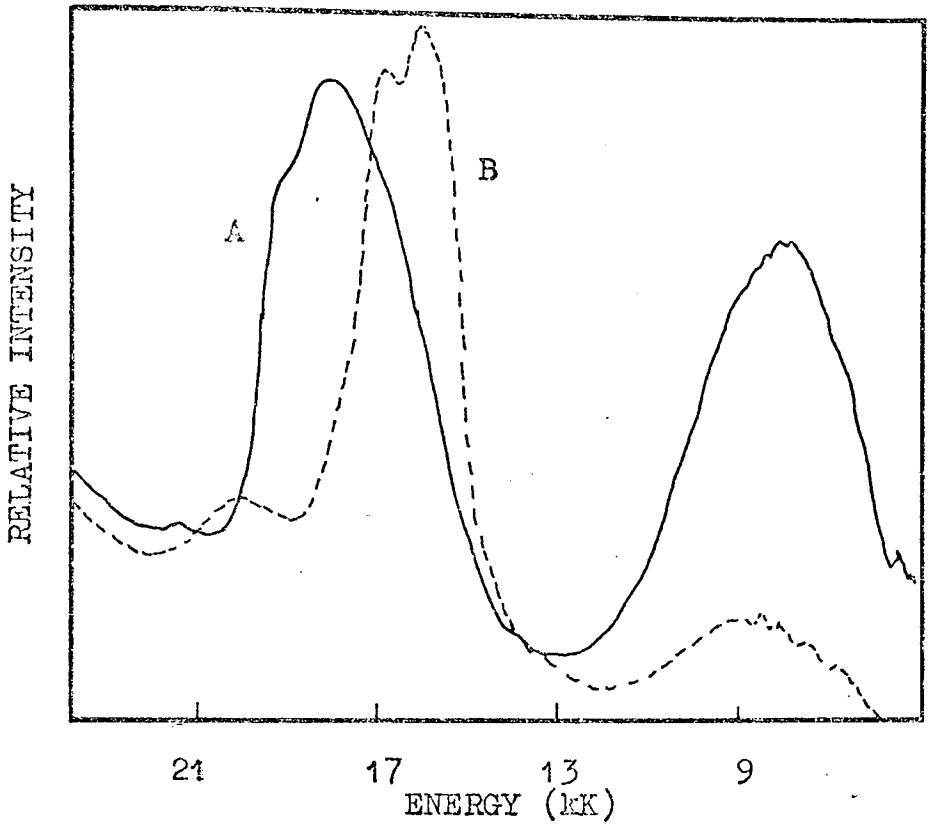


Fig. 3.13 A. Reflectance spectrum of $Co(i\text{-}BuNH_2)_4Br_2$

B. Solution spectrum of $Co(i\text{-}BuNH_2)_4Br_2$ in nitromethane.

with the solution spectrum of $Co(i\text{-}BuNH_2)_2Br_2$, Fig. 3.16, sect. 2.3.3. Both solution spectra have identical profiles. The peak in the near infrared is assigned to the transition $^4T_1 \leftarrow {}^4A_2$ while the high intensity peak in the visible is assigned to the transition $^4T_1(P) \leftarrow {}^4A_2$. Spectral evidence therefore indicates that the octahedral species dissociate to give tetrahedral species in solution;

$$\underset{\text{Octahedral}}{CoL_4X_2(\text{pink})} \xrightarrow{\text{nitromethane}} \underset{\text{Tetrahedral}}{CoL_2X_2(\text{blue})} + 2L$$

Nelson and co-workers have shown[114] that a similar transformation from octahedral configuration in the solid

state to tetrahedral configuration in solution occurs with the complexes CoL_4X_2, L = substituted pyridine; X = Cl, Br, I, CNS. In these cases addition of a slight excess of amine did not change the profile of tetrahedral absorption but on the addition of a large excess of amine the solutions became pink and the absorption spectra indicated the presence of octahedral species. They[114] explain this behaviour in terms of an equilibrium between neutral tetrahedral and octahedral complexes in solution:

$$CoL_2X_2(\text{tetrahedral}) + 2L \rightleftharpoons CoL_4X_2(\text{octahedral})$$

This behaviour was not observed with any of the complexes CoL_4X_2, L = aliphatic amine, X = Cl, Br, I, CNS. Once the tetrahedral species CoL_2X_2 had formed in solution, addition of a large excess of L did not change the profile of tetrahedral absorption. Even in solutions of the ligand the tetrahedral species still persisted. From these observations it is evident that complexes CoL_4X_2, L = substituted pyridine are more stable than complexes CoL_4X_2, L = aliphatic amine. Although steric effects may play a part in the apparent stability differences it seems likely that M → L π-back-bonding, as discussed by Nelson and co-workers,[104,114] is an important feature pertaining to the stability of the pyridine complexes.

It is quite feasible that the inability of the nitrogen in primary amines to back-accept electron density may result in the accumulation of a large amount of negative charge on the central metal cation of the complexes. Their tendency to rearrange to complexes having a lower coordination number

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may reflect their desire to reduce this negative charge.

Furthermore the apparent relative stabilities of these octahedral complexes having a particular ligand is in the order $CoL_4Cl_2 < CoL_4Br_2 < CoL_4I_2$. For example when L is iso-butylamine or iso-propylamine the chloro complex is stable only when saturated with free ligand. When L is sec-butylamine the chloro complex does not exist and the bromo complex is stable only when saturated with free ligand. In all these cases the iodo complex is relatively stable at ambient temperature and pressure in the absence of excess free ligand. These observations indicate the stability order Cl < Br < I for the complexes CoL_4X_2.

Since the aliphatic amine cannot act as a sink for electron density it is clear that any variation of electron density in the series CoL_4X_2 must be attributed to X. As the polarizability sequence for X is in the order Cl < Br < I it is expected that the ability of X to reduce a build up of negative charge on the central metal cation would be in the order I > Br > Cl. This is the sequence observed in the stability of the complexes CoL_4X_2.

The non-existence of the complex $Co(s\text{-}BuNH_2)_4Cl_2$ must therefore be attributed to a combination of steric and electrostatic factors. Assuming the polarizability of Cl to remain constant in $Co(i\text{-}BuNH_2)_4Cl_2$ and $Co(s\text{-}BuNH_2)_4Cl_2$ the latter complex would be expected to exist since the former complex was isolated in a fairly stable form. Clearly, therefore, the increased steric requirements of sec-butylamine over those of iso-butylamine is the ultimate factor preventing the formation of $Co(sec\text{-}BuNH_2)_4Cl_2$. By similar argument the failure to isolate the complex dichlorotetrakis-

(cyclohexylamine)cobalt(11) must be attributed to the fact that the steric requirements of cyclohexylamine are comparable to those of sec-butylamine. The dichlorotetrakis-(iso-propylamine) complex of cobalt(11) was isolated but was much more unstable with respect to dissociation than its corresponding iso-butylamine complex.

On the basis that each amine donates comparable amounts of electron density in complexes CoL_4X_2 (which is reasonable in view of the fact that they are all σ-bonded) and on the basis that the polarizability of X remains constant in each of the series CoL_4Cl_2, CoL_4Br_2, CoL_4I_2, the following stability sequence may be formulated for the complexes:

$$\begin{array}{ccccccc} CoL_4Cl_2 & > & CoM_4Cl_2 & > & CoN_4Cl_2^{*} & \simeq & CoP_4Cl_2^{*} \\ \wedge & & \wedge & & \wedge & & \wedge \\ CoL_4Br_2 & > & CoM_4Br_2 & > & CoN_4Br_2 & \simeq & CoP_4Cl_2 \\ \wedge & & \wedge & & \wedge & & \wedge \\ CoL_4I_2 & > & CoM_4I_2 & > & CoN_4I_2 & \simeq & CoP_4I_2 \end{array}$$

L, iso-butylamine; M, iso-propylamine
N, cyclohexylamine; P, sec-butylamine

* Non-existent

Since no π-bonding between metal and amine is possible for these complexes the vertical stability trends in the above table is totally a function of the polarizability of the Hal^{-1} ions. It may also be stressed that in these complexes the polarizability effect of the Hal^{-1} ions is to reduce the accumulation of negative charge on the metal cation. This may be contrasted to the well known examples of $[FeF_6]^{3-}$ and $[FeCl_4]^{-}$ where the effect of the

polarizability of F^- and Cl^- ions is to build up a negative charge on the metal cation.

It may be concluded therefore:

(a) In the complexes CoL_4X_2, L = aliphatic amine, the principle of electroneutrality is of major significance in deciding the coordination number. This is in complete agreement with postulations by Gill and Nyholm.[3]

(b) The ability of pyridine to participate in multiple bonding (and hence back-accept electron density) contributes significantly to the enhanced stability of complexes CoL_4X_2, L = pyridine, substituted pyridine, over those of CoL_4X_2, L = aliphatic amine. Stereochemical factors as structured determinants may be of much lesser importance in many cases.

Finally it has been stated already and shown, Table 3.15, that $10D_q$ is practically invarient in the octahedral complexes CoL_4X_2, L = aliphatic amine and thus independent of the steric nature of the amine. However in the complexes CoL_4X_2, L = substituted pyridine, Nelson and co-workers have shown[114] that the position of an alkyl substituent in pyridine can significantly affect the crystal field strength. An explanation consistent with M-ligand π-bonding was suggested. It would appear therefore that the non-variation of $10D_q$ in the octahedral complexes containing aliphatic amines is a consequence of the absence of M-L π-bonds.

3.2.3. Monomeric Tetrahedral Complexes CoL_2X_2, L = iso-butylamine, iso-propylamine, sec-butylamine, tert-butylamine, cyclohexylamine; X = Cl, Br, CNS.

All these complexes have an intense blue colour and their reflectance spectra indicate a basic tetrahedral stereochemistry for the cobalt atom. An indication of their departure from true C_{2v} symmetry may be obtained by studying the profile of the near infrared band i.e. the transition $^4T_1 \leftarrow {}^4A_2$. It has been stated already (sect. 3.2.1) that Ferguson [106] and Lever [105] have inferred the splitting of this transition in terms of a lowering of T_d symmetry. Slight splitting was observed in the ν_2 transition of the tetrahedral complexes $CoX_2.2NMe_3$, X = Cl, Br, I (sect. 3.3.1) and it was concluded that these complexes were slightly distorted.

In the complexes CoL_2X_2 splitting of the ν_2 transition was much more dramatic and pronounced, Fig. 3.14. Similar to the complex $Co(CNS)_2.2NMe_3$ splitting did not occur in the complexes $CoL_2(CNS)_2$, thus indicating that deviation from C_{2v} symmetry in these complexes is much less than in their halo analogues. Band assignments for the complexes are given in Table 3.18.

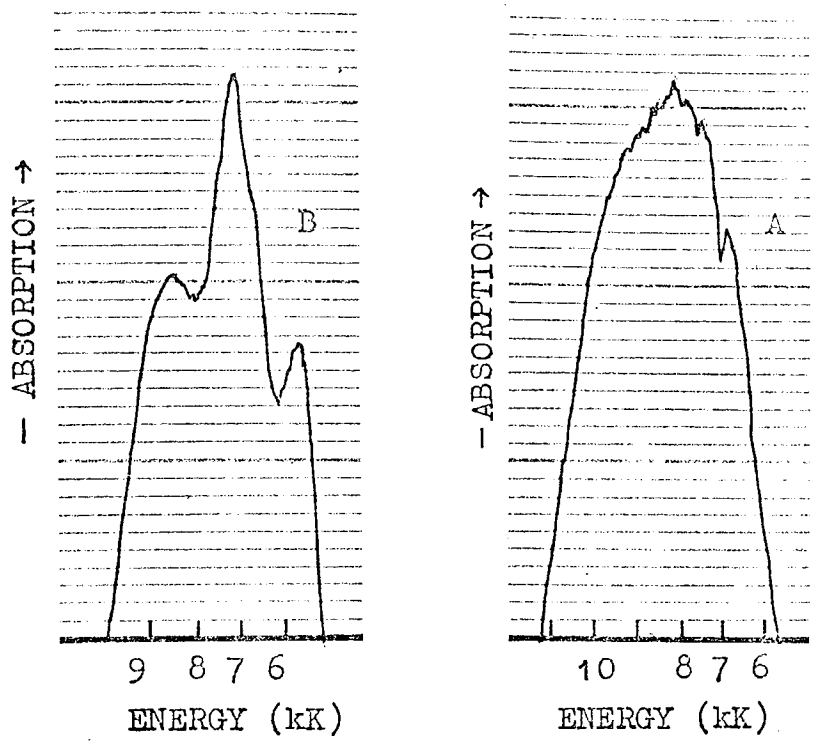


Fig. 3.14 Reflectance Spectra showing the $^4T_1 \leftarrow {}^4A_2$ transition in $Co(i\text{-}PrNH_2)_2(CNS)_2$, A, and in $Co(cyclohexylamine)_2Cl_2$, B.

TABLE 3.18

		$^4T_{1}(P) \leftarrow {}^4A_2$	$^4T_1 \leftarrow {}^4A_2$
L	X	Components of ν_3	Components of ν_2
Iso-butylamine	Cl	16.3, 15.8 sh	9.7 sh, 7.2, 6.1
Iso-butylamine	Br	16.2, 15.3 sh	8.6, 6.6
Sec-butylamine	Cl	16.2	8.8, 7.2, 5.8 sh
Sec-butylamine	Br	16.0	8.6, 7.0, 5.9 sh
Sec-butylamine	CNS	16.7	8.8
Iso-propylamine	Cl	16.2	9.0, 6.1

TABLE 3.18 contd.

Iso-propylamine	Br	16.2	9.5, 7.6
Iso-propylamine	CNS	16.8	8.3
Tert-butylamine	Cl	15.8	8.8. 7.0, 5.8 sh
Tert-butylamine	CNS	16.8	9.6 sh, 8.4
Cyclohexylamine	Cl	16.3	8.6, 7.1, 5.6
Cyclohexylamine	Br	15.6	8.4, 7.2, 5.9

sh, shoulder

Values of $10D_q$ and B were calculated by the method outlined by Lever[57,59,62] (see Appendix) using energy values for ν_2 and ν_3 transitions. For these calculations the centre of the near infrared band was assumed to be the transition $^4T_1 \leftarrow {}^4A_2$. The high energy component of the visible band was neglected as it was assumed to be mainly doublet in orgin. The centre of the remaining components of this absorption was taken to represent the energy of the transition $^4T_1(P) \leftarrow {}^4A_2$. Similar approximations were made by Lever and Nelson[105] in their calculations of $10D_q$ and B values for the complexes CoL_2X_2, L = substituted pyridine, X = Cl, Br, I, CNS.

TABLE 3.19

Approximate Mean Crystal Strength ($10D_q$) and Racah Parameter (B) for the complexes CoL_2X_2 (kK)

L	X	$10D_q$	B
Iso-butylamine	Cl	4.69	0.679
Iso-butylamine	Br	4.61	0.698
Sec-butylamine	Cl	4.51	0.683
Sec-butylamine	Br	4.51	0.683
Sec-butylamine	CNS	5.26	0.649
Iso-propylamine	Cl	4.52	0.645
Iso-propylamine	Br	4.52	0.645
Iso-propylamine	CNS	4.93	0.694
Tert-butylamine	Cl	4.49	0.661
Tert-butylamine	CNS	5.11	0.672
Cyclohexylamine	Cl	4.83	0.671
Cyclohexylamine	Br	4.76	0.700

The values of $10D_q$ fall within the range expected for tetrahedral cobalt(11) complexes, their values being approximately 4/9 those of their octahedral analogues, Table 3.15. However, due to the possible distortion of these tetrahedral complexes it is relevant to discuss only the trends in $10D_q$ values. Lever and Nelson have shown[105] that $10D_q$ values in the complexes CoL_2X_2, L = substituted pyridine, lie in the sequence I < Br < Cl < CNS. However in the complexes CoL_2X_2, L = aliphatic amine, the sequence Br ≃ Cl < CNS is observed.

This could be a consequence of the distortion of these complexes, which would introduce an inherent error in the calculation of $10D_q$. Splitting of the ν_2 transition was usually much greater in the chloro complexes than in their bromo analogues. For this reason values of $10D_q$ obtained for the complexes CoL_2Cl_2 may not be too significant.

The infrared spectrum of $Co(i\text{-}PrNH_2)_2Cl_2$ is shown in Fig. 3.15. Two metal-halogen vibrations, as expected for tetrahedral species ML_2X_2 having C_{2v} symmetry, are clearly visible at 323 cm^{-1} and 298 cm^{-1}. These vibrations are in the region expected for M-X stretching frequencies.[94]

TABLE 3.20

Frequencies of Co-X and CNS in the complexes CoL_2X_2, L = aliphatic amine; X = Cl, Br, CNS (cm^{-1})

L	X	(Co-X)	ν(C≡N)	ν(C-S)	δ(NCS)
Iso-butylamine	Cl	320, 297			
Iso-butylamine	Br	242,			
Sec-butylamine	Cl	318, 295 sh			
Sec-butylamine	Br	248			
Sec-butylamine	CNS	315, 275 sh	2078	828	474
Iso-propylamine	Cl	323, 298			
Iso-propylamine	Br	252			
Iso-propylamine	CNS	307, 280 sh	2078	828	486
Tert-butylamine	Cl	320 sh, 305			
Tert-butylamine	CNS	310, 295	2080, 2108	834	476

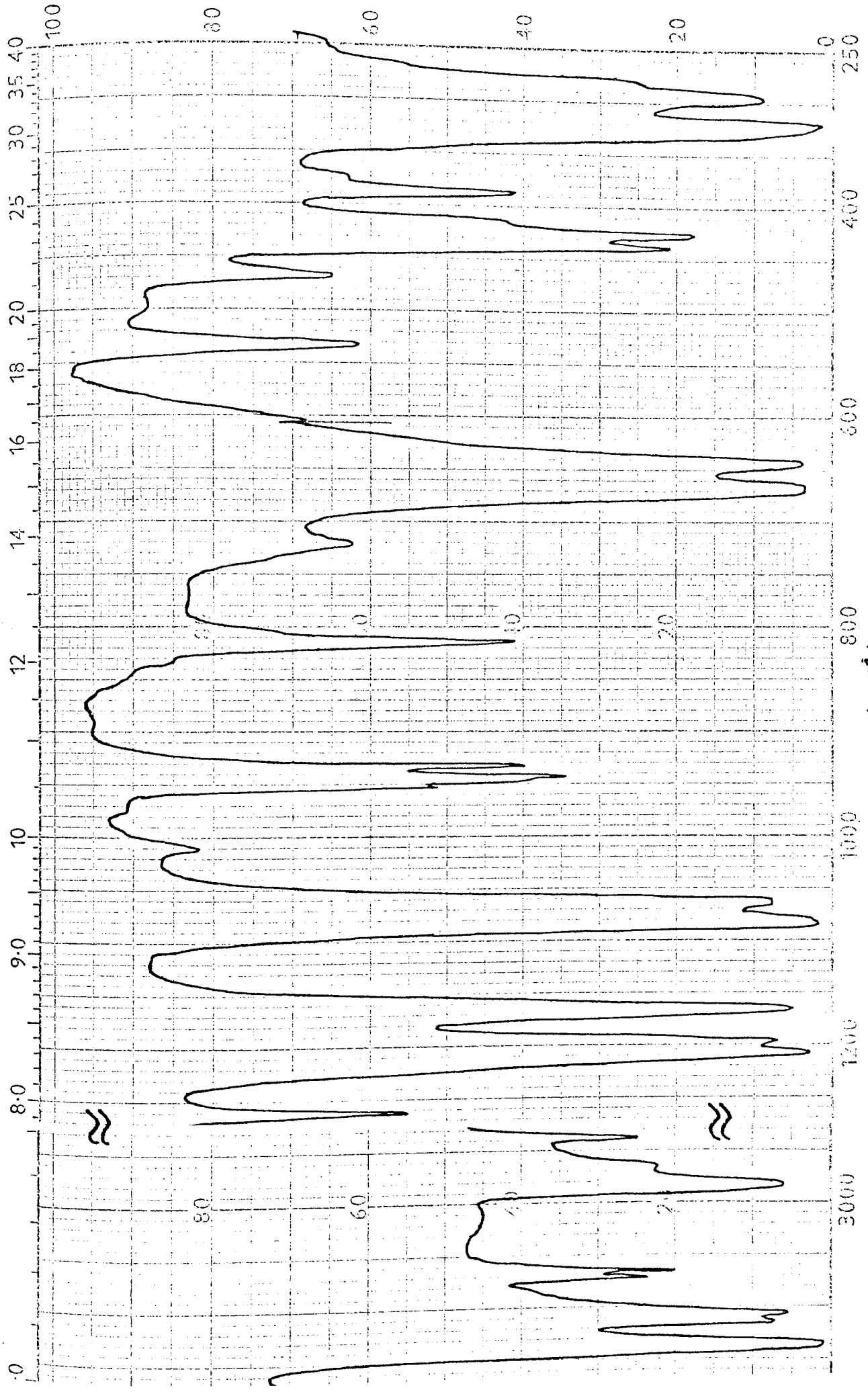


Fig.3.15. Infrared spectrum of $Co(i\text{-}PrNH_2)Cl_2$

TABLE 3.20 contd.

Cyclohexylamine	Cl	315, 290
Cyclohexylamine	Br	240

sh, shoulder.

The complexes CoL_2Cl_2, L = iso-butylamine, cyclohexylamine, also have well separated ν(Co-Cl) frequencies which occur at 320 cm^{-1}, 297 cm^{-1} for the iso-butylamine complex and 315 cm^{-1}, 290 cm^{-1}, for the cyclohexylamine complex. In the complex $Co(s\text{-}BuNH_2)_2Cl_2$ the two Co-Cl stretching vibrations seem to coincide and only one well defined band is visible at 318 cm^{-1}. The ν(Co-Cl) vibrations also coalesce in the complex $Co(t\text{-}BuNH_2)_2Cl_2$.

Only one Co-Br stretching vibration, which occurred around 240 cm^{-1}, was observed in the complexes CoL_2Br_2. However the second stretching vibration for these complexes is expected to occur below 200 cm^{-1}. This region was not examined in the present work.

All the complexes $CoL_2(CNS)_2$ have N-bonded thiocyanate groups, as deduced from the positions of $\nu(C{\equiv}N)$, ν(C-S) and δ(NCS), Table 3.20 (see also sect. 3.1.2). The complex $Co(t\text{-}BuNH_2)_2(CNS)_2$ is the only complex in which the C-N stretching vibration is split. However this is not unusual as the SCN-M-NCS group cannot be linear in tetrahedral complexes $CoL_2(CNS)_2$ and molecular symmetry requires a doubling of $\nu(C{\equiv}N)$ vibrations in these cases. Thus it is more unusual that only one C-N stretching vibration is observed in the other complexes $CoL_2(CNS)_2$ and it appears

likely that accidental degeneracy occurs in these cases. Splitting of the $\nu(C{\equiv}N)$ vibration has also been observed[110] in tetrahedral complexes of the type CoL_2X_2, L = substituted pyridine.

TABLE 3.21

Infrared Spectra for the complexes CoL_2Cl_2
L = aliphatic amine (cm^{-1}).

L = Iso-butylamine:	3280, 3240, 3148, 2690 b, 2870, 1590, 1510, 1470, 1390, 1375 sh, 1368 w, 1310, 1197, 1160, 1098, 1075 vw, 1022, 935, 878, 812, 722 w, 643, 544, 388 w, 320, 297.
L = Iso-propylamine:	3270, 3230, 3218, 3140, 3130, 2968, 2930 sh, 2878, 2730 vw, 1588, 1580, 1470, 1460 sh, 1445 vw, 1393, 1385 w, 1371, 1344, 1263. 1209, 1198 sh, 1167, 1082, 1065, 1010 vw, 942, 931, 812, 720 vw, 667, 645, 532, 438, 428, 388, 323, 298.
L = Sec-butylamine:	3262, 3218, 3144, 2968, 2930, 2880, 2800 sh, 1595 sh, 1588, 1518, 1462, 1380, 1230 sh, 1208, 1148, 1097, 1070 w, 1010 w, 1033 w, 990 w, 980, 910, 820 w, 774, 720 w, 655, 620 sh, 450 w, 385 w, 318, 295 sh.

TABLE 3.21 contd.

L = Tert-butylamine	3270 sh, 3258, 3220, 3150, 2978, 2900, 2814, 2718, 2608, 2504, 1592, 1580, 1515 w, 1530, 1405, 1372, 1300 sh, 1282 1220, 1155, 1137 w, 1025, 970 vw, 928 vw 905, 743, 720 w, 700 w, 685 vw, 650 b, 454, 425 w, 375 w, 348 w, 320 sh, 305, 280 sh.
L = Cyclohexylamine:	3258, 3220, 3120, 2922, 2858, 1569, 1469, 1452, 1438, 1382, 1282, 1270 vw, 1255 w, 1187, 1147 vw, 1110, 1074, 1038 w, 1063, 1030 w, 960, 888, 842, 790 w, 720 vw, 630, 620 sh, 557 w, 488 vw, 444, 428, 395 w, 278 w, 315, 290.

w, weak; vw, very weak; sh, shoulder; b, broad.

The N-H stretching vibrations are noticeably sharp in all the complexes CoL_2X_2, X = Cl, Br, CNS, (see Fig. 3.15). This is in contrast to their octahedral analogues where sharp N-H stretching vibrations were observed for the complexes $CoL_4(CNS)_2$ only. The broadness and shift to lower frequencies of these stretching vibrations in the halo complexes CoL_4X_2 was attributed to NH·····Cl association, a view which is now strongly supported from observations in the spectra of the tetrahedral complexes. Due to the

stereochemical arrangement of halogen and amine in tetrahedral complexes, NH····Cl linkage is not possible and thus the N-H vibrations appear sharp and in the region expected for free amine.

TABLE 3.22

Magnetic Moments and Molar Conductivities of the complexes CoL_2X_2

L	X	$\chi^1_M{}^*(10^{-6})$	μ_{eff}(BM, 18°-20°	Λ_M^{**}
Iso-butylamine	Cl	8580	4.50	18
Iso-butylamine	Br	8330	4.44	19
Sec-butylamine	Cl	8881	4.58	20
Sec-butylamine	Br	8521	4.49	19
Sec-butylamine	CNS	8478	4.48	28
Iso-propylamine	Cl	8989	4.61	18
Iso-propylamine	Br	8888	4.50	22
Iso-propylamine	CNS	8966	4.60	27
Tert-butylamine	Cl	9008	4.61	15
Tert-butylamine	CNS	8531	4.49	28
Cyclohexylamine	Cl	8749	4.55	16
Cyclohexylamine	Br	8764	4.55	18

* Corrected molar susceptibility in c.g.s. units

** Molar Conductivity in nitromethane (10^{-3}M.) ohm.$^{-1}$ mol.$^{-1}$ cm^2

Magnetic moment and susceptibility values for the complexes, Table 3.22, are comparable with those for the complexes $CoX_2 \cdot 2NMe_3$, Table 3.8, and are within the range expected for cobalt(11) in a tetrahedral environment. The complexes are soluble in a wide range of solvents, e.g. nitromethane, dimethylformamide, acetone and give solutions having a deep blue colour. Apart from splitting of the ν_2 transition for the halo complexes in the solid state the contours of solution spectra and reflectance spectra are not significantly different, Fig. 3.16.

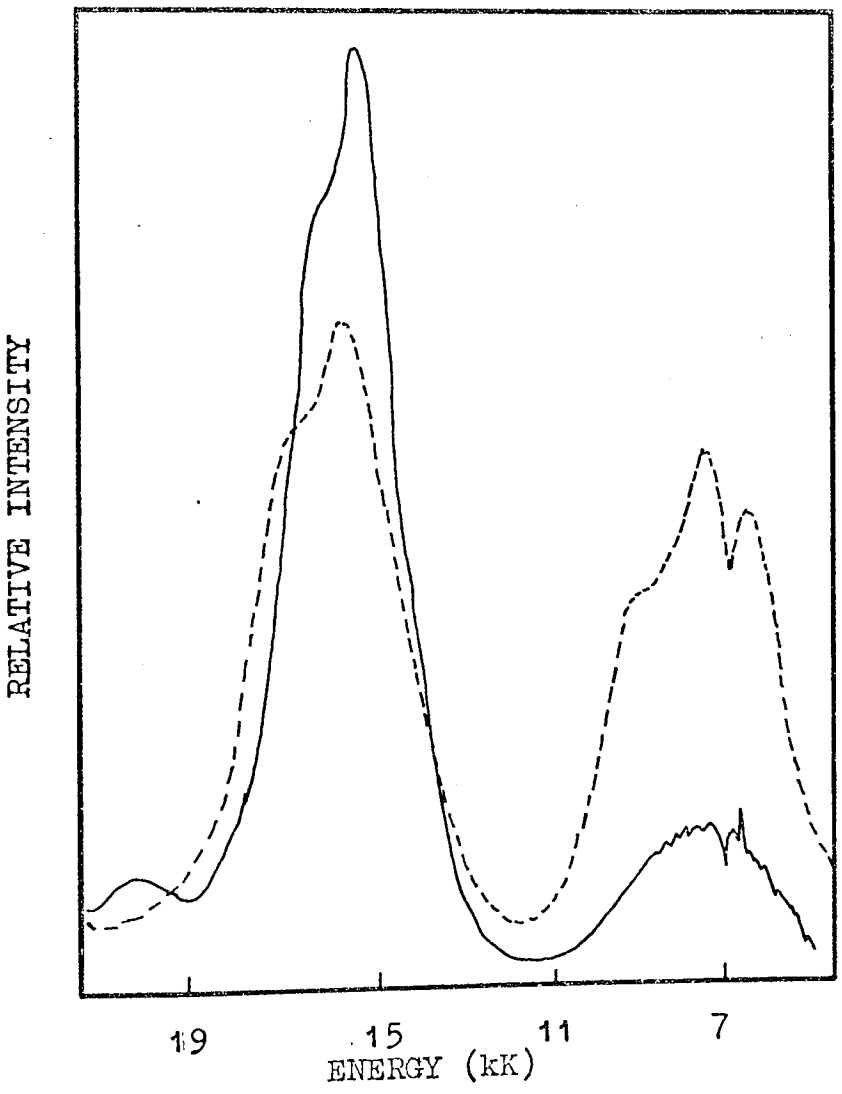


Fig. 3.16 Absorption spectrum of solid $Co(i\text{-}BuNH_2)_2Br_2$ (------) and in nitromethane (———)

Conductivity data, Table 3.22, indicates slight dissociation of the complexes in nitromethane. This was also evidenced by a slight enhancement of intensity in the visible band when excess amine was added. As was observed with the complexes $CoX_2 \cdot 2NMe_3$, sect. 3.2.1, the multiple nature of the ν_2 transition disappeared in solution. Again this is inferred to indicate that the halo complexes have a somewhat lower symmetry in the solid state than in solution and that deviation from C_{2v} symmetry is a consequence of lattice requirements in the solid state rather than the steric requirements of the ligands. Solution electronic spectra and estimated molecular weights for these complexes are tabulated in table 3.23.

TABLE 3.23

Solution Spectra (in nitromethane) and Estimated Molecular Weights (in tetrahydrofuran) for the complexes CoL_2X_2 (ϵ molar)

L	X	Abs.Maxima kK	M.W calculated	M.W found
Iso-butylamine	Cl	16.3sh(620),15.8(660),7.6(102)	276	298
Iso-butylamine	Br	16.0sh(680),15.8(820),8.0(132)	365	410
Sec-butylamine	Cl	16.3sh(590),15.4(725),7.0(110)	276	280
Sec-butylamine	Br	16.2sh(640),15.3(810),7.0(120)	365	390
Sec-butylamine	CNS	16.2(870), 8.2(182)	321	355
Iso-propylamine	Cl	16.0sh(640),15.8(690),7.5(125)	248	279
Iso-propylamine	Br	15.9sh(660),15.3(730),6.9(133	337	358

TABLE 3.23 contd.

Iso-propylamine	CNS	16.1(800), 8.1(166	293	340
Tert-butylamine	Cl	16.3sh(580),15.7(690),7.8(114)	276	280
Tert-butylamine	CNS	16.2(920), 8.1(165)	321	361
Cyclohexylamine	Cl	16.9sh(584),16.0(670),7.8(110)	328	371
Cyclohexylamine	Br	16.8sh(620),15.9(660),7.8(118)	417	480

sh, shoulder

3.2.4. Polymeric Octahedral Complexes $CoL_2(CNS)_2$, L = Iso-butylamine, Cyclohexylamine

The complexes $CoL_2(CNS)_2$, L = iso-propylamine, sec-butylamine, tert-butylamine, studied in the last section, have intense blue colours in the solid state and in solution. A tetrahedral structure was proposed for these complexes in the solid state and this structure was retained in solution. However the complex $Co(i\text{-}BuNH_2)_2(CNS)_2$ is lilac coloured and the complex $Co(cyclohexylamine)_2(CNS)_2$ is a pale pink. In solution both of these complexes have an intense blue colour similar to the complexes $CoL_2(CNS)_2$, L = iso-propylamine, sec-butylamine, tert-butylamine, in solution. On the basis of the following evidence from infrared spectroscopy, electronic spectroscopy and magnetic susceptibility measurements, it is proposed that the complexes $Co(i\text{-}BuNH_2)_2(CNS)_2$ and $Co(cyclohexylamine)_2(CNS)_2$ are thiocyanate bridged six coordinate in the solid state and monomeric tetrahedral in solution.

Polymeric octahedral complexes of the type $CoL_2(CNS)_2$, L = pyridine, substituted pyridine, are well known[110,115,116] and the most convincing evidence for bridging structures is found from a study of their infrared spectra.[110] The C-N stretching frequency for the complexes $CoL_2(CNS)_2$, L = iso-butylamine, cyclohexylamine, occurs at 2109 cm^{-1} and 2110 cm^{-1} respectively which is about 30 cm^{-1} higher than the corresponding vibration in the complexes $CoL_2(CNS)_2$, L = iso-propylamine, sec-butylamine, tert-butylamine, Table 3.24. This shift of the C-N stretching vibration to higher frequencies is characteristic of thiocyanate bridged complexes. For example $\nu(C\equiv N)$ occurs at 2060 cm^{-1} for the tetrahedral complex $Co(\alpha\text{-picoline})_2(CNS)_2$ but is shifted to 2099 cm^{-1} in the polymeric octahedral complex $Co(pyridine)_2(CNS)_2$.[110]

TABLE 3.24

A Comparison of CNS vibrations in tetrahedral and polymeric octahedral complexes having stoicheiometry $CoL_2(CNS)_2$ (cm^{-1})

L	$\nu(C\equiv N)$	$\nu(C-S)$	$\delta(NCS)$	$\nu(Co-NCS)$
		Tetrahedral		
Iso-propylamine	2078	828	486	307, 280 sh
Sec-butylamine	2078	828	474	315, 275 sh
Tert-butylamine	2080 2108	834	476	310, 295 sh
		Polymeric Octahedral		
Iso-butylamine	2109	772 w	461 472	252
Cyclohexylamine	2110	779	461 448	252

w, weak.

A shift to higher frequency is also observed in the C-S stretching frequency for polymeric complexes. In $Co(\beta\text{-picoline})_2(CNS)_2$ ν(C-S) occurs at 851 cm^{-1} but in $Co(pyridine)_2(CNS)_2$ ν(C-S) occurs at 787 cm^{-1}. Shifts to higher frequencies of similar magnitude, Table 3.24, were observed for the C-S stretching vibrations in the complexes $CoL_2(CNS)_2$, L = iso-butylamine, cyclohexylamine. According to Clark and Williams[110] the position of the thiocyanate bending vibration is almost independent of the stereochemistry and thus is of little value in distinguishing between polymeric and tetrahedral species. In the complexes of iso-butylamine and cyclobutylamine δ(NCS) occurred as well defined doublets in the 448 - 472 cm^{-1} region. However this splitting of δ(NCS) cannot be taken as criteria for bridging thiocyanate as similar splitting was observed [110] in the tetrahedral complexes $ZnL_2(CNS)_2$, L = α, β or γ-picoline.

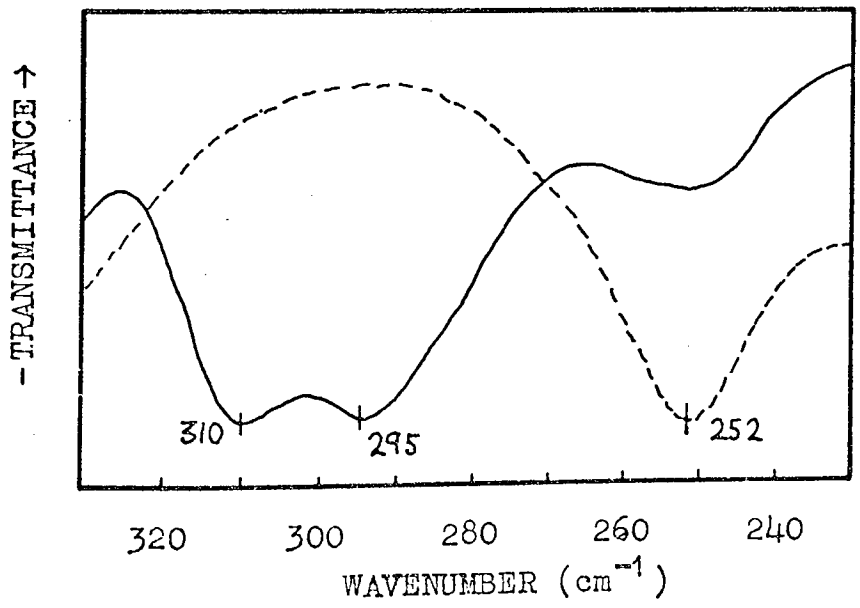


Fig. 3.17 Infrared spectra of $Co(tert\text{-}BuNH_2)_2(CNS)_2$ (———) and of $Co(i\text{-}BuNH_2)_2(CNS)_2$ (- - - -)

The most notable difference in the infrared spectra of octahedral bridged and tetrahedral iso-thiocyanate complexes occurs in the ν(M-NCS) frequencies. The metal-isothiocyanate vibrations for tetrahedral complexes occurs at significantly higher frequencies than the metal-isothiocyanate vibration for polymeric octahedral compounds. For example ν(Co-NCS) vibrations occur at 321 cm^{-1} and 287 cm^{-1} for the tetrahedral complex $Co(\alpha\text{-picoline})_2(CNS)_2$ while the Co-NCS stretching vibration for polymeric $Co(pyridine)_2(CNS)_2$ occurs at 268 cm^{-1}. [110] The spectra of $Co(t\text{-}BuNH_2)_2(CNS)_2$ and $Co(i\text{-}BuNH_2)_2(CNS)_2$ are shown in Fig. 3.17, and from the position of ν(Co-NCS) in the latter complex there can be little doubt regarding its polymeric nature.

Reflectance spectra for the complexes are shown in Fig. 3.18 and are clearly indicative of basic octahedral stereochemistry for the cobalt atom. They compare very well with the spectra of other octahedral complexes e.g. $Copy_4(CNS)_2$ and $Co(i\text{-}BuNH_2)_4(CNS)_2$, Fig. 3.11. The band in the near infrared is assigned to the $^4T_2 \leftarrow {}^4T_1$ (ν_1) transition while the multiple visible band is attributed to the $^4T_1(P) \leftarrow {}^4T_1$ (ν_3) transition. There is also a weak band on the high energy side of ν_3 in both of the complexes $CoL_2(CNS)_2$, L = iso-butylamine, cyclohexylamine. The low intensity of this band suggests that it is mainly spin-forbidden in origin. However it is not present in the spectra of monomeric thiocyanate octahedral species and thus it may reflect a lowering of symmetry in the polymeric octahedral complexes.

Magnetic moments, Table 3.25, were determined for both complexes and fall within the range expected for high-spin octahedral cobalt(11). They compare very well with the

values obtained by other workers[114,117] for bridging thiocyanate complexes of the type $CoL_2(CNS)_2$, L = substituted pyridine.

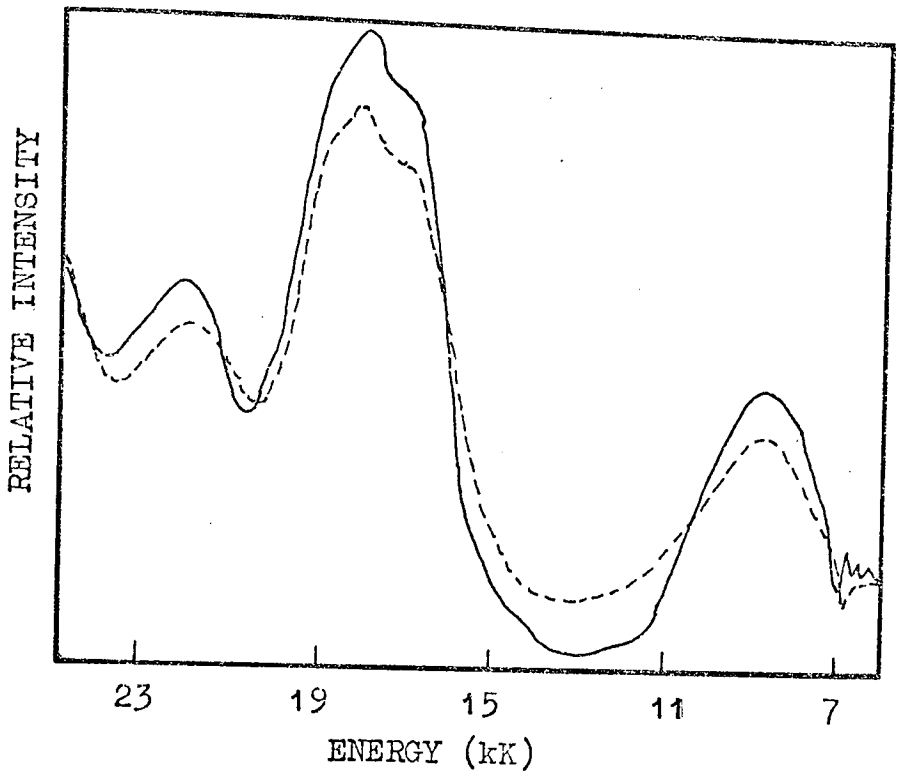


Fig.3.18 Reflectance Spectra of $Co(i\text{-}BuNH_2)_2(CNS)_2$ solid line, and of $Co(cyclohexylamine)_2(CNS)_2$, broken line.

TABLE 3.25

Reflectance Spectra (abs.max. kK) and Magnetic data for the complexes $CoL_2(CNS)_2$, L = iso-butylamine, cyclohexylamine.

L	$^4T_1(P) \leftarrow {}^4T_1$ ν_3	$^4T_2 \leftarrow {}^4T_1$ ν_1	$\chi^1_M{}^*(10^{-6})$	μ_{eff}(BM 18°20°)
Iso-butylamine	18.7,17.6 sh	8.9	10933	5.08
Cyclohexylamine	18.7,17.8 sh	8.8	11197	5.14

* Corrected molar susceptibility in c.g.s. units

The complexes dissolve in a wide range of solvents e.g. acetone, nitromethane, dimethylformamide, and give solutions having an intense blue colour. The position and profile of band absorption in these blue solutions is almost identical to that for the tetrahedral com plexes $CoL_2(CNS)_2$, L = iso-propylamine, sec-butylamine, tert-butylamine, in similar solvents. Thus it is assumed that the polymeric octahedral complexes have very labile thiocyanate bridges and dissociate readily in solution to give tetrahedral species:

$$n\text{Co(i-BuNH}_2)_2(\text{CNS})_2 \text{ (lilac)} \xrightarrow{\text{Acetone}} \text{Co(i-BuNH}_2)_2(\text{CNS})_2\text{(blue)}$$

polymeric octahedral — tetrahedral

Similar structural changes were observed by other workers[114,117] when polymeric thiocyanate complexes $CoL_2(CNS)_2$, L = substituted pyridine, were dissolved in chloroform.

3.3. Complexes of Chromium(111) chloride

As indicated in sect. 2.3.3. the pentakis-amine complexes $[Cr(RHN_2)_5X]X_2$, X = Cl, Br, I; R = methyl, ethyl, allyl, n-butyl, iso-butyl, have been prepared and characterized previously[30]. During the routine preparation of the chloropentakis-ethylamine complex an unexpected peak of moderate intensity, situated at 2300 cm^{-1}, was observed in

the infrared spectrum, Fig. 3.19.

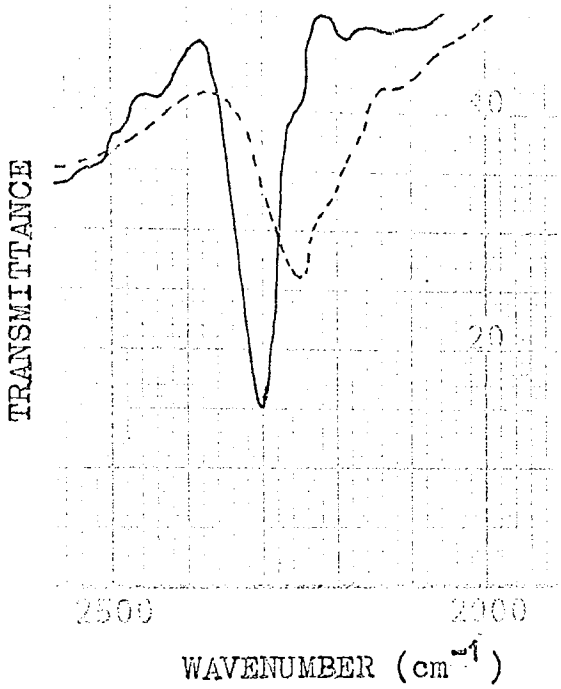


Fig. 3.19. Infrared spectrum (2500 - 2000 cm^{-1}) of $Cr[(EtNH_2)_5Cl]Cl_2$ prepared under open-air conditions (———) and of its thermal degradation products (-----)

Since this band is in the region expected for the C-N stretching frequency of nitriles the possible oxidation of some ethylamine to acetonitrile in the complex was immediately suspected. Partial proof that this did occur was obtained from the following experiment. The complex was gently heated in a slow stream of nitrogen over a period of two hours. The residue, which was also isolated by Mandal[28], showed no trace of absorption in the 2300 cm^{-1} region. The volatile thermal degradation products were collected in a nitrogen trap and the infrared spectrum at -30° revealed a band of diminished intensity situated at 2254 cm^{-1}. This band is in the region expected for $\nu(C\equiv N)$ in free acetonitrile and is shifted by 46 cm^{-1} to a lower frequency from that in the complex.

It is well known[94,118] that the C-N stretching frequency of nitriles is raised by about 40 cm^{-1} on coordination to a metal cation. For example Hathaway and Holah report[119] that $\nu(C{\equiv}N)$ for coordinated acetonitrile occurs at 2305 cm^{-1} in the complexes $MCl_3(MeCN)_3 \cdot MeCN$, M = Cr(111), V(111). Thus it is quite feasible that the band at 2300 cm^{-1} indicates the presence of some coordinated acetonitrile in the pentakis - ethylamine complex while the band at 2254 cm^{-1} in the thermal degradation products could be inferred to indicate the presence of some free acetonitrile.

This result is best interpreted if it is assumed that ethylamine becomes considerably activated upon coordination to chromium(111) chloride and in this unstable state is very susceptible to oxidation. A certain amount of polarization will always take place when any molecule and positive ion form a coordinate band and as a result reactivity changes can be expected in both the ligand and metal cation.

In general the electronic distortion in the ligand leads to an increase in activity th ough the degree and mode of activation may vary considerably. An example which comes to mind immediately is the chlorination and bromination of aromatic compounds whereby the halogen is activated as a result of its coordination to a Lewis acid such as $FeCl_3$.

The discovery of the first stable molecular nitrogen complex $[Ru(NH_3)_5N_2]X_2$, X = Br, I, BF_4, by Allen and Senoff[120] in 1965 resulted in intense research activity in this field. Numerous dinitrogen complexes are now well known but in most cases it was the changes in reactivity of the N_2 molecule, brought about upon coordination, that have received most attention. While the early reports[120,121]

that the N_2 molecule in the complex cation $[Ru(NH_3)_5N_2]^{2+}$ is reduced by alkaline $NaBH_4$ to give a 50% yield of ammonia have been shown[121,122] to be erroneous it is certain that the reactivity of the N_2 molecule is much enhanced upon coordination.

Since the nitrogen molecule, which is characterized by its inertness, is highly activated upon coordination to Ru(11) it might be expected that other molecules coordinated to the same metal would also show large increases in reactivity. It is not surprising therefore that McWhinnie et al. report[123] that methylamine becomes highly activated upon coordination to Ru(11) and is readily oxidized to cyanide under mild conditions.

However, the ability of Cr(111) to activate an amine was not expected to be comparable to that of Ru(11) and in the absence of further evidence the results with Cr(111) must be considered tentative only. No mechanism has yet been proposed for the reaction and the reduction products have not been identified. However oxygen is necessary for the reaction as demonstrated by the absence of the band at 2300 cm^{-1} when the complex is prepared in an inert atmosphere. The percentage conversion of ethylamine to nitrile appears to be very low and the oxygen uptake during the reaction could not be reliably estimated.

In view of this it is not surprising that the C, H, N analytical figures obtained by Parris and Feiner[31] clearly agree with the formulation of the complex as $[Cr(EtNH_2)_5Cl]Cl_2$ The presence of a small amount of contaminating complex such as $[Cr(C_2H_5NH_2)_4(CH_3CN)Cl]Cl_2$ would not be expected to change the C, H, N, analytical figures and the H analytical figure

would be expected to be too insensitive to reveal its presence.

The reaction of chromium(111) chloride with tribenzylamine (sect. 2.3.3) gave the 1:1 adduct $CrCl_3 \cdot NBz_3$. Broomhead and Dwyer[124] have reported 1:1 adducts of $CrCl_3$ with 2-2' bipyridyl and 1,10 phenanthroline but in general mono complexes of this type are little known. They[124] prepared the complexes by the reaction of the base with excess anhydrous chromium(111) chloride in boiling dimethylformamide. Both complexes, when first isolated, retained one molecule of solvent as a lattice component. This was readily removed under vacuum at 100^0 - 150^0.

Similarly the mono-tribenzylamine complex, prepared in acetone, was first isolated containing one molecule of acetone, $CrCl_3 \cdot NBz_3 \cdot$ acetone. In this case the solvent was weakly coordinated to the metal as evidenced by the position (1700 cm^{-1}) of the carbonyl stretching frequency in the infrared spectrum. The carbonyl frequency in free acetone occurs at 1712 cm^{-1} and is shifted to lower frequencies upon coordination to a metal cation. The acetone was readily removed by heating the complex in a vacuum at 120^0 - 130^0, and its absence was confirmed by the absence of carbonyl stretching frequency in the infrared spectrum.

The complex showed a strong M-halogen stretching frequency at 340 cm^{-1} and two absorption peaks were clearly visible in the reflectance spectrum at 14.2 kK and 20.2 kK. It was insoluble in most of the usual solvents but dissolved slightly in dimethylformamide and its absorption spectrum showed two peaks unshifted from those in the solid state.

Thus it appears that there is no structural change of the complex in solution. A magnetic moment of 3.82 BM (18^{o} - 20^{o}) indicated that the complex was spin-free and this value compares very well with the values obtained by Broomhead and Dwyer[124] for the 1:1 complexes of $CrCl_3$ with 2-2' bipyridyl and 1,10 phenanthroline.

It is interesting to note that tribenzylamine also reacts with chromium(vi) oxide in acetone to give the complex $CrO_3 \cdot NBz_3 \cdot$Acetone.[125] Similar to the complex of tribenzylamine with chromium(iii) chloride the acetone is readily removed under vacuum to give the 1:1 adduct $CrO_3 \cdot NBz_3$.

During the course of the work on amine complexes a number of complexes of chromium(iii) chloride with simple aliphatic ketones were isolated. As indicated in sect. 1.2.3 surprisingly little information is available on these complexes. This may be due in part to their very hygroscopic nature but is more likely due to the difficulties encountered in their isolation (see sect. 2.3.3.).

Acetone and diethylketone form the complexes $CrCl_3 \cdot 3Me_2CO$ and $CrCl_3 \cdot 3Et_2CO$ but 3-methylbutanone (3.MeBuCO) forms the complex $CrCl_3 \cdot 2(3\text{-MeBuCO})$. Complexes with cyclohexanone and 2-methylcyclohexanone were not isolated in the solid state but coordination of these ketones in solutions of the ligand was evidenced by the shift observed in their carbonyl stretching frequencies, Fig. 3.20.

Due to the very hygroscopic nature of all the complexes the positions of the carbonyl stretching frequencies were measured in solutions of the ligand. These are shown in

Fig. 3.20 and their positions are tabulated in Table 3.26

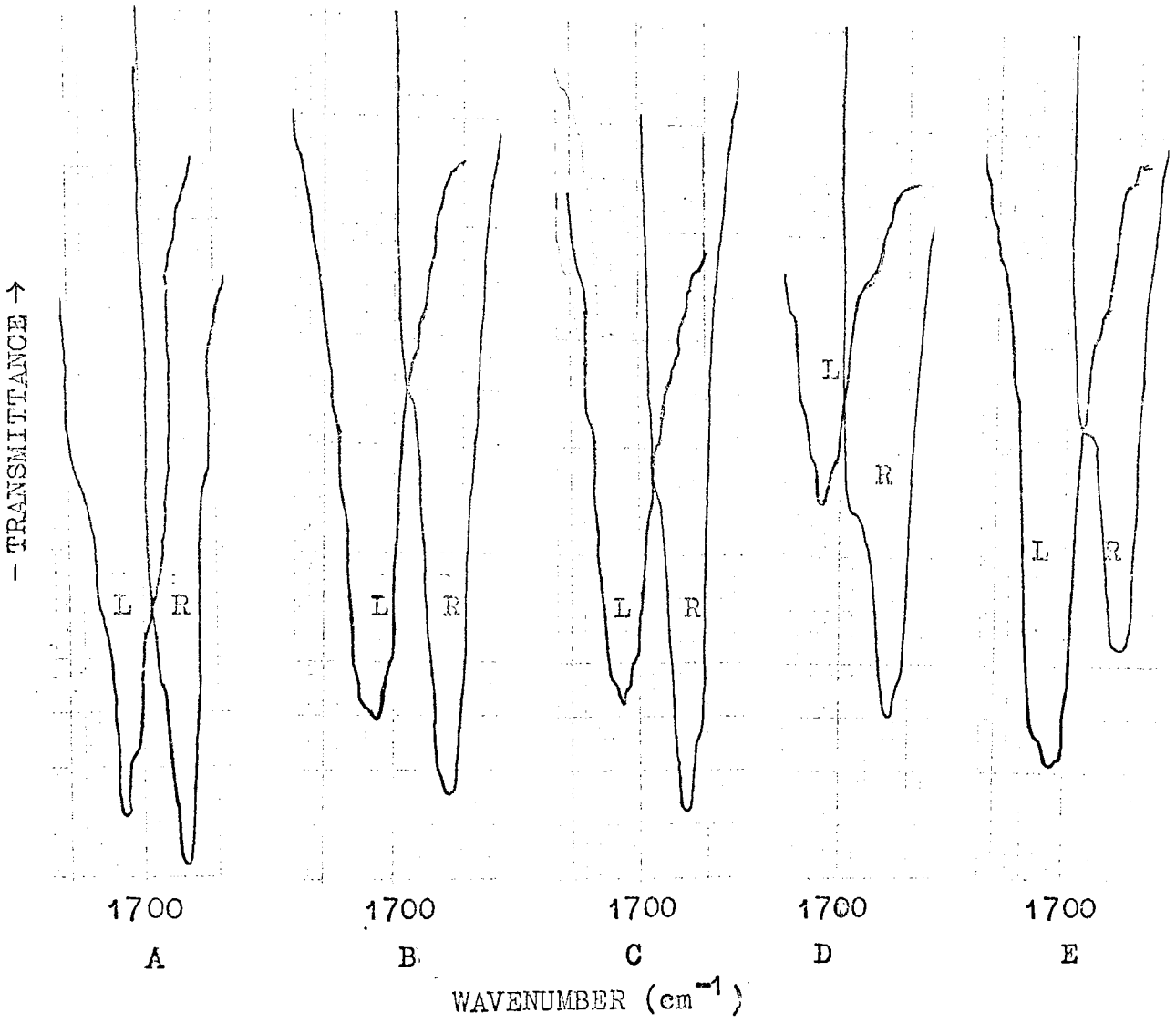


Fig.3.20. Infrared spectra showing the position of the carbonyl stretching frequency in free ketone (L) and on coordination with $CrCl_3$ (R): A, acetone; B, diethylketone; C, 3-methylbutanone; D, cyclohexanone; E, 2-methylcyclohexanone.

TABLE 3.26

Carbonyl Stretching Frequencies* of free ketones and of coordinated ketones (cm^{-1})

	Ketone	Complex	Shift
Acetone	1712	1674	38
Diethylketone	1715	1660	55
3-Methylbutanone	1712	1668	44
Cyclohexanone	1710	1660	50
2-Methylcyclohexanone	1712	1665	47

* Measured in solutions of the ligand.

Reflectance spectra of the complexes $CrCl_3.3Me_2CO$ and $CrCl_3.3Et_2CO$, Fig. 3.21, indicate octahedral stereochemistry for the chromium atom. All three spin-allowed transitions are clearly visible and are assigned to the transitions $^4T_2 \leftarrow {}^4A_2$ (near infrared), $^4T_1 \leftarrow {}^4A_2$ (visible) and $^4T_1(P) \leftarrow {}^4A_2$ (uv). The position of the third spin-allowed band compares very well with the calculated position of this band from ν_1 and ν_2, Table 3.27.

The reflectance spectrum of $CrCl_3.2(3\text{-MeBuCO})$ shows only slight difference to that of the other two ketone complexes. Thus it might be inferred that the complex is octahedrally coordinated, in which case the complex would probably be halogen-bridged similar to the ketone complexes of

titanium(111) chloride.[36]

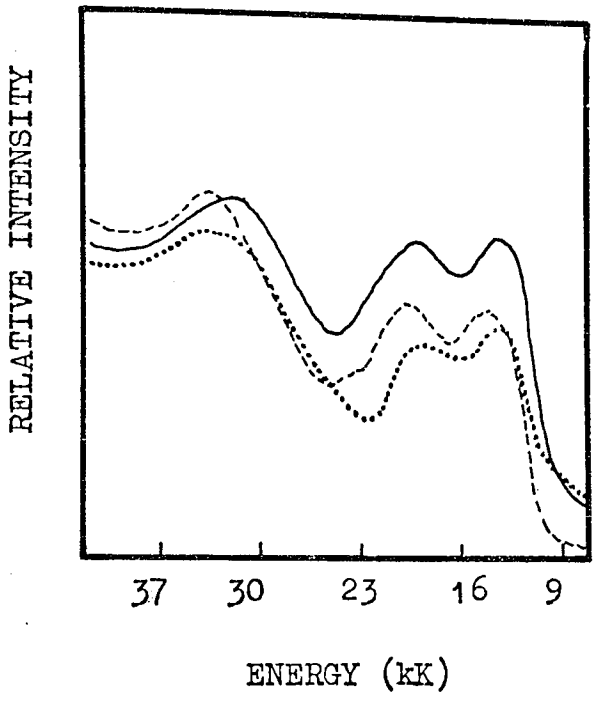


Fig. 3.21. Reflectance spectra of $CrCl_3 \cdot 3Me_2CO$ (———) $CrCl_3 \cdot 3Et_2CO$(-----) and of $CrCl_3 \cdot 2(3\text{-MeBuCO})$ (·····)

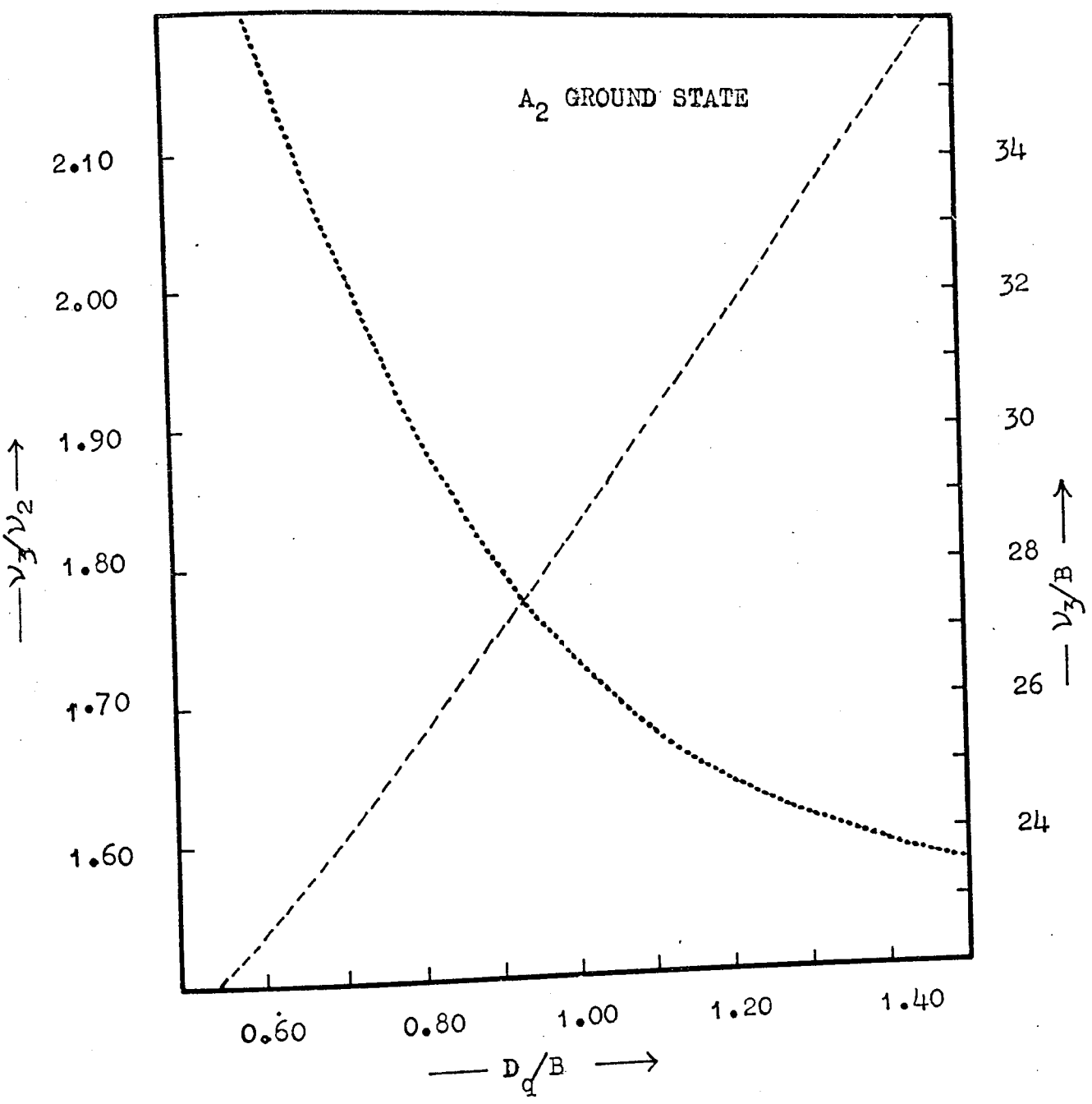
TABLE 3.27

Reflectance spectra for the complexes $CrCl_3 \cdot 3Me_2CO$ and $CrCl_3 \cdot 3Et_2CO$ (abs.max.kK)

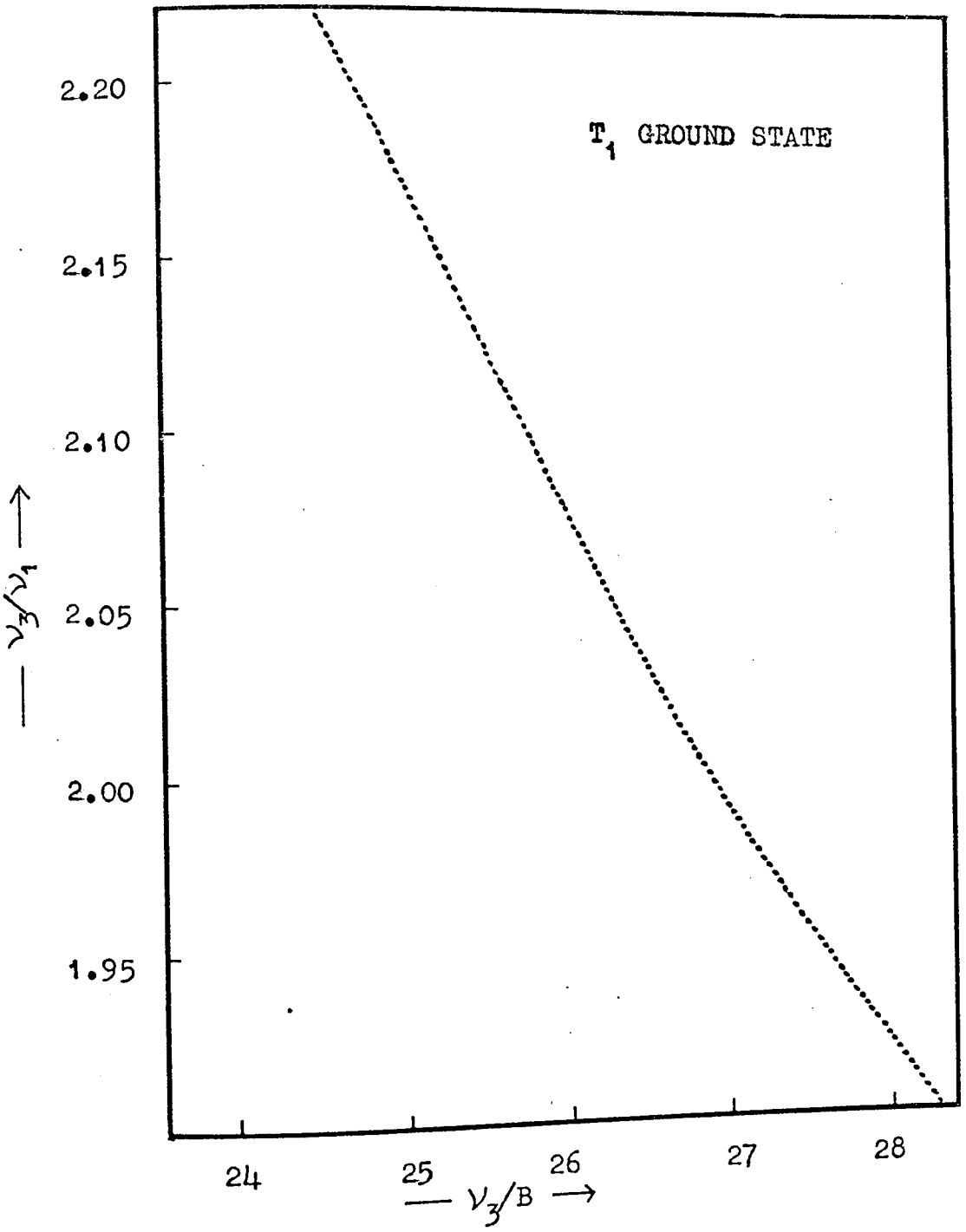
	$^4T_1(P) \leftarrow {}^4A_2$		$^4T_1 \leftarrow {}^4A_2$	$^4T_2 \leftarrow {}^4A_2$
	ν_3		ν_2	ν_1
	Obs.	Calc.		
$CrCl_3 \cdot 3Me_2CO$	31.0	30.8	19.6	14.0
$CrCl_3 \cdot 3Et_2CO$	33.2	31.8	20.1	14.5

APPENDIX

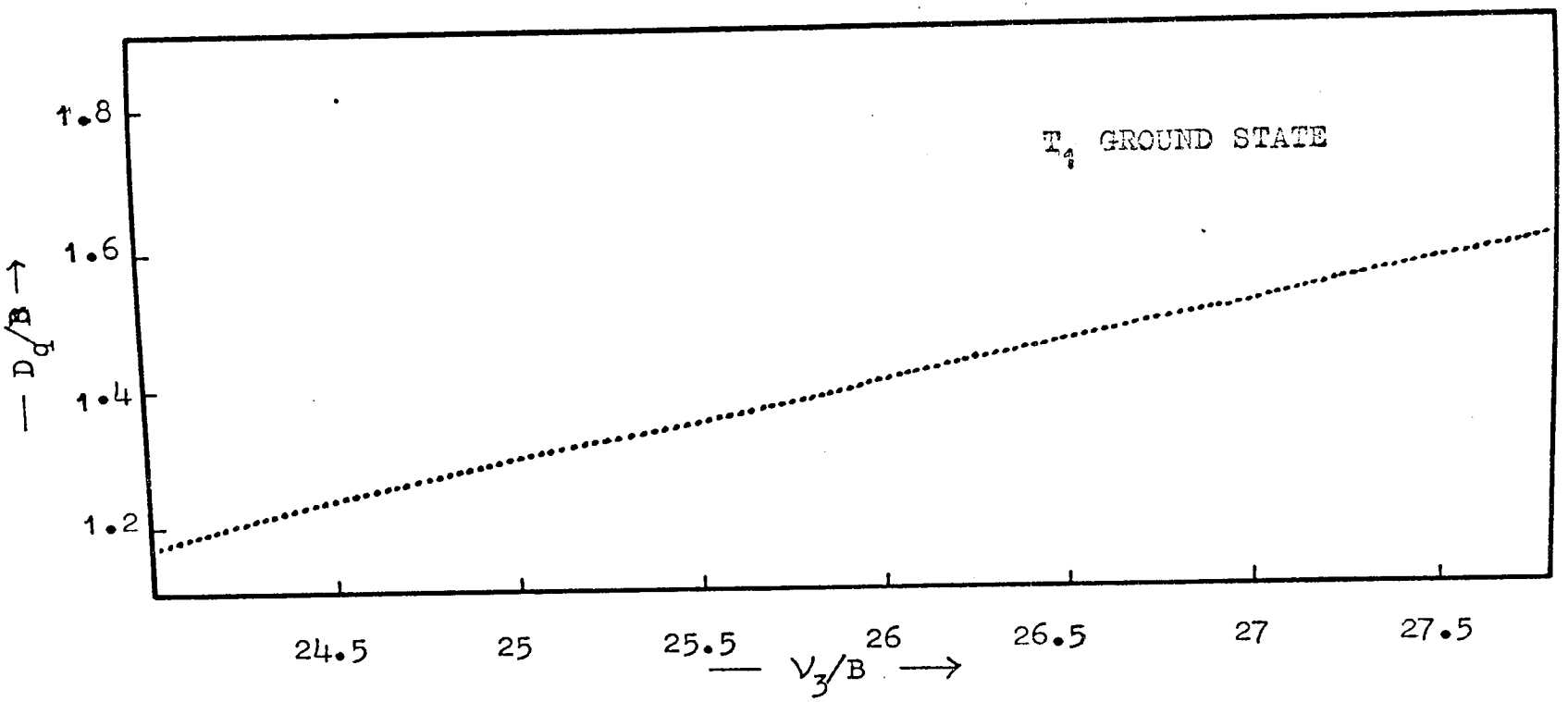
Transition Energy Ratio Diagrams
and
Calculations



The variation of the ratio ν_3/ν_2 (.....) and ν_3/B (-----) with D_q/B for high spin A_2 ground state ions.



The variation of the ratio ν_3/ν_1 with ν_3/B for high spin T_1 ground state ions.



The variation of the ratio D_q/B with ν_3/B for high spin T_1 ground state ions.

CALCULATIONS

$Ni(i\text{-}BuNH_2)_4Br_2$ - A_2 ground state

ν_3 = 26.9 kK, ν_2 = 16.7 kK $\quad \nu_3/\nu_2 = 1.611$

$D_q/B = 1.32$; $\nu_3/B = 33.6$

$10D_q = 10.57$ kK; $B = 0.801$ kK

$Co(s\text{-}BuNH_2)_2(CNS)_2$ - A_2 ground state

ν_3 = 16.7 kK, ν_2 = 8.8 kK $\quad \nu_3/\nu_2 = 1.897$

$D_q/B = 0.81$; $\nu_3/B = 25.7$

$10D_q = 5.26$ kK; $B = 0.649$ kK

$Co(i\text{-}PrNH_2)_4Cl_2$ - T_1 ground state

ν_3 = 17.5 kK, ν_1 = 8.7 kK $\quad \nu_3/\nu_1 = 2.011$

$D_q/B = 1.49$; $\nu_3/B = 26.73$

$10D_q = 9.64$ kK; $B = 0.610$ kK

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