PROPERTIES OF SOME COMPOUNDS OF THE METALS OF MEDIUM ATOMIC WEIGHT WITH HETEROCYCLIC LIGANDS AND THE MORE READILY POLARIZABLE ANIONS

by

BALAVANTRAI GULABBHAI NAIK

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SUMMARY

Part I

The coordination behaviour of 2-benzoylpyridine (PhCOpy) with some transition metal cations was investigated. 2-benzoylpyridine is believed to be a weak-field, bidentate (NO-co-ordination) ligand. Complexes of 2-benzoylpyridine with the perchlorates, chlorides, bromides and iodides of manganese (II), cobalt (II) and nickel (II) are described. Some compounds of zinc (II), cadmium (II) and magnesium (II) were studied for comparison. With the exception of $Mn(PhCOpy)X_2$ (X = Cl or Br) and $Cd(PhCOpy)Cl_2$, all compounds isolated were bis-complexes but the metal ions are six-co-ordinate in all cases.

The complexes, $[Mn(PhCOpy)_2(EtOH)_2](ClO_4)_2$; $[Co(PhCOpy)_2(OH)_2](ClO_4)_2$ and $[Ni(PhCOpy)_2(EtOH)_2](ClO_4)_2$ with ionic perchlorate groups, and $[Co(PhCOpy)_2(ClO_4)_2]$ and $[Ni(PhCOpy)_2(ClO_4)_2]$ with weakly coordinated perchlorate groups were characterised. In nitromethane, it was established that $[Co(PhCOpy)_2X_2]$ (X = Cl or Br) dissociates to the pseudo-tetrahedral complex, $[Co(PhCOpy)X_2]$. The two forms of $Ni(PhCOpy)_2Cl_2$ are believed to be the two isomers of the trans-dichloro-complex. $[Mn(PhCOpy)X_2]$ (X = Cl or Br) and $[Cd(PhCOpy)Cl_2]$ are polymeric. The compounds $M(PhCOpy)_2I_2$, (M = Co, Ni, Zn or Cd) are isomorphous and form isomorphous groups with $M(PhCOpy)_2Cl_2$, [M = Co, Ni(green and yellow)].

Part II

The compounds investigated have all been of one or the other of two types, namely $[(\text{pyridine base})_4 (M)^{2+}(I_3^-)_2]$

(M = first row divalent transition metal ion) or $[(\text{pyridine base})_4 (\text{M}')_2^{2+} (\text{CNSI}_2)_2]$, (M' = Ni(II)) only and pyridine base = pyridine, β-picoline or γ-picoline in both cases. Some I_3^- compounds of manganese(II), iron (II), cobalt (II) and cadmium (II) with pyridine bases were crystallised from acetonitrile. Acetonitrile was retained as an uncoordinated, lattice component. $\text{M}^{II}(\beta\text{-picoline})_4(I_3)_2$ (M = Fe, Mn or Cd) could not be crystallised.

Little information concerning the structure of the above compounds was obtained from physical examinations. The most informative data was derived from the measurement of the magnetic susceptibilities. High-spin octahedral complexes, $[\text{M}(\text{pyridine base})_4 (I_3)_2]$ (M = Mn, Fe or Co) and planar or "tetragonally distorted octahedral" nickel (II) complexes, $\text{Ni}(\text{pyridine base})_4\text{X}_2$ $[\text{X} = I_3^-$ or $(\text{NCS-I}_2)^-]$ were characterised. Study of the magnetic susceptibilities at various temperatures is described for nickel (II) complexes only. The bonding nature of $(\text{CNS-I}_2)^-$, as Ni-NCS-I_2^- is discussed.

The compounds $\text{Cd(py)}_4(I_3)_2$; $\text{Cd}(\gamma\text{-pic})_4(I_3)_2\ 2(\text{CH}_3\text{CN})$, and the polymerisation reactions involved in cadmium - γ-picoline-iodine are described.

The conductivity study of all compounds in nitromethane and in dimethylsulphoxide, and the absorption spectra of I_3^- ions in acetonitrile and in 1,2-dichloroethane are described.

This work was carried out between 1968 and 1972 at The University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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CONTENTS

PART I

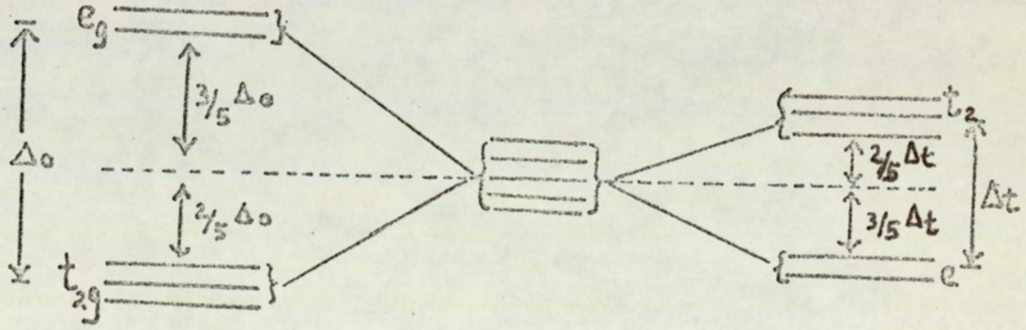
Study of the compounds of 2-Benzoylpyridine with salts of some divalent metals

CHAPTER 1

INTRODUCTION

The properties of d-block transition metal complexes depend on the number of d-electrons in the metal ion and their electrostatic interaction with the surrounding ions, atoms or molecules. In a free ion the d-orbitals are degenerate but this degeneracy will be lifted when the d-electrons interact with the surrounding ions, atoms or molecules (often called ligands).

There are two main theories which explain the change in the d-orbital energies, they are the molecular orbital theory and the crystal field theory. The crystal field theory is described first. In an octahedral environment[1a] of six negative charges, the metal ion has two groups of d-orbitals: the triply degenerate t_{2g} (dxz, dyz and dxy) and the doubly degenerate e_g (dx^2-y^2, dz^2) orbitals. The e_g orbitals are of higher energy than the t_{2g} orbitals. In the tetrahedral environment the t_2 orbitals are of higher energy than the e orbitals (fig.1).



octahedral complexes tetrahedral complexes

Fig.1.

A further splitting of the d-orbital will arise in the octahedral complex by withdrawal of two trans-ligands. (These two trans-ligands lie on the Z-axis). The degeneracy of the e_g orbitals lifts first, the dz^2 orbital becoming more stable than the $d(x^2 - y^2)$ orbital. At the same time the threefold degeneracy of the t_{2g} orbitals is also lifted. The dyz and dzx orbitals will remain equivalent to one another, but they become more stable than the dxy orbital (fig.2).

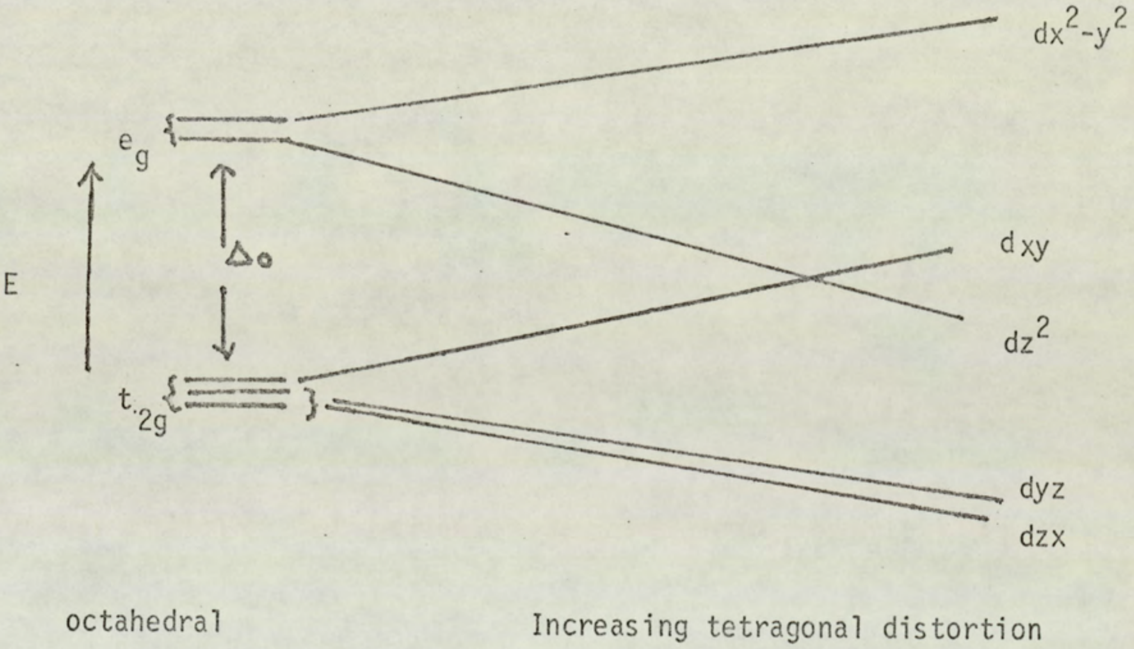


Fig. 2.

The crystal field theory does not provide any information about orbital overlap (or covalent bonding) between the metal ion and the surrounding ligand atoms. Therefore certain modification is required in simple crystal field theory. A modified crystal field theory is that in which the orbital overlap is involved using all parameters of interelectronic interactions. These parameters are namely, the spin-orbit coupling constant, λ, and the interelectronic repulsion parameters which may be the Condon and Shortley parameters (F_2 and

F_4) or the Racah parameters (B and C). They are related:

$$B = F_2 - 5F_4$$

$$C = 35F_4$$

The Racah parameters have a small advantage in that if they are employed, the separation between terms of the same spin-multiplicity within a configuration involve only the parameter B. The separation between states of different multiplicity involve both B and C. With the Condon-Shortley parameters, the separation between terms, even of the same multiplicity, in general are functions of both F_2 and F_4.

The simple molecular orbital is now considered for an octahedral complex (ML_6)[1b]. There are nine valence shell orbitals of the metal ion to be taken for σ and π-bonding. Six of these dz^2, dx^2-y^2, s, px, py and pz have lobes lying along the metal-ligand bond direction and are suitable for σ-bonding, whereas the other three dxy, dxz and dyz are suitable for π-bonding. Figure(3) shows a molecular orbital energy diagram for an octahedral complex formed between the metal ion of the first transition series and six ligands which do not have a π-orbitals. The T_{2g} orbitals do not point at the ligand orbitals and hence are not involved in σ-bonding. They remain unchanged in energy.

If the ligand possess π-orbitals, the effect of π-bonding will vary, depending on the energy of the ligand π-orbitals relative to the energy of metal T_{2g} orbitals and also depending on whether the ligand π-orbitals are filled or empty. Figure 4(a) indicates a situation where the ligands have empty π-orbitals of higher energy than the metal T_{2g} orbitals. The net result is to stabilize the metal T_{2g} orbitals with respect to the metal E_g^* orbitals. In effect,

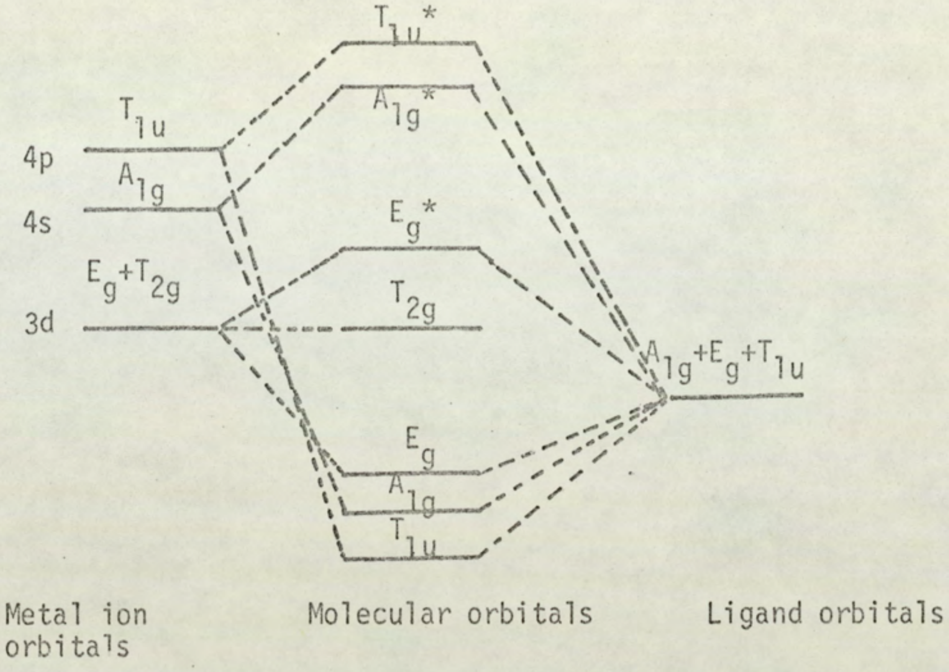


Fig. 3. A qualitative molecular orbital energy level diagram for an octahedral complex between a metal ion of the first transition series and six ligands which do not have π-orbitals

The * mark ~~suggests~~ indicates antibonding

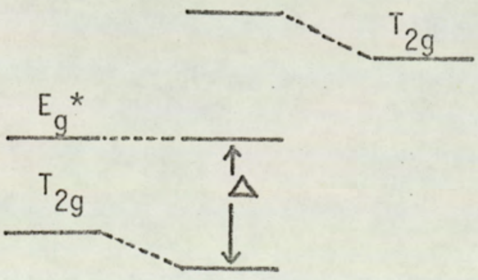


Fig. 4(a)

Ligands have π-orbitals of higher energy than the metal T_{2g} orbitals.

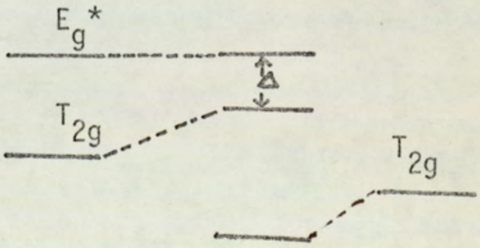


Fig. 4(b)

Ligands have π-orbitals of lower energy than the metal T_{2g} orbitals.

π-interaction gives a great Δ value than the case, if there were only σ-interactions. The second important situation is shown in figure-4(b), in which the ligands possess only filled π-orbitals of lower energy than the metal T_{2g} orbitals. The interaction here destabilizes the T_{2g} orbitals relative to the Eg* orbitals and thus the Δ value becomes less.

There is another important case in which the ligands such as CO, CN or pyridine have both bonding and antibonding p_{π}-orbitals (fig.5).

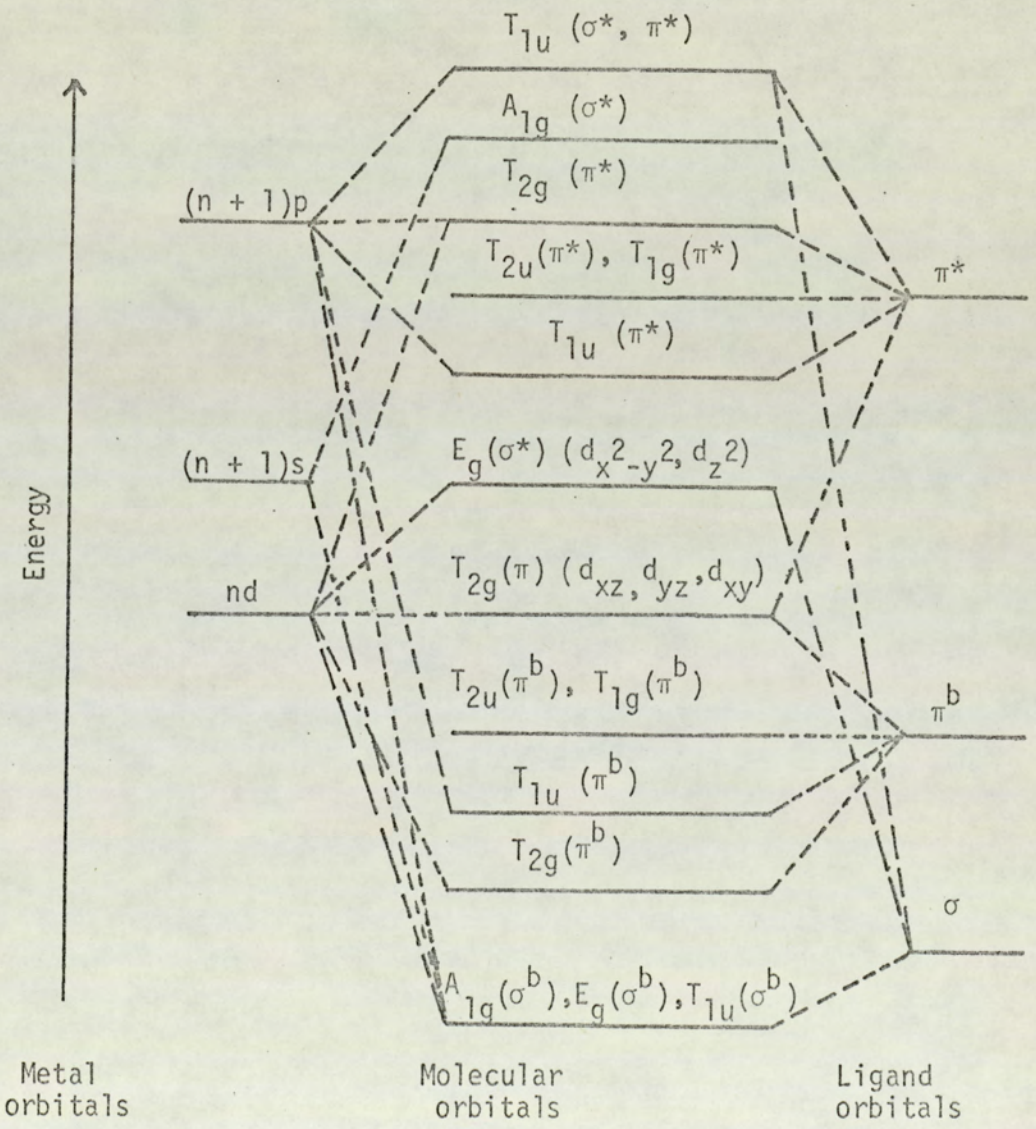


Fig.5. A qualitative molecular orbital diagram for an $M(CO)_6$ or $[M(CN)_6)]^{n-}$ compound. (Ref.2)

The size of Δ is most readily measured spectroscopically by observing the energy of the electronic transition between the t_{2g} and e_g orbitals of the metal ion. The electronic transitions occur at particular wavelengths in the near infrared, visible and near ultraviolet region of the spectrum and they are called d-d transitions. The magnitude of Δ depends on the ligand and on the nature of the transition metal ion.

It is possible to arrange the ligands in order of the magnitude of ligand field (Δ) produced or experienced[3a], such an ordered sequence being known as the 'Spectrochemical series'. The ligands are arranged according to the increase in the Δ value with any constant metal ion and metal ions are arranged in order of increased Δ developed with a constant ligand group. The more common ligands are now placed in the following order:

$$I^- < Br^- < SCN^- \sim Cl^- < NO_3^- < F^- < \text{Urea} \sim OH^- \sim ONO^-$$
$$\sim HCOO^- < (C_2O_4)^{2-} < H_2O < NCS^- < \text{glycine}^- \sim EDTA^{4-}$$
$$< \text{py} \sim NH_3 < \text{en} \sim \text{den} \sim \text{tren} < \text{dipy} < \text{phen} < NO_2^- \ll CN^-$$

The interelectronic repulsion forces between d-electrons are decreased by complex formation. The metal ions or ligand groups can be arranged in a series according to the value of B', the Racah interelectronic repulsion parameter[3b]. In other words the common ligands can be arranged in order of their ability to cause electron-cloud expansion. This order is almost independent of the metal ion. Such a series is called Nephelauxetic series, i.e. cloud expanding series. The series are based on the order in which B' increased toward free ion value B. The ligands are placed in the following order:-

$F^- > H_2O >$ Urea $> NH_3 > (C_2O_4)^{2-} \sim$ en $> NCS^-$

$> Cl^- \sim CN^- > Br^-$

The d-group transition metals have a remarkable ability to form complexes with various ligands such as pyridine,2,2'-bipyridyl, 1,10-phenanthroline and their substituted derivatives. The metal complexes with these heterocyclic amines have high biological activity. The toxicity of 2,2'-bipyridyl and 1,10-phenanthroline metal complexes to mice and rats, bacteriostatic and bacteriocidal properties and action on enzymes have been demonstrated by Dwyer et al[5]. Recently Gillard[6] has found that the rhodium complexes of pyridine and its alkyl substituent show antibacterial activities.

The co-ordination compounds of pyridine, substituted pyridines, quinoline and iso-quinoline with transition metal ions have been studied extensively and accurately in the solid state and in solution in organic solvents[7-16]. The stability of these complexes depends upon many factors such as basicity of ligand, steric interaction, π-bonding and the perturbing effect of the ligand field on the energy of d-electrons.

However, the substituent group on the pyridine ring could produce some differences in the co-ordinating ability of ligand and properties of the metal complex. Thus the substitution of electron attracting groups such as $-COCH_3$, $-CONH_2$, $-COOCH_3$, $-CN$ and $-Cl$ causes the electron density on the pyridine ring to be lowered which results in a weakening of the ligand → metal σ-bond but enhances the tendency to metal → ligand π-bonding, whereas the electron-releasing substituents such as $-CH_3$, $-CH_2OH$ increase the electron density on the pyridine ring and enhance the σ-bond strength and weakening the π-bond.

The position of the substituent in the pyridine ring decides the solid state stereochemistry. The basicity of amine changes such as the position of substituent is altered. For monosubstituted pyridines, the γ-substituents are more basic than the others and thus forming more stable complex with metal ions. The basicity of the ligands as judged by their pKa values (in water at 25°C)[17] are: pyridine:5.22; 2-picoline:5.96; 3-picoline:5.63; 4-picoline:5.98; quinoline:4.58. The π-acceptor properties may be altered significantly by substitution. Nelson[18] et al, explained these properties in terms of the different charge densities and charge distribution in the pyridine ring. Thus in fig.6 , 1*, 3* and 5* positions in the pyridine ring are those of greatest electron density and 2, 4 and 6 positions those of least electron density.

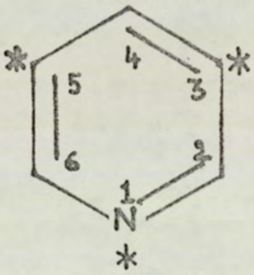


Fig. 6.

So any back co-ordinated charge from metal to the pyridine ring (M→L π-bonding) will be localized mainly on the 2, 4 and 6 positions. And therefore in complexes with 3-picoline, back co-ordination will be inhibited in comparison with 4-picoline and pyridine. It was found that the greater π-acceptor capacity of quinoline and iso-quinoline compared to pyridine may be attributed to the more extensive delocalization of π-electrons in the quinoline and iso-quinoline.

The metal-ligand stretching frequencies are greatly affected by substitution in the pyridine ring. Wong and Brewer[19] found that the frequencies of the Cu(II) complexes (M-Nitrogen stretching frequency) are appreciably changed by the effect of different substituents in the 4-position of the pyridine ring and decrease in the order:

$$CH_3 > CH_2OH > H > COCH_3 > CONH_2 \approx COOCH_3 > CN$$

the M-N stretching frequency in Cu complex:

$$285 > 276 > 268 > 265 > 264 \approx 264 > 243 \quad cm^{-1}$$

Cattalini et al.[20] who worked with Gold(III), pyridine and substituted pyridines pointed out that M-ligand stretching frequencies appear to increase with increase in the base strength of the ligands.

(The pKa values are in order of 4CN-py < py < 3me-py < 4-me-py < 2 -me-py < 3,5-lutidines < 2,6-lutidines < 2,4-lutidines)

The Au-ligand stretching frequency of $AuCl_3$. ligand ($AuCl_3.L$) is taken here and it is in the order:

4CN-py < py < 3-me-py < 4-mepy < 3,5-lutidines < 2,4-lutidines

$$\begin{matrix}249\\227\end{matrix} < \begin{matrix}249\\239\end{matrix} < 234\ cm^{-1} < 286\ cm^{-1} < 289\ cm^{-1} < 306\ cm^{-1}$$

The sterically hindered group present in the pyridine ring may affect the stability of the metal complexes. Nelson et al.[7,8], Buffagni at al.[12-14] and Curran et al.[21] independently found that for α-picoline and α-lutidines the maximum number of moles of ligand which can coordinate to each of the metal ions Co(II) or Ni(II), is limited to two. Since pyridine, β-picoline, γ-picoline,[7,8,21] and β-lutidines[13,14] tend to form stable octahedral complexes of the stoichiometry ML_4X_2 (where M = Co(II) or Ni(II) and X = halide or pseudohalide); the limitation of the stoichiometry of α-picoline and α-lutidines to ML_2X_2 complexes may be largely due to steric effects.

Körös, Nelson et al.[11] examined a series of complexes of Co(II), Ni(II) and Zn(II) with pyridine, mono-substituted pyridine, quinoline and iso-quinoline in chloroform. They found that in the presence of excess of the appropriate amine, the ML_2X_2 (where M = Co(II), X = halide or pseudohalide) exist in equilibrium with the corresponding mononuclear octahedral complex.

The equilibrium process is as follows:

$$\underset{\text{(Tetrahedral)}}{ML_2X_2} + 2L \rightleftharpoons \underset{\text{(Octahedral)}}{ML_4X_2}$$

They also found that higher crystal field stabilization in an octahedral field and lower crystal field stabilization in tetrahedral field for Ni(II) ion than for a Co(II) ion indicates that the tetrahedral complexes of Nickel (II) are less likely than with Co(II) ion.

Moreover the M → L π-bonding is dependent upon the nature of anionic ligand (X) present in the complex. The more polarizable the anionic ligand (X) (e.g. I^-), the more charge is transferred to the metal ion and this enhances the release of non-bonding "d" electrons to antiboding π-orbitals of amine. Their effectiveness in promoting M → L π-bonding is in the order of 1>Br>Cl>NCO>NCS. This order remains the same for complexes with a variety of substituted pyridines.

The position of pyridine in the spectrochemical series is close to that of ammonia, suggesting rather normal σ-bonding[22]. Bostrup and Jørgensen[23] found that the highest number of pyridine ligands introduced with certainty in a complex was four such as in $[Ni(Py)_4(H_2O)_2]^{2+}$ and $NiPy_4Cl_2$ (where py = pyridine). They have estimated that for Nickel (II) nitrate in pyridine, $\Delta = 10{,}200\text{cm}^{-1}$; for $Nipy_4(SCN)_2$, Δ is 10,200 cm^{-1}.

Rosenthal and Drago[24] have estimated a Δ value for the hexakis-pyridine Ni(II) cation. The equilibrium studies on solution of Ni(II) tetrafluoroborate or of Ni(II) perchlorate in nitromethane in the presence of an excess of pyridine, supported an existence of a six co-ordinate pyridine complex of Nickel (II). The spectrochemical parameters, $\Delta = 9850\ \mathrm{cm}^{-1}$ and $\beta = \frac{B'}{B} = 0.83$ were calculated from the spectrum assigned to an octahedral $\mathrm{Ni(py)_6}^{2+}$ species.(B' is the Racah B values for the complex and B is the Racah B values for the free ion. The interelectronic repulsion forces between d-electrons are decreased by complex formation).

The complexes of highly conjugated polyheterocyclic ligands such as 1,10-phenanthroline and 2,2'-bipyridyl are well known for their stereochemistry, their usefulness in analytical chemistry and their ability to stabilize unusual valence states of some of the metals. They can act as moderately good π-acceptors when complexed with transition metal ions[25]. These ligands are very weak bases and usually form monoprotonated species. The pKa[26] values at 25°C are: 2,2'-bipyridyl = 4.5; 1,10-phenanthroline = 4.98.

2,2'-bipyridyl forms high spin tris-complexes with V(II), Mn(II), Co(II), Ni(II) and Cu(II) but forms low spin complexes with Cr(II) and Fe(II)[25,27]. The corresponding 1,10-phenanthroline compounds have similar properties to their 2,2'-bipyridyl analogs. The tris-bipyridyl or phenanthroline-Fe(II) complexes are anomalously high in the stability sequence. The stepwise formation constants for bipyridyl and phenanthroline complexes with divalent metal ions were obtained by Irving and Mellor[26]. They found that, for Fe(II), the trend is $K_1 > K_2 \ll K_3$ and thus Fe(II) tris-bipyridyl and phenanthroline complexes do not follow the usual Irving-Williams order of stabilities.

Jørgensen[28] obtained Δ values of Nickel(II) complexes with ethylenediamine, 2,2'-bipyridyl and 1,10-phenanthroline and suggested that the spectro-chemical position of 2,2'-bipyridyl and 1,10-phenanthroline is higher than ethylenediamine. The Δ values of tris-complexes of ethylenediamine, 2,2'-bipyridyl and 1,10-phenanthroline are:

$\left[Ni(en)_3\right]^{2+}$ = 11,200 cm^{-1}; $\left[Ni(bipy)_3\right]^{2+}$ = 12,650 cm^{-1} and $\left[Ni(phen)_3\right]^{2+}$ = 12,700 cm^{-1}. Palmer and Piper[29] have investigated the polarized crystal spectra of the tris-bipyridyl complexes of Ni(II), Co(II) together with Fe(II), Ru(II) and Cu(II). They obtained values of $\Delta = 12,800\ cm^{-1}$ and Racah parameter $B' = 710\ cm^{-1}$ from the spectrum of the tris-(2,2'-bipyridyl) Nickel(II) ion. This value of the Racah parameter B' in the complex represents a 30% reduction of the free ion value. The tris-(2,2'-bipyridyl) complex of Fe(II) was found to be spin paired having a ground state $^1A_{1g}$.

Robinson, Curry and Busch[30] skilfully used the Δ values of Nickel(II)-trisdimethine complexes as a measure to the critical values for spin pairing in the respective Fe(II) complexes. They concluded that ligands of $\Delta < 12,500\ cm^{-1}$ with respect to Nickel(II) gave spin free Fe(II) complexes while ligands of $\Delta > 12,500\ cm^{-1}$ with respect to Nickel(II) gave spin paired Fe(II) complexes. Thus a critical value for spin pairing in the respective Fe(II) complexes was given by the same authors[30] as $\Delta = 12,500 \pm 800\ cm^{-1}$.

The complexes of a substituted derivative of 2,2'-bipyridyl and 1,10-phenanthroline with various transition metal ions have been studied[4,31,32]. The substitution in 2,2'-bipyridyl and 1,10-phenanthroline may lead to increased stability of the metal complexes due to increased basic strength or π-acceptor properties of the ligand; on the other hand, substitution can lower the stability of complexes because of the ligand's lower basic strengths or by virtue of steric hindrance caused by the substituent groups[4,31,32]. The substitution[4] of the electrophilic bromo or nitro group in the 4,4'-position of bipyridyl or 4,7-position in phenanthroline lowers the base strength and hence reduces the stabilities of the metal complexes In the case of the 2-methylphenanthroline complexes the stability constant drops because of the steric effects of the large methyl groups present in the α-position to the metal-nitrogen bond. Irving and Mellor[32] found that, when the more sterically hindered 2,9-dimethyl-phenanthroline ligand is used, the stability constants become smaller, and K2/K1 for Cu(II) is greater than unity.

2,2'2"-Terpyridyl is believed to be a more highly conjugated amine than 2,2'-bipyridyl[31] and behavesas a weak base. Mono and bis-complexes of 2,2',2"-terpyridyl (terpy) with various metal ions have been studied by Hogg and Wilkins[33]. The Δ value estimated as 12,740 cm^{-1} for $Ni(terpyridyl)_2^{2+}$ ion. They believed that terpyridyl has a larger crystal field strength than bipyridyl. This conclusion was made from the observation of d-d transition bands in bis-(2,2',2"-terpyridyl) Ni(II) ion. Using a recent Δ value obtained by Palmer and Piper for $Ni(bipy)_3^{2+}$ as $\Delta = 12,800\ cm^{-1}$ then terpyridyl and bipyridyl were seen to be of similar ligand field strength. The mono-terpyridyl complex, Fe(terpy) Br_2 was found to be a high spin complex with a moment of 5.10 B.M; whereas the bis-complex of terpyridyl-Fe(II) was known to be a diamagnetic.

The other systems which have been extensively studied [34-40] are those in which 2-pyridyl groups such as 2,2'-bipyridyl are insulated by the introduction of the group, > X.R (where X = N or C and R = H or O). These ligands are: di-2-pyridylamine and di-2-pyridylketone.

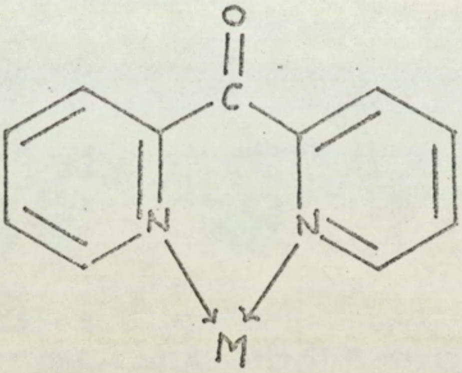
Pyridine nitrogens are co-ordinated to the metal ions in both ligands which form six-membered chelating ring system.

Di-2-pyridylamine is potentially a bidentate ligand. It forms bis-, and tris-complexes with iron(II)[34,35], cobalt(II)[36] and nickel(II)[35,37]. In di-2-pyridylamine, the group -NH is inserted between the two pyridyl groups and this would impede conjugation between the two pyridyl rings. The Δ value estimated as 11,200 cm^{-1} from the spectra of the nickel(II) complexes ($^3T_{2g} \leftarrow {}^3A_{2g}$ band). All iron(II) complexes[34,35], with di-2-pyridylamine are found to be high spin ($^5T_{2g}$ ground state), except for $FeL_2(CN)_2$ compound, which is diamagnetic ($^1A_{1g}$ ground state; L = di-2-pyridylamine). Goodgame and Burbridge[34] obtained Δ value as 12,000 cm^{-1} from the spectra of the iron(II)- di-2-pyridylamine complexes. Thus di-2-pyridylamine produced a stronger ligand field than ethylenediamine, $\Delta = 11{,}400\ cm^{-1}$ for $Fe(en)_3^{2+}$; but a weaker one than 1,10-phenanthroline. (Δ value for $Fe(Phen)_3^{2+}$ is 13,00 cm^{-1})[41].

McWhinnie et al.[35] presented the following spectrochemical series of bivalent metal ions for di-2-pyridylamine:

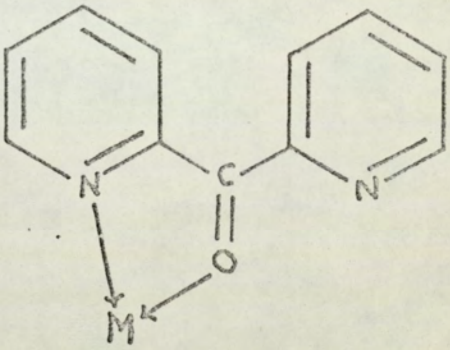
$$Fe(II) > Co(II) \sim Ni(II)$$

Osborn and McWhinnie[38] first considered di-2-pyridylketone (pyCOpy) as a ligand, in which the group > C = O is the insulating group between two pyridyl groups. Since then a number of the transition metal complexes of di-2-pyridylketone have been reported[39,40,42]. Di-2-pyridylketone is believed to be an ambidentate ligand[38]. It can co-ordinate to a metal ion either via nitrogen atoms of the two pyridyl groups (N,N-co-ordination) or nitrogen atom of one pyridyl group and the oxygen atom of the carbonyl group (N,O-co-ordination) figure 7(a) and 7(b).



N,N-coordination

Fig. 7(a)



N,O-coordination

Fig. 7(b)

The N,N-co-ordination and N,O-co-ordination, for di-2-pyridylketone, can be differentiated by observing the position of the carbonyl stretching frequency which shifts characteristically to a lower wave number on co-ordination. Moreover, in di-2-pyridylketone complexes a complication[39] also arises due to the hydration or alcoholation across the ketone double bond (figure 8).

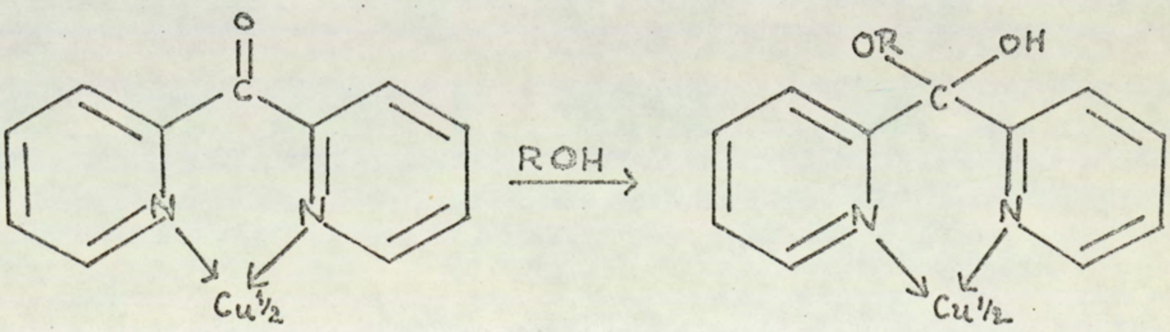


Fig.8.

Morgan[40] compared di-2-pyridylketone with other bidentate ligands such as acetylacetone, salicyclic acid etc., in that all form six-membered ring systems. The similarity of di-2-pyridylketone is found to be more close to an acetylacetone. Both ligands have π-electron systems and are of the same symmetry, C_{2v}.

Copper(II) halide and perchlorate complexes with di-2-pyridylketone have been prepared[38]. The N,N-co-ordination and N,O-co-ordination were observed in Cu(II)-perchlorate complexes with di-2-pyridylketone. One $[Cu(pyCOpy)_2(H_2O)_2](ClO_4^-)_2$ has ionic perchlorate groups and co-ordinated water molecules. $[\nu_3(F_2)$ for ClO_4^- is at ∿ 1100 cm^{-1} and ν(OH) is at 3550 cm^{-1}.$]$[38] The ligand, di-2-pyridylketone, is N,O-co-ordinated. The carbonyl stretching is assigned at 1445 cm^{-1}. Dehydration of the above copper(II) complex affords bis(pyCOpy) copper(II)-perchlorate. The infrared study of this complex suggests that perchlorate groups were co-ordinated $[$for $\nu(ClO_4)$: $\nu_1(A_1)$,952 cm^{-1}; $\nu_6(B_1)$,1055 cm^{-1}; and $\nu_8(B_2)$, 1130 $cm^{-1}]$ [38]. The carbonyl frequency, ν(CO) at 1700 cm^{-1}, indicates a free carbonyl group i.e.N,N-co-ordination.

Feller and Robson[39] found that the complex, $Cu(pyCOpy)_2(H_2O)_2 SO_4$, like other solvated di-2-pyridylketone - Cupric complexes[38] showed a strong band at 1445 cm^{-1*} in its infrared spectrum. The di-2-pyridylketone is suggested to be N,N-chelated in these complexes. They[39] proposed that the disappearance of carbonyl stretching frequency ν(CO), or an inexplicably large shift of carbonyl band in solvated copper(II) complexes, can be attributed to hydration or alcoholation across the ketone double bond:

$$>C=O \;+\; ROH \;\rightarrow\; >C(OH)(OR)$$

The visible absorption spectrum[39] of $Co(pyCOpy)_2Cl_2$ in dimethylformamide solution clearly indicates the presence of a tetrahedral cobalt(II). The maxima at λ max,14900(ε,250) and

16,400*cm^{-1}(ε,190) were assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition. *($1 \times 10^{-6} cm^{-1}$=10 nm).In the presence of an excess of the ligand, di-2-pyridylketone, the complex Co(pyCOpy)$_2$Cl$_2$ exists in equilibrium with the corresponding octahedral complex. The equilibrium process in dimethylformamide is as follows:

$$\underset{\text{Octahedral}}{Co(pyCOpy)_2\,Cl_2} \overset{DMF}{\rightleftharpoons} \underset{\text{Tetrahedral}}{Co(pyCOpy)\,Cl_2 + pyCOpy}$$

In the ketonic ligand, the co-ordination is accompanied by a characteristic shift in the carbonyl stretching frequency to a lower wavenumber in the infrared spectrum. The complexes of many ketonic ligands with various transition metal ions have been reported[43-45]. Scagliavini and Tartarini[43] first used benzophenone as a ligand with transition metal ions when preparing unstable solid TiCl$_4$-benzophenone. The carbonyl stretching frequency in the free ligand, benzophenone, is at 1675 cm^{-1} but when it is complexed with various metal ions, the carbonyl band is shifted to a lower wavenumber: e.g. ν(CO) is at 1550 cm^{-1} in VCl$_4$ $\cdot$ 2phCOph[44]; 1560 cm^{-1} in TiCl$_3$ $\cdot$ 2phCOph[45].

Bridgeland et al.[44] reported a maxima in the diffuse reflectance spectra at 14,300 cm^{-1} ($^2B_{1g} \leftarrow {}^3B_{2g}$) and 20,400 cm^{-1} ($^2A_{1g} \leftarrow {}^2B_{2g}$) and magnetic moment, μ_{eff} = 1.70 B.M. for tetrachloro-bis(benzophenone) vanadium (IV).

The following spectrochemical series with respect to vanadium(IV) have been presented by these workers[44]:

phenanthroline ~ bipyridyl > ethyleneglycoldimethylether > 1,4-dioxan > pyrazine > benzophenone > 2,6-dimethylpyrazine > tetrahydropyran > tetrahydrofuran > Cl .

Fowles et al.[45] prepared complexes of titanium(III)-chloride with ketones of the type $TiCl_3 . 2R_2CO$, where R = CH_3, C_2H_5 or C_6H_5. For all these three ketone-Ti(III) compounds, co-ordination results in an appreciable lowering of the carbonyl stretching frequency: R = Me, ν(CO) was at 1675 and 1560 cm^{-1}* (in free ligand,Me_2CO, ν(CO) was found at 1715 cm^{-1}) Et, 1655 cm^{-1} (Et_2CO, 1720 cm^{-1}*) and Ph, 1560 cm^{-1}* (Ph_2CO,1680 cm^{-1}*). The visible spectra of titanium(III)chloride complexes were reported. The complex $TiCl_3.2Ph_2CO$ has maxima at 15,600 cm^{-1}*and 25,600 cm^{-1}* in the visible region of the spectrum.

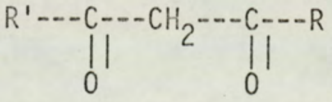
* [Approximate wavelengths of colours: Ultraviolet- <400 mμ; Visible (Violet,400-450 mμ; Blue,450-500 mμ; Green-500-570 mμ; Yellow,570-590 mμ; Orange,590-620 mμ; Red,620-760mμ);Infrared > 760mμ] [51(d)]

*(Note: 1mμ = 1x10^{-7}cm^{-1}= 1 nm)

They[45] presented the following spectrochemical series with respect to titanium(III):

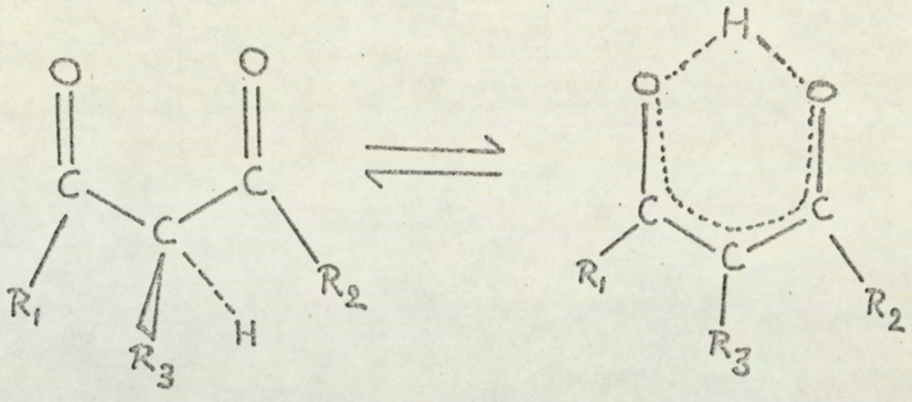
Methylcyanide ∼ ethylcyanide > H_2O > morpholine >
dimethylketone ∼ diethylketone ∼ benzophenone > tetrahydrofuran

Other ketonic ligands of the type X-COR (where X contains a potentially co-ordinate group) have also been used for complex formation, e.g. β-diketones,



$$R'\text{---}\underset{\overset{||}{O}}{C}\text{---}CH_2\text{---}\underset{\overset{||}{O}}{C}\text{---}R$$

. Fackler has reviewed the large number of complexes of β-diketones. β-Di-ketones which have at least one proton on the carbon atom between the carbonyl groups, exhibit keto-enol tautomerism (fig.9).



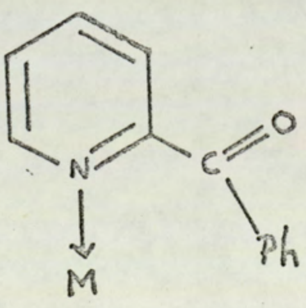
"keto" form "enol" form

Fig.9

The complexes of many ligands are reviewed[46] including benzoylacetone, dibenzoylmethane, acetylacetone, trifluoroacetylacetone etc.

In the present work, metal complexes of 2-benzoylpyridine (PhCOpy) are studied. The ligand, 2-benzoylpyridine is studied since it should provide a good analogue for N,O-co-ordination in di-2-pyridylketone[38], and enable N,O-co-ordination to be recognised by spectroscopic properties.

The 2-benzoypyridine is an ambidentate ligand and may co-ordinate to a metal ion in one of the following three possible ways:



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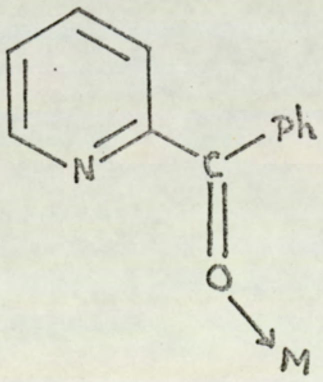

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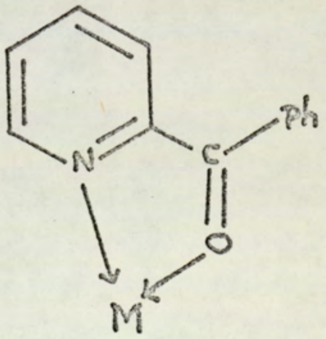


(1) (2) (3)

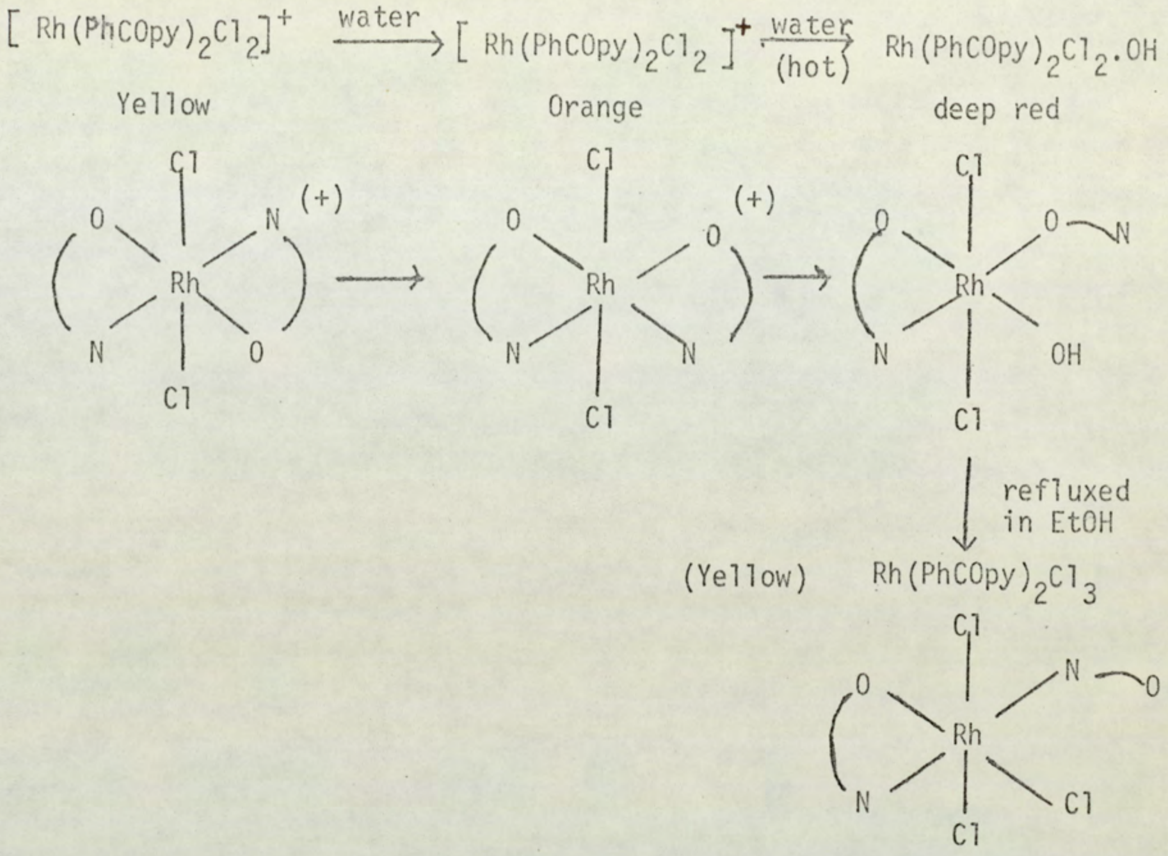
Ph = phenyl group

The above (1) and (2) possibilities were only found in Rh(III) complexes[48]. The mono-dentate (i.e. N-bonded or O-bonded) 2-benzoylpyridine complexes of first transition metal ions were not isolated.

The known complexes of 2-benzoylpyridine will now be described. Hemmerich and Fallab[47] first reported the copper(II) complex of 2-benzoylpyridine in which the molecule was acting as a bidentate ligand. McWhinnie and Osborn[38,48] studied the complexes of copper(II) perchlorate, halides; zinc(II)halide[38] and rhodium(III) complexes[48], with 2-benzoylpyridine. The ligand, 2-benzoylpyridine (PhCOpy) was found to be N,O-co-ordinated in both copper(II) and zinc)II) complexes. The shift in the carbonyl stretching frequency was similar in both zinc(II) and copper(II) and suggested weak interaction between carbonyl group and metal ions. The infrared spectrum of green bis-(2-benzoylpyridine)copper(II) perchlorate suggests the perchlorate groups to be weakly co-ordinated to copper.

Some rhodium (III) complexes with 2-benzoylpyridine (PhCOpy) have been prepared[48]. The complex, $Rh(PhCOpy)Cl_2$, $Rh(PhCOpy)Cl_4$ is formed by the reaction of $RhCl_3$ and 2-benzoylpyridine in ethanol. The cation $(Rh(PhCOpy)_2Cl_2)^+$ has been obtained as perchlorate in yellow and orange isomeric forms, both isomers have trans- chloride ligands. The substitution reaction of the trans-dichlorobis (PhCOpy)Rh(III) has been described by the same authors[48] who suggested that the ligand, 2-benzoylpyridine was found to be co-ordinated to rhodium(III) in all three possible ways (i.e. N,O, -O and N-bonded 2-benzoylpyridine, page 19)

The reaction proceeds via an isomeric form of $(Rh(PhCOpy)_2Cl_2)^+$, as follows:



Some rhodium (III) complexes of other 2-pyridylketones (py-CO.R) have been prepared[49] in which the group, R, has been varied: R = amino phenyl, 2-m-aminobenzoylpyridine ($pyCOPhNH_2$); R = methyl, 2-acetylpyridine(pyCOMe); R = nitrophenyl, 2-m-nitrobenzoylpyridine ($pyCOPhNO_2$). The rhodium(III) complexes of 2-acetylpyridine, 2-m-amino-, and 2-m-nitrobenzoylpyridine were found to be similar to $Rh(PhCOpy)Cl_2 . Rh(PhCOpy)Cl_4$[48]. The conductivity data of these complexes in dimethylformamide solution indicates some ion association in dilute solution. The position of the carbonyl stretching frequency, ν(CO) in each of these complexes suggested that the carbonyl group is co-ordinated to the rhodium(III) cations.

CHAPTER 2

EXPERIMENTAL

(A) CHEMICALS:

The 2-benzoylpyridine used, was obtained from the "KOCH-LIGHT LABORATORIES LTD"., England., and used with no purification. The metal perchlorates and metal iodides (except CdI_2 and ZnI_2) were synthesised in the laboratory.

(B) SOLVENTS:

All solvents were purchased and were purified by standard methods[50]. The purification methods are described on page- 82 in the second part of this thesis.

(C) ANALYSIS:

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

Metals were also analysed gravimetrically, e.g. Nickel as Nickel-dimethylglyoximate, $Ni(C_4H_7O_2N_2)_2$;[51a] and Cobalt as $Co(C_5H_5N)_4(SCN)_2$[51(b)]. Halides (chloride, bromide, iodide) were determined volumetrically by Volhard's method[51(c)].

(D) SPECTRA:

(i) Diffuse Reflectance Spectra:

Diffuse reflectance spectra (30000-4000 cm^{-1})* were recorded for finely powdered specimens against a magnesium oxide (or lithium fluoride) reference using a "UNICAM-SP-700" spectrophotometer with an 'SP-735' diffuse reflectance attachment.

(ii) Solution Spectra:

Solution Spectra (30000-13300 cm^{-1})*, were measured using a Perkin Elmer Spectrophotometer No.137" with 1 cm, 2 cm and 4.0 cm matched silica cells respectively.

(iii) Infrared Spectra (4000 -625 cm^{-1})*:

Perkin Elmer Spectrophotometers "PE-237" and "457" were used to record spectra for paraffin oil mulls.

(iv) Far Infrared Spectra:

Far infrared spectra (to 200 cm^{-1}) were recorded for paraffin oil mulls in cesium iodide supports using a Perkin Elmer Spectrophotometer, "PE-225"

* Note: 10^{-7}cm = 1 millimicron (mμ) = 10^{-9}meter = 1 nm

(E) CONDUCTIVITY:

Molar conductivities of freshly prepared solutions (10^{-3}M) in purified nitromethane were determined with a "Mullard" conductivity bridge, using a standard conductivity cell type E7591/B and cell constant 1.36. The detailed theory and choice of solvent is described in the second part of this thesis,page - 85.

(F) MAGNETISM:

Magnetic susceptibilities were determined by the Gouy method at room temperature. The Gouy tube was calibrated with $Hg[Co(NCS)_4]$ (taking $\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 20°C)[52a]. The tube calibration was checked by measuring the magnetic susceptibility of $[Ni(en)_2S_2O_3]$ for which a value of χ_g equal to $(10.60 \pm 0.1) \times 10^{-6}$ c.g.s. units at 19°C was obtained. This agrees satisfactorily with the literature values[53]. A Stanton Instruments Ltd. balance, model S.M.12 was used. The diamagnetic susceptibility of 2-benzoylpyridine was determined in the laboratory, at room temperature and other diamagnetic corrections were made from Pascal's constants as listed by Figgis and Lewis[52b]. (χ_g for 2-benzoylpyridine = -124.3×10^{-6} c.g.s. units at 24°C). The detailed theory of magnetic susceptibility, its calculation and diamagnetic corrections are described in the second part of this thesis, page 94..

(G) X-RAY POWDER PHOTOGRAPHY

X-Ray powder, photographs were taken using Cukα radiation. (The "SOLUS-SCHALL", London generator and "Phillips" camera and X-ray tubes were used.)

CHAPTER 3

Nickel(II), Cobalt(II) and Manganese(II) halides and perchlorate complexes with 2-benzoylpyridine and also some new complexes of Zinc(II), Cadmium(II) and Magnesium(II) halides with 2-benzoylpyridine

In this chapter the preparations, characterisations, and the spectroscopic and magnetic properties are presented for the following new nickel(II), cobalt(II) and manganese(II) complexes. Some complexes of Cd(II), Zn(II) and Mg(II) are also described.

Complex	Preparation	Solid State & solution data	Discussion of structure
$Ni(PhCOpy)_2(ClO_4)_2$	p 26	Table 1 & 5	p 46
$Ni(PhCOpy)_2Cl_2$(green)	p 27	"	p 51
$Ni(PhCOpy)_2Cl_2$(yellow)	p 27	"	p 51
$Ni(PhCOpy)_2Br_2$	p 27	"	p 53
$Ni(PhCOpy)_2I_2$	p 28	"	p 53
$Co(PhCOpy)_2(H_2O)_2(ClO_4)_2$	p 28	Table 2 & 6	p 55
$Co(PhCOpy)_2(ClO_4)_2$	p 29	"	p 55
$Co(PhCOpy)_2Cl_2$	p 29	"	p 56
$Co(PhCOpy)_2Br_2$	p 29	"	p 56
$Co(PhCOpy)_2I_2$	p 30	"	p 56
$Mn(PhCOpy)_2(EtOH)_2(ClO_4)_2$	p 30	Table 3 & 4	p 60
$Mn(PhCOpy)Cl_2$	p 31	"	p 60
$Mn(PhCOpy)Br_2$	p 31	"	p 60
$Mn(PhCOpy)_2I_2$	p 31	"	p 60
$Zn(PhCOpy)_2I_2$	p 32	Table 8	p 61

Complex	Preparation	Solid State & solution data	Discussion of structure
$Cd(PhCOpy)Cl_2$	p 32	Table 8	p 61
$Cd(PhCOpy)_2I_2$	p 32	"	p 61
$Mg(PhCOpy)_2I_2(H_2O)_2$	p 32	"	p 61

PREPARATIONS

1. Nickel(II) complexes of 2-benzoylpyridine:

Diperchloratobis-(2-benzoylpyridine)nickel(II)

Nickel(II) perchlorate hexahydrate (2m.moles,0.53g) was heated under reflux for 30 minutes with 2,2'-dimethoxypropane (10 ml). 2-Benzoylpyridine (4m.moles,0.73g) in 2,2'-dimethoxypropane (5ml) was added and the solution was heated under reflux for a further 30 minutes. The green crystals deposited from the solution after one hour were filtered and washed with fresh solvent. The product was dried over P_4O_{10} in a vacuum desiccator. Yield of green solid: 1.3g

(Found: C,46.3; H,2.7; N,4.7; Ni,9.42%; $C_{24}H_{18}Cl_2N_2NiO_{10}$ requires:C,46.2; H,2.9; N,4.5; Ni,9.40%)

If ethanol was used as solvent, the perchlorate complex was obtained with co-ordinated solvent molecules. Thus a green diethanolodiperchlorato bis-(2-benzoylpyridine) nickel(II) was prepared.

(Found: C,46.5; H,4.38; N,3.95; Ni,8.28%. $C_{28}H_{30}Cl_2N_2NiO_{12}$ requires:C,46.9; H,4.29; N,3.90; Ni,8.20%)

However treatment of this compound at 137°C in vacuo over 72 hours afforded diperchloratobis-(2-benzoylpyridine) nickel(II)

Dichlorobis-(2-benzoylpyridine)nickel(II).(green form):

2-Benzoylpyridine(7.3g, 40m.moles) in cold ethanol (50 ml) was added to nickel(II) chloride hexahydrate (20 m.moles,4.8g) in cold ethanolic solution (50 ml). The resulting solution was refluxed for half an hour. After the solution had refluxed for half an hour, it was allowed to cool and the green solid was filtered off and washed with fresh solvent (ethanol) and dried over P_4O_{10} in a vacuum desiccator. Yield of the green solid: 6.4g.

(Found: C,58.5; H,3.8; N,5.6; Ni,11.90; Cl,14.5%. $C_{24}H_{18}Cl_2N_2NiO_2$ requires: C,58.2; H,3.7; N,5.7; Ni,11.84; Cl,14.3%)

Dichlorobis-(2-benzoylpyridine)nickel(II).(yellow form):

Dissolution of above green solid in ethanol affords a green solution which becomes yellow on addition of benzene. If the volume of the solution is reduced, a yellow solid dichlorobis-(2-benzoylpyridine)nickel(II) separates out.

(Found: C,58.2; H,3.8; N,5.6; Ni,11.89; Cl,14.3% $C_{24}H_{18}Cl_2N_2NiO_2$ requires: C,58.2; H,3.7; N,5.7; Ni,11.84; Cl,14.3%)

This yellow isomeric form was stable for many months after removal of the free ligand. However, contamination by the ligand resulted in reversion to the green form. The isomerisation reaction (yellow → green) was rapid in molten 2-benzoylpyridine.

Dibromobis-(2-benzoylpyridine)nickel(II)

2-Benzoylpyridine(7.3g, 40m.moles) in cold ethanol (50 ml) was added to nickel(II) bromide trihydrate (4.5g, 20 m.moles) in cold ethanolic solution (50 ml). The resulting solution was refluxed for half an hour and the red solid was filtered off and washed with ethanol.

The compound was dired over P_4O_{10} in vacuum desiccator. Yield of red solid: 9.0g.

(Found: C,49.1; H,3.2; N,4.7; Ni,10.23; Br,27.0% $C_{24}H_{18}Br_2N_2NiO_2$ requires: C,49.3; H,3.1; N,4.8; Ni,10.03, Br,27.3%)

Diiodobis-(2-benzoylpyridine)nickel(II)

This compound was prepared as above bromo-compound. The yield of dark green solid, 12.5g.

(Found: C,42.5; H,2.8; N,4.4; Ni,8.70; I,37.50% $C_{24}H_{18}I_2N_2NiO_2$ requires: C,42.4; H,2.7; N,4.1; Ni,8.64; I,37.40%)

2. Cobalt(II) complexes of 2-benzoylpyridine:

Diaquobis-(2-benzoylpyridine)cobalt(II)perchlorate

Cobalt(II)perchlorate hexahydrate (2m.moles, 0.54g) was heated under reflux for 30 minutes with 2,2'-dimethoxypropane (10 ml). 2-Benzoylpyridine (4m.moles, 0.73g) in 2.2'-dimethoxypropane (5 ml) was added and the resulting solution was heated under reflux for a further 30 minutes. Bright orange crystals deposited from the solution after one hour, were filtered off and washed with fresh solvent. The orange solid was dried over P_4O_{10} in a vacuum desiccator. Yield = 1.6g.

(Found: C,42.8; H,3.7; N,4.3; Co,9.0% $C_{24}H_{22}CoCl_2N_2O_{12}$ requires: C,43.6; H,3.4; N,4.3; Co,8.93%)

If ethanol was used as solvent, the perchlorate complex was obtained with co-ordinated solvent molecules. Thus an orange diethanolodiperchloratebis-(2-benzoylpyridine)cobalt(II) was prepared.

(Found: C,46.95; H,3.96; N,3.82; Co,8.10% $C_{28}H_{30}CoCl_2N_2O_{12}$ requires: C,49.90; H,4.19; N,3.91; Co,8.23%)

However treatment of the both diquo- and diethanolo-cobalt(II) perchlorate compounds at 137^{o}C in vacuo over 72 hours afforded the yellow-orange solid, diperchloratobis-(2-benzoylpyridine) cobalt(II) with a weight loss corresponding to the loss of two mole of water or ethanol respectively.

Dichlorobis-(2-benzoylpyridine)cobalt(II)

2-Benzoylpyririne (7.3g, 40m.moles) in cold ethanol (50 ml) was added to cobalt(II) chloride hexahydrate (20 m.moles, 4.76g) in cold ethanolic solution (50 ml). The resulting solution was refluxed for half an hour. After the solution had refluxed, it was allowed to cool and the yellow-brown solid was filtered off, washed with ethanol and finally dried over P_4O_{10} in a vacuum desiccator. Yield of yellow-brown solid, 7.1g.

(Found: C,57.8; H,3.8; N,5.8; Co,11.85; Cl,13.9% $C_{24}H_{18}CoCl_2N_2O_2$ requires: C,58.0; H,3.7; N,5.7; Co,11.90; Cl,14.3%)

Dibromobis-(2-benzoylpyridine)cobalt(II)

This compound was prepared as the above chloro-compound. Yield of yellow-brown solid: 10.5g.

(Found: C,49.2; H,3.3; N,4.9; Co,10.3; Br,26.0% $C_{24}H_{18}Br_2CoN_2O_2$ requires: C,49.3; H,3.1; N,4.8 Co,10.10; Br,27.3%)

In a similar preparation using acetone as a solvent and an anhydrous cobalt(II)bromide afforded a green solid,$Co(PhCOpy)_2Br_2\cdot$acetone. Yield of the green solid,4.49g.

(Found: C,49.9; H,4.0; N,4.2; Co,9.65; Br,24.8% $C_{27}H_{24}Br_2CoN_2O_3$ requires: C,50.0; H,3.8; N,4.4; Co,9.8; Br,24.8%)

Infrared evidence supported the presence of acetone, $\nu_{C=O}$ (acetone) occured at 1713 cm^{-1}. However treatment of acetone adduct at 137^{o}C in vacuo over 1 hour afforded the yellow-brown solid, $Co(PhCOpy)_2Br_2$; with a weight loss corresponding to the loss of one mole of acetone. The infrared spectrum of this compound showed no band at 1713 cm^{-1}.

(Found: C,49.2; H,3.21; N,4.5; Co,10.20; Br,26.5% $C_{24}H_{18}Br_2CoN_2O_2$ requires: C,49.3; H,3.10; N,4.8; Co,10.10; Br,27.3%)

Diiodobis-(2-benzoylpyridine)cobalt(II)

This compound was prepared as above chloro-compound. A dark-brown solid was obtained. Yield: 12.2g.

(Found: C,42.0; H,2.7; N,4.5; Co,8.81; I,37.2% $C_{24}H_{18}CoI_2N_2O_2$ requires: C,42.40; H,2.67; N,4.12; Co,8.76; I,37,37%)

3. Manganese(II) halide and perchlorate complexes with 2-benzoylpyridine:

Diethanolobis-(2-benzoylpyridine)manganese(II)perchlorate

2-Benzoylpyridine(40m.moles,7.3g) in cold ethanol (50 ml) was added to manganese(II) perchlorate hexahydrate (20m.moles,5.26g) in cold ethanolic solution (50 ml). The resulting solution was refluxed for half an hour. After that, it was allowed to cool and poured into an evaporating dish. The dish was then placed over P_4O_{10} in a vacuum desiccator and the solution was allowed to evaporate slowly under vacuum. Orange crystals were formed after one week, which were dried further to remove free solvent. Yield of an orange solid: 10.8g

(Found: C,46.9; H,4.18; N,3.93; Mn,7.5% $C_{28}H_{30}Cl_2MnN_2O_{12}$ requires: C,47.2; H,4.25; N,3.98; Mn,7.7%)

Diiodobis-(2-benzoylpyridine)manganese(II)

2-Benzoylpyridine (40m.moles,7.3g) in cold ethanol (50 ml) was added to manganese(II) iodide tetrahydrate (20 m.moles,7.6g) in an ethanolic solution (50 ml). The resulting solution was refluxed for half an hour. On the solution being cooled, diethylether was used to induce cystallisation. The red-brown crystals were filtered off, washed with diethylether and dried over P_4O_{10} in a vacuum desiccator. Yield of red solid: 9.8g.

(Found: C,42.6; H,2.7; N,4.1; Mn,8.25; I,37.8% $C_{24}H_{18}I_2MnN_2O_2$ requires: C,42.7; H,2.7; N,4.2; Mn,8.13; I,37.6%)

The following manganese(II) complexes were isolated in metal to ligand ratio of 1:1 only. All attempts made to prepare metal to ligand ratio of 1:2 resulted in formation of only 1:1 complexes.

Dichloromono-(2-banzoylpyridine)manganese(II):

2-Benzoylpyridine (20 m.moles 3.66g) in cold ethanol was added to manganese(II)chloride tetrahydrate (3.96g, 20 m.moles). The resulting solution was refluxed for half an hour and was allowed to cool. Diethylether was used to induce crystallisation. The yellow crystals obtained, were filtered off, washed with diethylether and dried over P_4O_{10} in a vacuum desiccator. Yield of yellow solid: 6.1g.

(Found: C,46.3; H,3.1; N,4.3; Mn,18.1; Cl,23.0% $C_{12}H_9Cl_2MnNO$ requires:C,46.5; H,3.0; N,4.5; Mn,17.77;Cl,22.9%)

Dibromomono-(2-benzoylpyridine)manganese(II):

A similar procedure was used as outlined in the above chloro-compound of manganese(II). Yield of the yellow solid: 6.4g.

(Found: C,36.6; H,2.4; N,4.1; Mn,14.0; Br,40.1% $C_{12}H_9Br_2MnNO$ requires: C,36.2; H,2.3; N,4.2; Mn,13.8; Br,40.2%.

4. Zinc(II), Cadmium(II) and Magnesium(II) complexes with 2-benzoylpyridine

The general procedure which was outlined for nickel(II) and cobalt(II) complexes was used for the preparation of the following compounds:

Diidobis-(2-benzoylpyridine)zinc(II):

Yield of the yellow solid: 10.5g.

(Found: C,42.30; H,2.42; N,4.20; I,36.96; $C_{24}H_{18}I_2N_2O_2Zn$ requires: C,42.0; H,2.65; N,4.12; I,37.01%)

Diiodobis-(2-benzoylpyridine)cadmium(II):

Yield of the yellow solid: 12.8g.

(Found: C,39.2; H,2.37; N,3.81; Cd,15.2; I,34.7% $C_{24}H_{18}CdI_2N_2O_2$ requires: C,39.33; H,2.48; N,3.86; Cd,15.34; I,34.64%)

Diaquobis-(2-benzoylpyridine)magnesium(II)iodide:

Yield of the yellow solid: 8.3g.

(Found: C,42.2; H,3.4; N,4.1; I,38.0% $C_{24}H_{22}I_2MgN_2O_4$ requires: C,42.3; H,3.3; N,4.1; I,37.5%)

Dichloromono-(2-benzoylpyridine)cadmium(II):

In this complex, all attempts made to prepare metal to ligand ratio of 1:2 resulted in the formation of 1:1 complex only.

Yield of the white solid: 9.0g.

(Found: C,38.8; H,2.31; N,3.80; Cl,24.4; Cd,30.42% $C_{12}H_9CdCl_2NO$ requires: C,39.3; H,2.48; N,3.82; Cl,24.35;Cd,30.60%).

RESULTS

Solid state data for the complexes of 2-benzoylpyridine with nickel(II), cobalt(II) and manganese(II) are described in Tables 1, 2 and 3 respectively. Solid state data for Cd(II),Zn(II) and Mg(II) complexes of 2-benzoylpyridine are described in Table 8. Solution spectra and conductivity measurements for the manganese(II), nickel(II) and cobalt(II) complexes are given in Tables 4,5 and 6 respectively. Figure -10 and Table 7 show the effect of addition of an excess of 2-benzoylpyridine to a nitromethane solution of dibromobis-(2-benzoylpyridine)cobalt(II).

X-Ray powder photographs are given on pages-44 & 45 and its data (d-spacings measurements) are given in Tables 9 and 10.

Figure -13 shows the ionic and weakly co-ordinated perchlorate groups in nickel(II) and cobalt(II) complexes of 2-benzoylpyridine.

TABLE 1

Solid state data for complexes of Nickel(II)with 2-Benzoylpyridine

Complex	†Magnetic moment		Infrared spectra (in cm^{-1}) §			Diffuse Reflectance spectrum (maxima in cm^{-1})§
	μ_{eff} B.M.	Temp °C	ν(CO)	ν(MX)	ν(ClO$_4$)	
$Ni(PhCOpy)_2(ClO_4)_2$ (Green)	3.0	21.6	1614	-	1132_s 1037_s 915_{ms}	$24,400_{sh}$; 15,800; 10,400.
$Ni(PhCOpy)_2Cl_2$ (Green)	3.23	18.6	1615	238_s	-	24,700; 14,700; $12,200_{sh}$ 8,800.
$Ni(PhCOpy)_2Cl_2$ (Yellow)	3.04	19.5	1614	261^*_s	-	$24,800_{sh}$; $22,900_{sh}$ 14,600; 9,000.
$Ni(PhCOpy)_2Br_2$ (Red)	3.16	21.2	1615) 1605)	-	-	28,500; $25,400_{sh}$ 19,600; 9,700.
$Ni(PhCOpy)_2I_2$ (Dark-green)	3.17	20.0	1618) 1608)	-	-	24,600; 16,200; 9,400

s - strong; ms - medium strong; sh - shoulder

* Uncertain due to ligand absorption in this region

§ 1×10^4 cm^{-1} = 1000 nm

† The positive values of μ are obtained for paramagnetic substances.

TABLE 2

Solid state data for complexes of cobalt(II) with 2-Benzoylpyridine

Complex	†Magnetic moment		Infrared spectra (in cm^{-1}) §			Diffuse Reflectance spectrum
	μ_{eff} B.M.	Temp. ^{o}C	$\nu(CO)$	$\nu(MX)$	$\nu(ClO_4)$	(maxima in cm^{-1})§
$[Co(PhCOpy)_2(H_2O)_2]$ $(ClO_4)_2$ (Orange)	4.30	21.4	1620	-	1117_s	29,700; 9,500.
$Co(PhCOpy)_2Cl_2$ (Yellow-brown)	5.18	21.0	1610	249_s	-	23,600; 20,100; 17,000; 9,500.
$Co(PhCOpy)_2Br_2$ (Yellow-brown)	4.85	21.7	1615	-	-	29,800; 25,700 23,500; $19,700_{sh}$; 16,500; $14,500_{sh}$; 9,400.
$Co(PhCOpy)_2Br_2\cdot$ acetone (Green)	5.00	21.6	1713) 1630)	-	-	23,000; 16,900; 13,900.
$Co(PhCOpy)_2I_2$ (Dark-brown)	4.56	21.0	1615	-	-	26,700; 22,800; $18,400_{sh}$;$15,900_{sh}$

s - Strong sh - shoulder

§ 1×10^6 cm^{-1} = 10 nm and 1×10^4 cm^{-1} = 1000 nm

† The positive values of μ are obtained for paramagnetic substances.

TABLE 3

Solid state data for complexes of manganese(II) with 2-Benzoylpyridine

Complex	†Magnetic moment		Infrared spectra (in cm^{-1}) §			Diffuse Reflectance spectra
	μ_{eff} B.M.	Temp ^{o}C	$\nu(CO)$	$\nu(MX)$	$\nu(ClO_4)$	(maxima in cm^{-1})§
$Mn(PhCOpy)Cl_2$ (Yellow)	6.78	21.7	1630	267^{*}_{m} 250_{s} 238_{s}		29,300; $23,500_{sh}$;
$Mn(PhCOpy)Br_2$ (orange-yellow)	6.64	21.6	1620	-	-	29,500; $27,700_{sh}$; 23,200; $16,500_{sh}$;
$Mn(PhCOpy)_2I_2$ (Red-brown)	5.63	21.0	1632_{sh} 1625_{sh} 1620	-	-	27,000; $20,700_{sh}$; 16,600.
$[Mn(PhCOpy)_2(EtOH)_2](ClO_4)_2$ (Orange-yellow)	6.11	21.8	1622	-	1095_{b}	29,200; 24,000; 16,300.

s - strong, m - medium, b - broad, sh - shoulder

* Uncertain due to ligand absorption in this region.

§ 1×10^6 cm^{-1} = 10 nm and 1×10^4 cm^{-1} = 1000 nm.

† The positive values of μ are obtained for paramagnetic substances.

TABLE 4

Solution spectra and conductivities of Manganese(II)complexes of 2-Benzoylpyridine

Complex	Solvent	Solution spectra (Maxima in cm^{-1})§	†Conductivity Data Λ_M(in 10^{-3}M) MeNO$_2$	Temp ^{o}C
Mn(PhCOpy)Cl_2	Nitro-methane	Insoluble in nitromethane	-	23^{o}C
Mn(PhCOpy)Br_2	"	27,700(150)*	20	22.5
Mn$(PhCOpy)_2I_2$	"	25,600(860); 16,900$_{sh}$(50)	34	23.0
$[Mn(PhCOpy)_2(EtOH)_2](ClO_4)_2$	"	24,900(30)	156	23.0

TABLE 5

Solution spectra and conductivities of Nickel(II)complexes of 2-Benzoylpyridine

Complex	Solvent	Solution spectra (Maxima in cm^{-1})§	†Conductivity Data Λ_M(in 10^{-3}M) MeNO$_2$	Temp ^{o}C
$[Ni(PhCOpy)_2](ClO_4)_2$	Nitro-methane	16,000(17)*	159	19.0
$Ni(PhCOpy)_2Cl_2$ (Green)	"	26,300(410); 14,300(34)	6	19.5
$Ni(PhCOpy)_2Cl_2$ (Yellow)	"	26,300(400); 14,200(31)	8	19.3
$Ni(PhCOpy)_2Br_2$	"	26,100(610); 14,400(31)	36	19.0
$Ni(PhCOpy)_2I_2$	"	24,600(190); 16,450(100)	76	19.0

Notes for Table 4&5.

* Apparent extinction coefficient calculated from observed optical density and total concentration of metal.

§ 1×10^{6} cm^{-1} = 10 nm and 1×10^{4} cm^{-1} = 1000 nm.

† Λ_M = Molar conductivity = Ohm^{-1} $mole^{-1}$ cm^{2}.

TABLE 6

Solution spectra and conductivities of cobalt(II)complexes of 2-Benzoylpyridine

Complex	Solvent	Solution Spectra (maxima in cm^{-1})§	Conductivity Data	
			† Λ_M (in 10^3M) $MeNO_2$	Temp ^oC
$[Co(PhCOpy)_2(H_2O)_2](ClO_4)_2$	Nitro-methane	26,200(1030); 19,300(55)*	137	22.0
$Co(PhCOpy)_2Cl_2$	"	26,200(690); 16,900(160) 16,000(120); 15,000(180)	21	21.8
$Co(PhCOpy)_2Br_2$	"	25,800(930); $17,500_{sh}(125)$ 16,400(170); 15,200(160) 14,500(175)	27	22.0
" "	chloro-form	24,200(940); 17,700(130)	-	-
$Co(PyCOpy)_2Br_2\cdot$ acetone	"	24,300(930); 17,900(130)	-	-
$Co(PhCOpy)_2I_2$	nitro-methane	24,900(15) $15,100_{sh}(62)$ $14,100_{sh}(75)$	54	22.0

* Apparent extinction coefficient calculated from observed optical density and total concentration of metal.

§ $1 \times 10^6\ cm^{-1}$ = 10 nm and $1 \times 10^4\ cm^{-1}$ = 1000 nm.

† Λ_M = Molar conductivity = $Ohm^{-1}\ mole^{-1}\ cm^2$

TABLE 7

** Solution Spectra of $Co(PhCopy)_2X_2$ in the presence of Added Ligand

Solid = $Co(PhCopy)_2Br_2$; Solvent = CH_3NO_2; L = 2-Benzoylpyridine.

Solution	Solution Spectra in cm^{-1} §
10^{-3} M Co L_2Br_2	25,800(930)*, $17{,}540_{sh}$(110), 16,200(155), 15,000(160), 14,300(210)
10^{-3} M Co L_2Br_2 + x10 ML	26,700(1400), 17,600(120), 16,260(115) 15,000(105) 14,500(150)
10^{-3} M Co L_2Br_2 + $x10^{-4}$ML	26,690(1235), $17{,}670_{sh}$(117), 16,150(145) 14,880(140), 14,270(165)
10^{-3}M Co L_2Br_2 + 10^{-2} ML	25,950(1345), 17,500(140), $16{,}400_{sh}$(117) $14{,}700_{sh}$(40)
10^{-3} M Co L_2Br_2 + 10^{-1} ML	25,700(2000), 24,200(1150), 17,800(147)

$Co(PhCopy)_2Cl_2$ gives similar spectra on addition of ligand.

* Apparent extinction coefficient calculated from observed optical density and total concentration of metal.

§ 1 x 10^4 cm^{-1} = 1000 nm.

** (See figure-10,)

TABLE 8

Physical data for complexes of Mg(II), Cd(II) and Zn(II) with 2-Benzoylpyridine

Compound	Colour	§Infrared data (in cm^{-1})		Conductivity Data	
		$\nu(CO)$	$\nu(MX)$	†Δ_M in $10^{-3}M$ $MeNO_2$	Temp °C
$[Mg(PhCOpy)_2I_2\ 2H_2O]$	Yellow	1625	-	42	23
$Zn(PhCOpy)_2I_2$	Yellow	1620	-	24	23
$Cd(PhCOpy)_2I_2$	Yellow	1638	-	16	23
$Cd(PhCOpy)Cl_2$	White	1635	*269_{sh} *263_{sh} 234_s	Insoluble in nitromethane at 23°C.	-

* uncertain due to ligand absorption in this region

sh - shoulder, s - strong;

§ (1×10^4 cm^{-1} = 1000 nm)

†Δ_M = Molar conductivity = Ohm^{-1} $mole^{-1}$ cm^2 .

TABLE 9

d-spacings from the X-ray powder photographs of the complexes of Ni(II), Co(II)and Cd(II)chloride with 2-benzoylpyridine

$Ni(PhCOpy)_2Cl_2$ (green form)	$Ni(PhCOpy)_2Cl_2$ (Yellow form)	$Co(PhCOpy)_2Cl_2$	$Cd(PhCOpy)Cl_2$
8.50_s	8.50_s	8.20_s	8.51_s
7.00_s	6.90_s	7.00_w	7.00_w
5.59_s	5.58_s	5.70_s	5.68_s
4.59_s	4.57_s	4.60_s	4.70_s
4.15_s	4.17_s	4.10_m	4.20_m
3.85_s	3.82_s	3.78_w	3.80_s
3.55_m	3.52_m	$3.55_{v.w}$	3.60_m
3.37_m	3.40_m	3.36_w	3.40_m
3.20_s	3.18_s	3.23_w	3.12_s
2.90_m	2.87_w	2.95_m	2.92_m
2.80_m	2.78_m	2.80_s	2.80_s
2.67_w	$2.65_{v.w}$	$2.70_{v.w}$	$2.68_{v.w}$
$2.58_{v.w}$	$2.57_{v.w}$	$2.58_{v.w}$	$2.60_{v.w}$
$2.43_{v.w}$	$2.43_{v.w}$	2.40_w	2.40_w
2.36_m	2.35_m	2.37_w	2.35_w
$2.23_{v.w}$	$2.20_{v.w}$	$2.28_{v.w}$	$2.25_{v.w}$
$2.08_{v.w}$	$2.07_{v.w}$	$2.14_{v.w}$	2.08_w
$2.05_{v.w}$	$2.02_{v.w}$	$2.00_{v.w}$	$2.02_{v.w}$
1.97_w	1.95_w	1.95_w	$1.94_{v.w}$
$1.88_{v.w}$	$1.87_{v.w}$	$1.88_{v.w}$	$1.87_{v.w}$
$1.83_{v.w}$	$1.80_{v.w}$	$1.80_{v.w}$	$1.80_{v.w}$
$1.75_{v.w}$	$1.73_{v.w}$	$1.74_{v.w}$	$1.76_{v.w}$

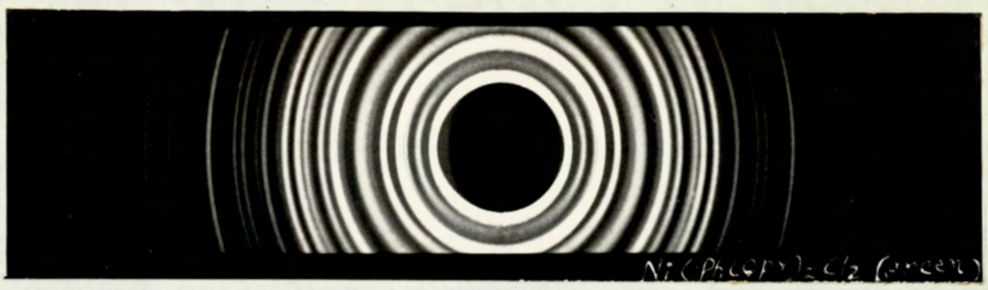
s - strong, m - medium, w - weak, v.w. - very weak.

TABLE 10

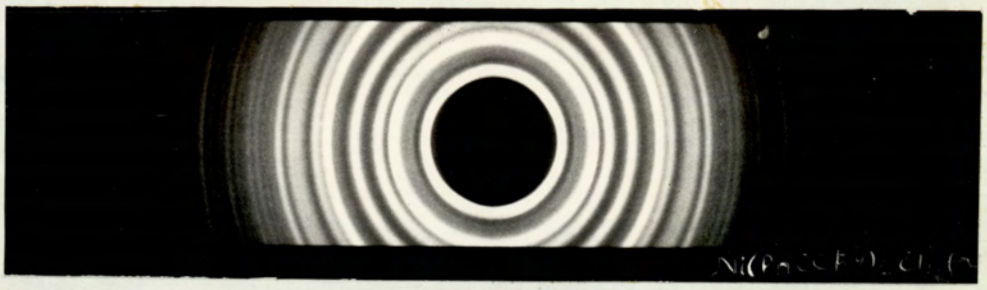
d-spacings from the X-ray powder photographs of the complexes of Ni(II), Co(II), Cd(II) and Zn(II) iodide with 2-Benzoylpyridine

$\mathrm{Ni(PhCOpy)_2I_2}$	$\mathrm{Co(PhCOpy)_2I_2}$	$\mathrm{Zn(PhCOpy)_2I_2}$	$\mathrm{Cd(PhCOpy)_2I_2}$
10.0_{s}	9.9_{s}	9.88_{s}	10.0_{s}
7.00_{s}	6.80_{s}	6.80_{s}	7.0_{s}
6.20_{m}	6.50_{m}	6.30_{m}	6.20_{m}
5.50_{s}	5.65_{m}	5.60_{m}	5.55_{s}
5.10_{s}	5.20_{m}	5.22_{s}	5.20_{s}
4.45_{s}	4.50_{s}	4.40_{s}	4.20_{s}
4.10_{s}	3.95_{m}	4.10_{w}	3.90_{s}
3.65_{m}	3.65_{m}	3.68_{m}	3.66_{m}
3.50_{w}	3.55_{w}	3.50_{m}	3.50_{m}
3.35_{m}	3.32_{m}	3.35_{m}	3.30_{m}
3.00_{s}	3.20_{m}	$3.10_{v.w}$	3.10_{s}
2.92_{w}	$2.95_{v.w}$	2.95_{w}	2.95_{m}
2.80_{w}	2.77_{w}	$2.75_{v.w}$	2.77_{m}
2.58_{m}	2.60_{w}	2.60_{w}	2.58_{m}
2.49_{w}	$2.45_{v.w}$	2.48_{w}	2.48_{w}
$2.30_{v.w}$	$2.25_{v.w}$	$2.25_{v.w}$	2.27_{m}
$2.08_{v.w}$	$2.10_{v.w}$	$2.12_{v.w}$	2.10_{m}
$1.77_{v.w}$	$1.75_{v.w}$	$1.76_{v.w}$	$1.75_{v.w}$
$1.67_{v.w}$	$1.65_{v.w}$	$1.67_{v.w}$	1.67_{w}
$1.53_{v.w}$	$1.55_{v.w}$	$1.52_{v.w}$	$1.52_{v.w}$

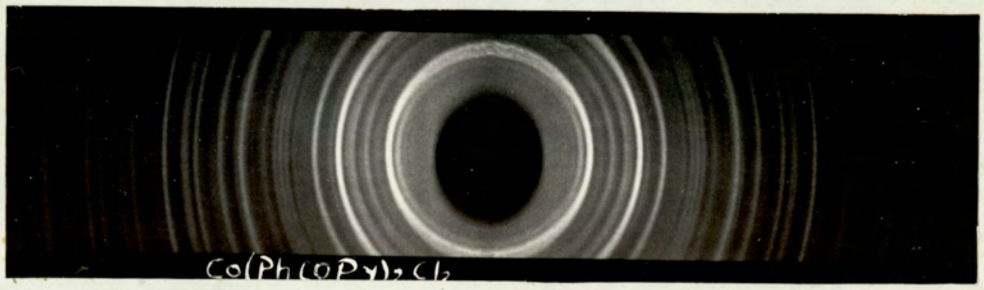
s - strong, m - medium, w - weak, v.w. - very weak.



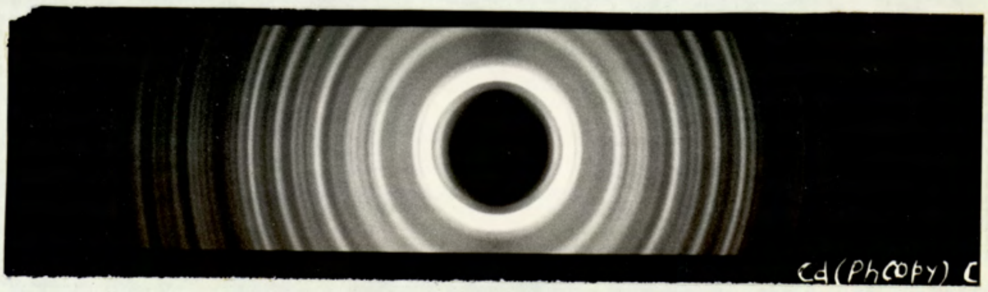
Dichlorobis-(2-benzoylpyridine)nickel(II) (green form)



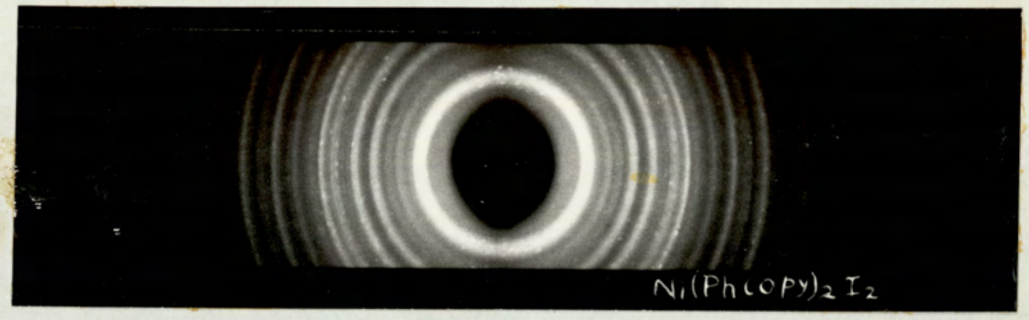
Dichlorobis-(2-benzoylpyridine)nickel(II) (yellow form)



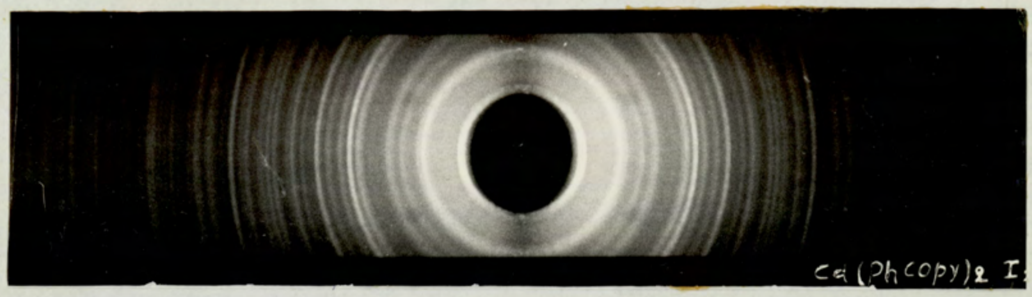
Dichlorobis-(2-benzoylpyridine)cobalt(II)



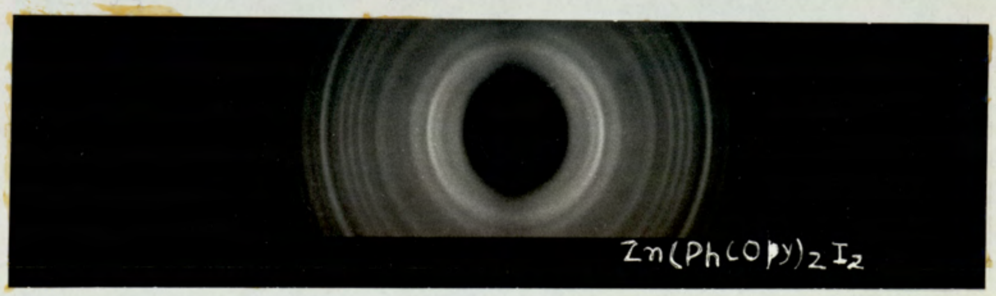
Dichloromono-(2-benzoylpyridine)cadmium(II)



Diiodo*bis*-(2-benzoylpyridine)nickel(II)



Diiodo*bis*-(2-benzoylpyridine)cadmium(II)



Diiodo*bis*-(2-benzoylpyridine)zinc(II)

DISCUSSION

1. Nickel(II) Complexes with 2-benzoylpyridine:

All nickel(II) compounds isolated with 2-benzoylpyridine were bis-complexes and the metal ions are located in very distorted octahedral environments. Characteristic shifts of the carbonyl group frequency, $\nu(CO)$, for 2-benzoylpyridine to lower wave number were noted on co-ordination which indicates that 2-benzoylpyridine functions solely as a bidentate ligand.

The spectra of nickel(II) complexes can readily be interpreted by referring to the energy level diagram for d^8 ions (fig.11(a)). The ground state of nickel(II) in an octahedral co-ordination is $^3A_{2g}$, $(t_{2g})^6\ (e_g)^2$. It is seen from the energy level scheme (fig.11 (b)), that nickel(II) in regular octahedral co-ordination will always possess two unpaired spins. This is not the case for axially distorted nickel(II). There are three spin allowed transitions for a typical octahedral nickel(II) complex and they are the $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P). These bands occur in the range of *7,000-13,000; *11,000-20,000 and *19,000-29,000cm^{-1} regions respectively. In addition two spin forbidden bands, to ^1E_g and to $^1T_{2g}$ are frequently observed [(not shown in Fig.11 (a))]. Octahedral nickel(II) complexes have relatively simple magnetic behaviour and all of them should have the magnetic moments ranging from 2.9 to 3.4 BM. (*1 x 10^4 cm^{-1} = 1000 nm).

A. Complexes with Nickel(II) Perchlorate:

Reaction of 2-benzoylpyridine with nickel(II) perchlorate hexahydrate in 2.2'-dimethoxypropane affords a green complex of stoichiometry $Ni(PhCOpy)_2(ClO_4)_2$. If ethanol was used as solvent

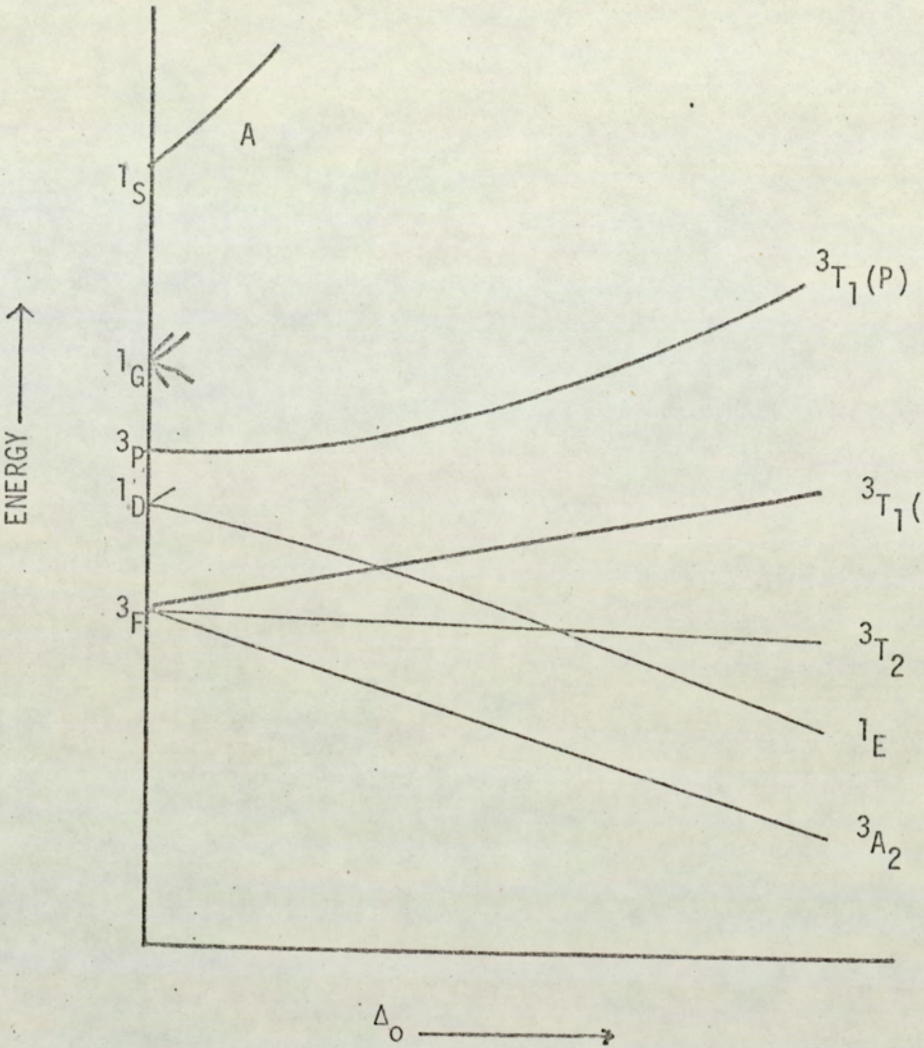


Figure: 11(a) Partial energy level diagram for a d^8 ion in an octahedral field.

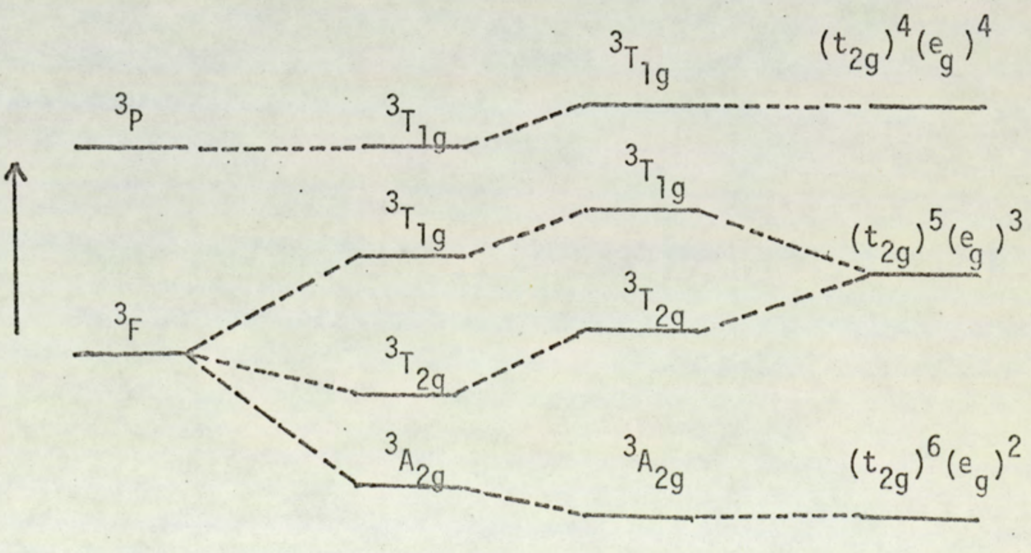
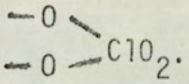
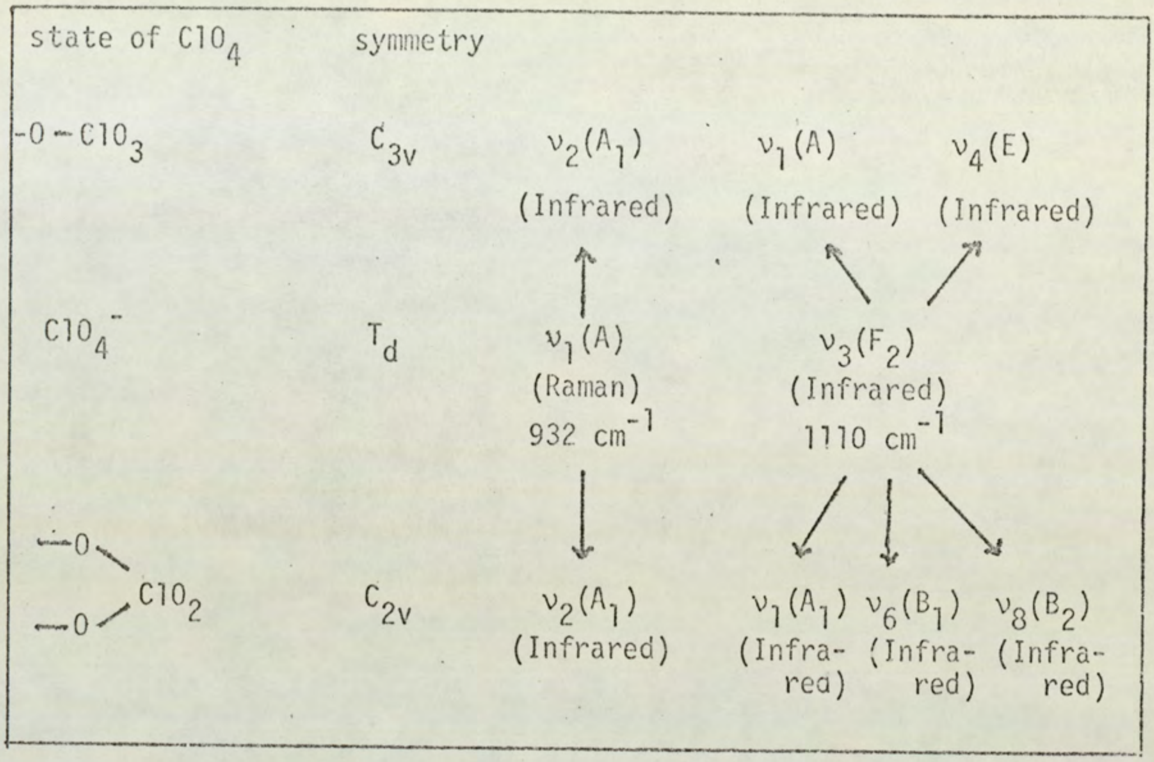


Figure: 11(b) Energy level scheme for the triplet states in octahedral coordinated Nickel(II) complexes.

a green perchlorate complex of stoichiometry $Ni(PhCOpy)_2(ClO_4)_2$.2EtOH was obtained with co-ordinated solvent molecules. The carbonyl stretching frequency, $\nu(CO)$, for $Ni(PhCOpy)_2\ (ClO_4)_2$ is at 1614 cm^{-1} and for $Ni(PhCOpy)_2(ClO_4)_2$.2EtOH is at 1610 cm^{-1}, which indicates NO-co-ordination of 2-benzoylpyridine in both complexes. (The carbonyl stretching frequency in 2-benzoylpyridine is at 1665 cm^{-1} but when it is complexed with various metal ions, the carbonyl band is shifted to a lower wavenumber).

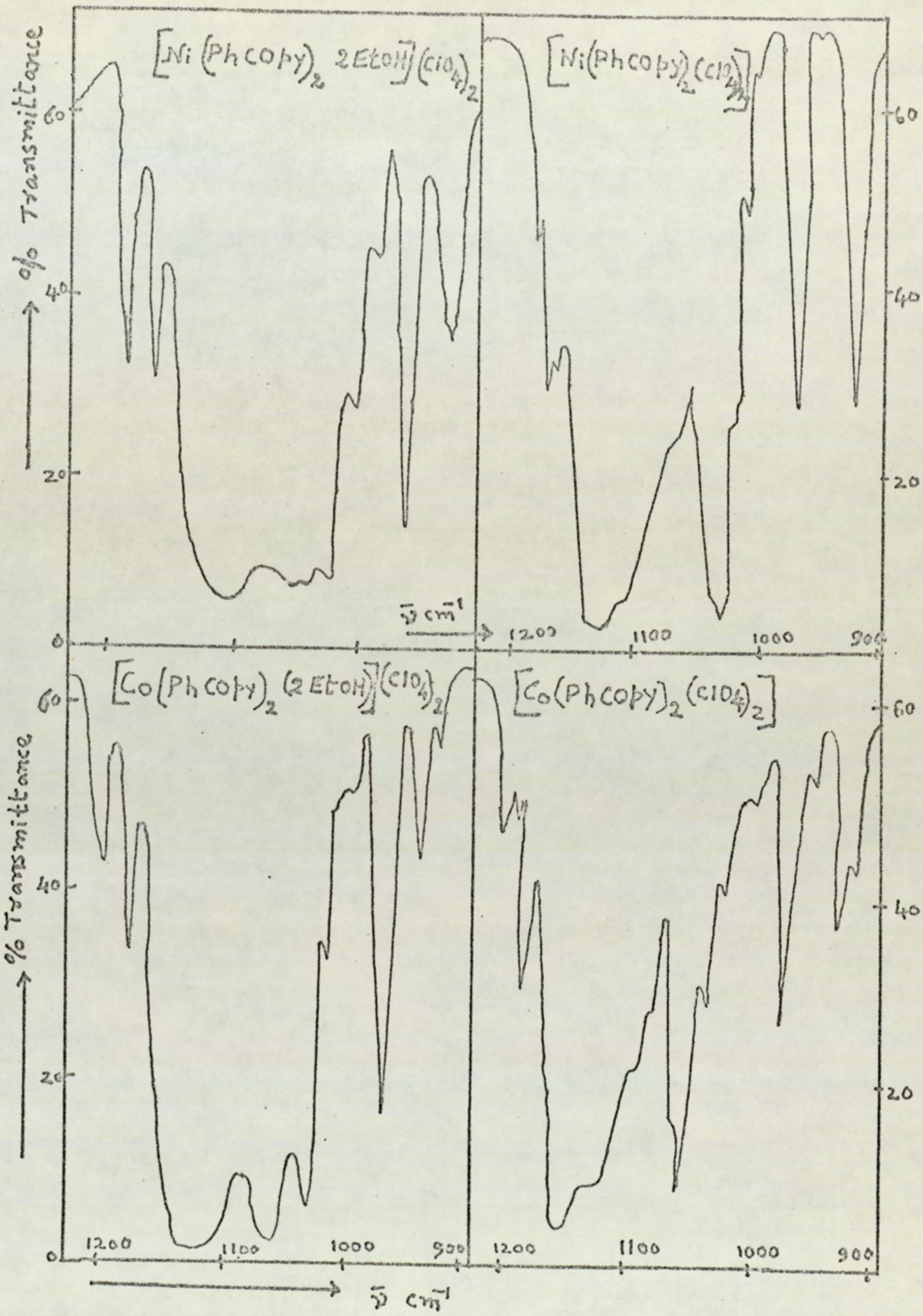
The number and position of infrared bands associated with the perchlorate group have been used to indicate whether the group is a monodentate ($-O-ClO_3$), an ionic (ClO_4^-) or a bidentate ligand,  $\begin{matrix}-O\\-O\end{matrix}\!>ClO_2$.[54] . An ionic perchlorate group has T_d symmetry and has a strong infrared active bands $\nu_3(F_2)$ at 1110 cm^{-1} and a weak band at 932 cm^{-1}, which corresponds to $\nu_1(A)$, is theoretically forbidden in the infrared. When a perchlorate group functions as a monodentate ligand, the co-ordinated oxygen is no longer symmetrically equivalent to the other three and the effective symmetry of the group is lowered to C_{3v}. The frequency $\nu_3(F_2)$ of the ionic perchlorate group is resolved into $\nu_1(A)$ and $\nu_4(E)$. Also the frequency ν_1 of the ionic perchlorate group becomes frequency $\nu_2(A_1)$ which is infrared active. When a perchlorate group functions as a bidentate ligand, the symmetry of the group is reduced to C_{2v}, and the frequency ν_3 of the ionic perchlorate group has its degeneracy completely resolved, giving $\nu_1(A_1)$, $\nu_6(B_1)$ and $\nu_8(B_2)$, all of which are infrared active. Also the frequency ν_1 of the ionic perchlorate becomes $\nu_2(A_1)$ which is infrared active. This is illustrated in fig.12.



Some vibrations of the ClO_4 group as a function of symmetry

Figure 12.

The complex $Ni(PhCOpy)_2(ClO_4)_2$ has two infrared bands in the solid state at 1132 and 1027 cm^{-1} which corresponds $\nu_1(A)$ and $\nu_4(E)$ and it has a band at 915 cm^{-1} corresponding to $\nu_2(A_1)$. Since the splitting of frequency $\nu_3(ClO_4)$ is not very pronounced in this complex (fig.13), the (ClO_4) groups are considered to be weakly co-ordinated, The interaction of the anion with with the metal being sufficient to favour a spin-triplet ground state at room temperature and to cause splitting of $\nu_3(ClO_4)$ and to allow some intensity for $\nu_1(ClO_4)$[54]. The conductivity data (Table-5) of $Ni(PhCOpy)_2(ClO_4)_2$ indicates an extensive ionic dissociation of the perchlorate groups in nitromethane solution, although the solution spectrum remains consistent with the presence of a six-co-ordinate species. (The complex is 1:1 electrolyte in nitromethane solution.) The magnetic moment and diffuse reflectance spectra (Table 1) support an octahedral environment about the nickel(II) ion. Reaction of nickel(II) perchlorate hexahydrate and 2-benzoylpyridine in ethanol



Infrared spectra in the region associated with some vibrations of the perchlorate group.

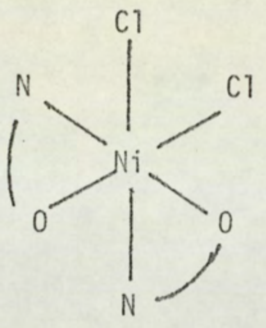
Figure - 13.

gives $Ni(PhCOpy)_2(EtOH)_2(ClO_4)_2$, in which the perchlorate groups are definitely ionic (fig.13). This complex has a broad single band corresponding to $\nu_3(F_2)$ at ~ 1110 cm^{-1}* in the solid state spectrum. However treatment of $Ni(PhCOpy)_2(2EtOH)(ClO_4)_2$ at 137°C in vacuo over 72 hours affords diperchloratodi- (2-benzoylpyridine)nickel(II) where again there is infrared evidence for some degree of perchlorate co-ordination in the complex.*(1×10^4 cm^{-1} = 1000 nm).

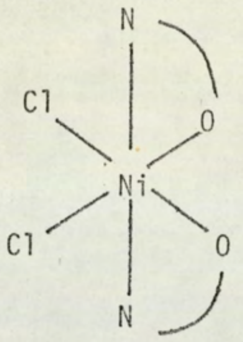
B. Complexes with Nickel(II) halides:

Reaction of hydrated nickel(II) chloride and 2-benzoylpyridine affords the green solid $Ni(PhCOpy)_2Cl_2$. Addition of benzene to an ethanolic solution of green $Ni(PhCOpy)_2Cl_2$ gives a yellow solid of the same composition. As previously stated, if the yellow isomer is carefully washed free of free ligand it is stable for many months. However failure to remove any contaminating ligand results in reversion to the green form in a matter of days. The isomerisation reaction (yellow → green) was very rapid in molten 2-benzoylpyridine. The two isomers of the composition, $C_{24}H_{18}Cl_2NiN_2O_2$, clearly contain six-co-ordinate nickel(II) and equally clearly the detailed environment of the metal differs in the two cases. Nitromethane solutions of green or yellow $Ni(PhCOpy)_2Cl_2$ are green and nonconducting and both isomers give identical solution spectra which are in turn not identical with either set of solid state data. The magnetic moments and diffuse reflectance spectra are different in both cases. (Table-1)

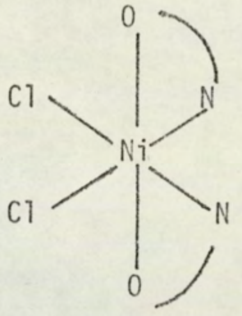
The isomers may be related as cis- and trans-dichloro-compounds or they may have similar arrangements of halogen ligands and differ with respect to the co-ordination of 2-benzoylpyridine (e.g.mutually cis- or trans- 2-pyridyl group), three such isomers being possible for a cis-dichloro-compound and two for a trans-dichloro-compound.



(1)



(2)



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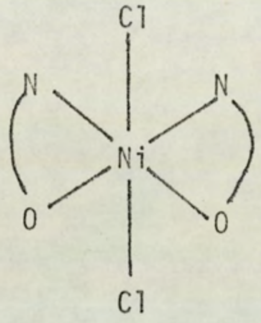

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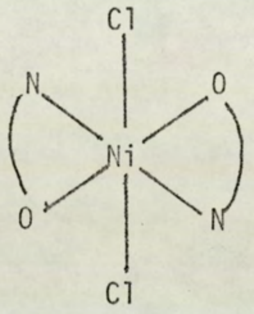


(5)

X-Ray powder photographs of the two compounds are identical (Table 9). This initially surprising result probably implies that the nickel chlorine spacings are similar in the two complexes since it will be these heavier atoms that will be primarily responsible for the X-Rays being scattered. Thus it is unlikely that the complexes (yellow and green) differ as cis- and a trans-dichloro-compounds. The two complexes are isomorphous with $Co(PhCOpy)_2Cl_2$ which shows, in common with the compound $Ni(PhCOpy)_2Cl_2$(green), a single cobalt-chlorine stretching frequency. Thus it is believed that these two isomers are formed as the trans-dichloro compound. The yellow isomer which gives a simpler spectrum below 17000 cm^{-1}, is considered to contain cis-2-pyridyl groups (dxz ≡ dyz) and the green isomer to contain trans-2-pyridyl groups (dxz ≢ dyz). The far infrared data (Table 1) support this with the more complex spectrum for yellow isomer, $Ni(PhCOpy)_2Cl_2$, being consistent with the noncentrosymmetric microsymmetry.

Reaction of hydrated nickel(II) bromide and 2-benzoylpyridine affords the red solid $Ni(PhCOpy)_2Br_2$. The nitromethane solution of this compound is green and nonelectrolyte. The carbonyl frequency is at 1615 cm^{-1} showing that the ligand 2-benzoylpyridine is NO-co-ordinated in this complex ($\nu(CO)$ for free 2-benzoylpyridine is at 1665 cm^{-1}.) The magnetic moment (3.16 B.M.) and solid state and solution spectra (Tables 1 & 5) in the visible region, suggest an octahedral environment for the nickel(II) cations.

The reaction of hydrated nickel(II) iodide and 2-benzoylpyridine affords the dark green solid $Ni(PhCOpy)_2I_2$. The 2-benzoylpyridine is NO-co-ordinated in this complex ($\nu(CO) = 1618\ cm^{-1}$). The molar conductance of this complex suggest some ionic dissociation in nitromethane solution. The diffuse reflectance spectra and magnetic moment, (3.17 B.M.), (Table 1), indicate an octahedral co-ordination about the nickel(II) cation.

2. Cobalt(II) complexes with 2-benzoylpyridine:

All cobalt(II) complexes with 2-benzoylpyridine are six-co-ordinated, high spin complexes. The metal ions are located in very distorted octahedral environments. The 2-benzoylpyridine is NO-co-ordinated in all complexes and characteristic shifts of the carbonyl group frequency, $\nu(CO)$, to a lower wave number were noted on co-ordination.

In octahedral co-ordination the ground state for Cobalt(II) ion, can be either $^4T_{1g}\ (t_{2g})^5\ (e_g)^2$ or $^2E_g\ (t_{2g})^6(e_g)^1$ depending upon the strength of the ligand field. Thus for weak ligand fields the $^4T_{1g}\ (t_{2g})^5\ (e_g)^2$, is the ground state and for a stronger ligand field the $^2E_g\ (t_{2g})^6(e_g)^1$ becomes the ground state. However, a strong field ligand will be required for spin pairing in cobalt(II) ion ($\Delta \geqslant 15000\ cm^{-1}$)[1c]

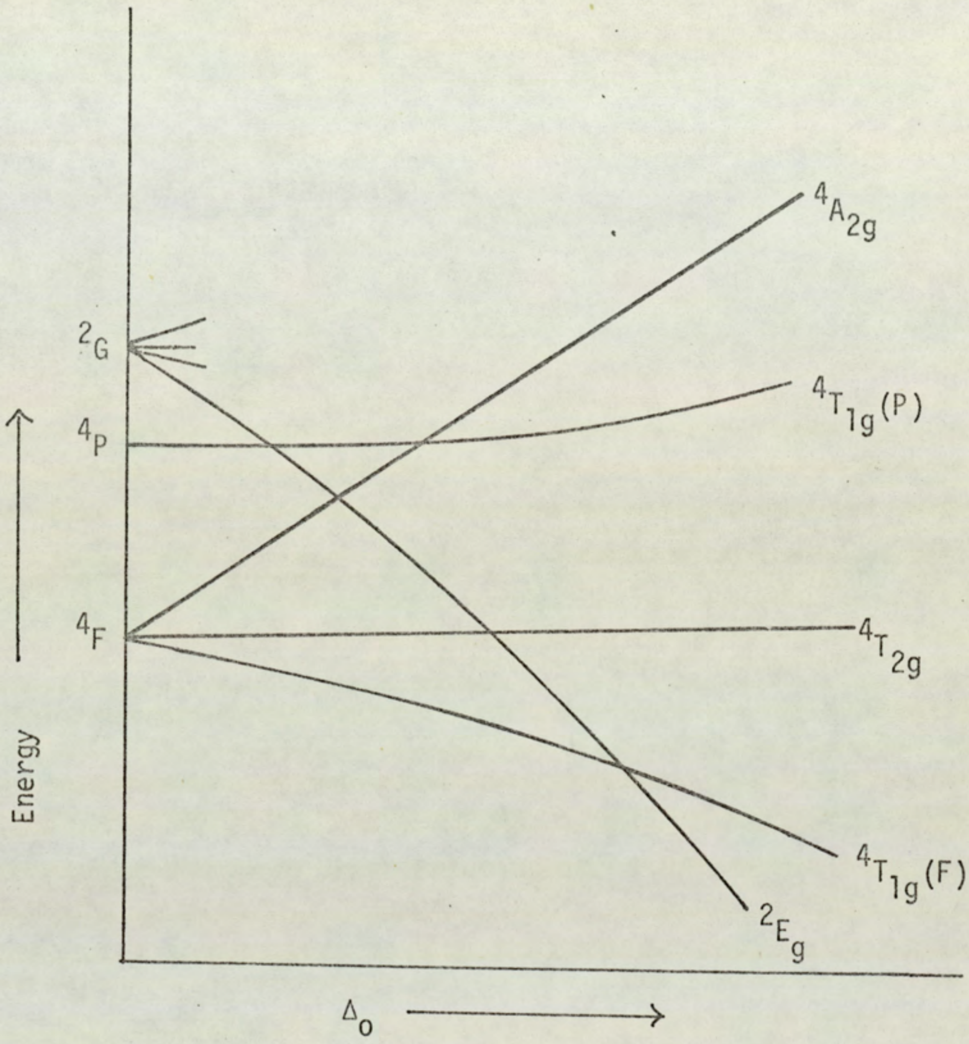


Fig. 14. A partial energy level diagram for Co(II) ion in an octahedral field. (The ^2E_g(G) becomes the ground state in sufficiently high fields).

The 2-benzoylpyridine is considered to be a weak field ligand (a value of Δ=10000cm^{-1}with respect to nickel(II) may be estimated) and therefore all cobalt(II) complexes of 2-benzoylpyridine were considered as high-spin complexes having the ground state $^4T_{1g}$ $(t_{2g})^5(e_g)^2$, in octahedral co-ordination. The octahedral cobalt(II) ion should have three spin-allowed d-d transitions and they are arranged in order of increasing energy:

$^4T_{1g}(F) \rightarrow {}^4T_{2g}$; $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (fig.14)

The $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition appears near ~ 12000cm^{-1} as a very weak peak and generally it is not observed[1d]. The high spin octahedral cobalt(II) compounds have magnetic moments ranging from 4.7 to 5.2 B.M.

A. Complexes with cobalt(II) perchlorate

Reaction of hydrated cobalt(II) perchlorate with 2-benzoylpyridine in 2,2'-dimethoxypropane affords an orange solid, diaquo*bis* -(2-benzoylpyridine) cobalt(II) perchlorate. The position of carbonyl stretching frequency indicated that 2-benzoylpyridine was NO-co-ordinated in this complex. The infrared spectrum showed the presence of water (ν(OH) = 3400 cm^{-1}) and showed that the perchlorate groups were ionic ($\nu_3(ClO_4)$ = 1117 cm^{-1}) (fig.12). Thus from the position of ν(OH) and $\nu_3(ClO_4)$, the complex is formulated as $[Co(PhCOpy)_2(H_2O)_2]$ $(ClO_4)_2$. The magnetic moment (4.30 B.M.) and visible spectra of the complex indicates an octahedral co-ordination about the cobalt(II) ion (Table 2). The effective magnetic moment is rather low but this is possibly due to quenching of the orbital contribution by the low symmetry ligand field rather than an indication of the presence of some cobalt(II) ions in another spin state. If ethanol was used as a solvent, the perchlorate complex was obtained with co-ordinated solvent molecule of the stoichiometry $Co(PhCOpy)_2(EtOH)_2(ClO_4)_2$. However treatment of both diaquo-and diethanolo- complexes at 137°C in vacuo over 72 hours afforded diperchlorato bis(2-benzoylpyridine) cobalt(II). There is infrared evidence for some degree of perchlorate co-ordination in this complex (fig.13). The reaction is accompanied by loss of $\nu(OH)$ and by splitting of $\nu_3(ClO_4)$ and increasing intensity for $\nu_1(ClO_4)$. The conductivity of $Co(PhCOpy)_2(ClO_4)_2$ indicates an extensive ionic dissociation of the perchlorate groups in nitromethane solution.

B.Cobalt(II) halides complexes with 2-benzoylpyridine

Reaction of 2-benzoylpyridine and hydrated cobalt(II) halides in ethanol affords the yellow brown solid of composition $Co(PhCOpy)_2X_2$ (X = Br or Cl) and the dark-brown solid, $Co(PhCOpy)_2I_2$. A similar reaction with anhydrous cobalt(II) bromide in acetone affords the green solid, $Co(PhCOpy)_2Br_2 \cdot$acetone. The infrared spectrum of the acetone adduct supports the presence of acetone, $\nu(CO) = 1713\ cm^{-1}$. Heating of the adduct in vacuo afforded the yellow-brown solid $Co(PhCOpy)_2Br_2$ and the infrared band at 1713 cm^{-1} disappeared. The 2-benzoylpyridine is NO-co-ordinated in each of these halides complexes. The far infrared spectrum of $Co(PhCOpy)_2Cl_2$ shows a single cobale-chlorine stretching frequency. Thus in the solid state the chloro and the bromo complexes are considered to be trans-dichloro(and dibromo)-bis-(2-benzoylpyridine) cobalt(II). The magnetic moments and the visible spectra in the solid state for each of these halide complexes, $Co(PhCOpy)_2X_2$ where X = Cl,Br,I are consistent with an actahedral environment about the cobalt(II) ion (Table 2).

Although $Co(PhCOpy)_2X_2$ (X = Cl or Br) does not undergo complete ionic dissociation, the nitromethane solutions of these complexes are intensely coloured (dark-green) and the spectra (Table 7) bears no relation to those of the solid state. The visible absorption spectrum of $Co(PhCOpy)_2Br_2$ in nitromethane solution clearly indicated the presence of a tetrahedral cobalt(II) species. (λ max 14,270 cm^{-1}, (ε = 212) and 16,130 cm^{-1} (ε = 154) may be assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition.) The chloro compound gives the similar spectra in nitromethane solution. Addition of varying amounts of 2-benzoylpyridine to the nitromethane solutions of chloro or bromo complexes causes the intense band centered at 15000cm^{-1}(which associated with the tetrahedral species) to decrease in intensity and the spectra becomes more characteristic of "octahedral" species. A more detailed study of this phenomenon with the complex, dibromobis(2-benzoylpyridine) cobalt(II), revealed an isobestic point at 16000cm^{-1}as the ligand concentration was increased with the cobalt concentration constant (fig.10). The solution studies in nitromethane suggest the following equilibria to be established:

$$Co(PhCOpy)_2X^+ + X^- \rightleftharpoons \underset{\text{'octahedral'}}{Co(PhCOpy)_2X_2} \rightleftharpoons \underset{\text{tetrahedral}}{Co(PhCOpy)X_2} + PhCOpy$$

The solution spectra of $Co(PhCOpy)_2Br_2$ and its acetone adduct are identical in both nitromethane and chloroform, the latter solvent favouring an "octahedral" species in solution. The solid-state data of both compounds are marginally sensitive to the presence of acetone, which is however readily lost. These differences may arise from direct cobalt-acetone interaction in the crystals or by modification of the lattice by acetone sufficiently to alter the site symmetry in the complex.

The conductivity data of $Co(PhCOpy)_2I_2$ indicates some ionic dissociation in nitromethane solution and the spectra bears no relation to that of solid state. The solution spectrum of this complex, in nitromethane, is complicated due to charge transfer from metal to ligand. However tetrahedral species can easily be observed in the solution spectra. The X-Ray data suggests that this compound is isomorphous with many other compounds of the type $M(PhCOpy)_2I_2$(Table 9).

3. Manganese(II) complexes with 2-benzoylpyridine

The manganese(II) perchlorate and iodine compounds with 2-benzoylpyridine were isolated as bis-complexes and the manganese(II) ion is located in six co-ordinate environments in both cases. The chloro- and bromo- complexes were isolated as mono-complexes with 2-benzoylpyridine. The shift of the carbonyl stretching frequency $\nu(CO)$, for 2-benzoylpyridine to lower wave number in the manganese(II) complexes indicated that the ligand is NO-co-ordinated.

The bright orange to red-brown colour of manganese(II) complexes of 2-benzoylpyridine is quite striking when compared with most of the manganese(II) salts which are very pale pink in octahedral surroundings. This intense colour is attributed to the charge transfer bands which extend far into the visible region. It is this phenomenon that prevents one from getting any useful electronic absorption data from solid state and solution spectra. The reason is that the charge transger bands mask the weak spin-forbidden d $\leftrightarrow$ d transitions.

In a high-spin octahedrally co-ordinated manganese(II) complex, the ground state for manganese(II) ion is $^6A_{1g}$ $(t_{2g}{}^3\, e_g{}^2)$. Since this is the only sextet level present, the d $\leftrightarrow$ d transitions are all spin-forbidden and thus give rise to very weak absorption bands.

(The spin-forbidden transitions give absorption bands $\sim$100 times weaker than those for similar but spin-allowed transitions)[1e]. There are six absorption bands in the visible and near ultraviolet region of the spectrum for manganese(II) complexes. They all correspond to the spin-forbidden transitions and are assigned from the ground state to various excited states in order of increasing energy:

$^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$; $^6A_{1g} \rightarrow {}^4T_{2g}(^4G)$; $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$; $^6A_{1g} \rightarrow {}^4T_{2g}$ (^4D) $^6A_{1g} \rightarrow {}^4E_g(^4D)$ and $^6A_{1g} \rightarrow {}^4T_{1g}(^4P)$. (fig. 15(a))

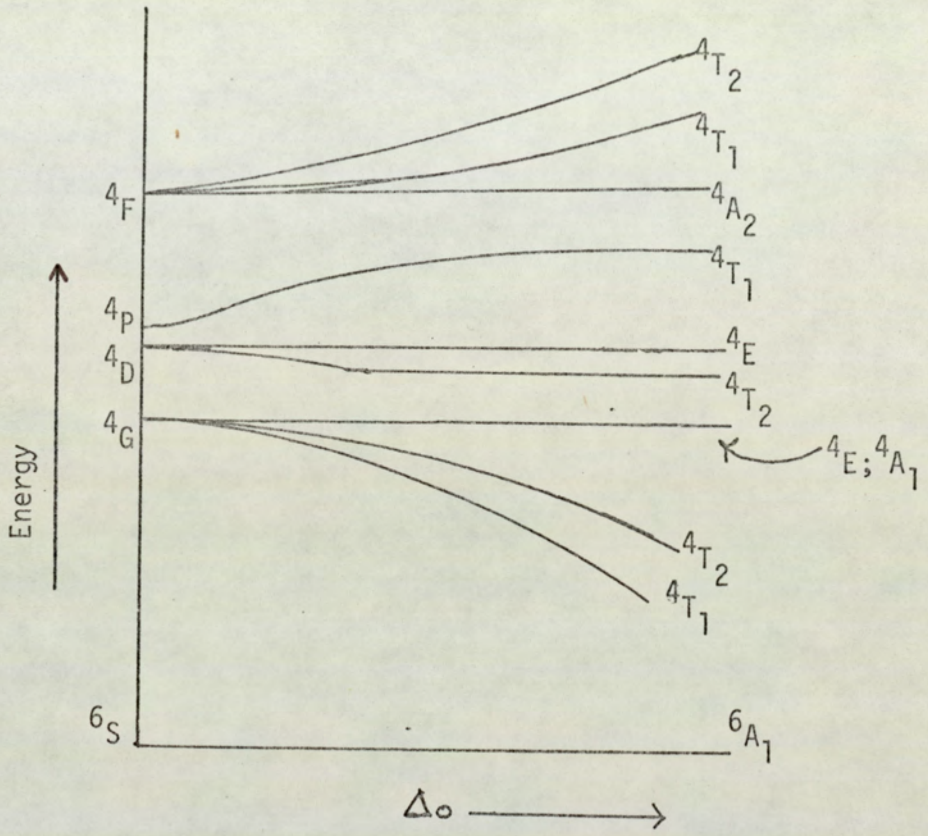


Fig. 15a. Partial energy level diagram for the Mn(II) ion, showing only the ^6S state and the quartet states.

The magnetic moment for a high-spin manganese(II) complex is 5.92 B.M. This value of magnetic moments does not alter much in the manganese(II) complexes with weak field ligands like 2-benzoylpyridine. This is not surprising because neither crystal fields nor the spin-orbit coupling alone can remove the sixfold degeneracy of the ground state of the manganese(II) ion.

A. Manganese(II) perchlorate complex with 2-benzoylpyridine

Reaction of hydrated manganese(II) perchlorate with 2-benzoylpyridine in ethanol affords a bright orange complex of stoichiometry, $Mn(PhCOpy)_2(ClO_4)_2$. 2EtOH. The position of $\nu(CO)$ for this complex is at $1622 cm^{-1}$ which indicates NO-co-ordination of 2-benzoylpyridine.

The infrared spectrum showed the presence of co-ordinated solvent molecules ($\nu(OH) = 3390\ cm^{-1}$) and also suggests that the perchlorate groups were ionic. A broad infrared band centered at $\sim 1100\ cm^{-1}$, which corresponds to $\nu_3(ClO_4)$ has been observed. The magnetic moment (6.1 B.M.) of this complex is consistent with six-co-ordinated high-spin manganese(II) compounds. The visible spectrum of this complex, in the solid state, was very weak and therefore it could not give any structural information. The conductivity data of $Mn(PhCOpy)_2(ClO_4)_2$. 2 EtOH, indicates an extensive ionic dissociation of the perchlorate groups in nitromethane solution. {(The complex is 1:1 electrolyte in nitromethane solution, (table 4).} The complex is therefore formulated as $\left[Mn(PhCOpy)_2\ 2EtOH\right]\ (\overset{ClO_4}{\cancel{C0l}_4})_2$. The infrared spectra also supported this conclusion for the solid state.

B. Manganese(II) halide complexes with 2-benzoylpyridine

The reaction of hydrated manganese(II) iodide with 2-benzoylpyridine in ethanol affords the red-brown complex of the stoichiometry $Mn(PhCOpy)_2I_2$. The 2-benzoylpyridine is NO-co-ordinated in this complex, $\nu(CO) = 1620\ cm^{-1}$. The molar conductance of this complex indicates some ionic dissociation in nitromethane

The magnetic moment, 5.6B.M, is consistent with octahedrally co-ordinated high-spin manganese(II) compounds. The visible spectrum of this complex, in the solid state, is very weak. A considerable simplification of the solid state spectrum is to be expected.

As previously stated (p.31) the dichloro- and dibromo- manganese (II) complexes with 2-benzoylpyridine were isolated in metal to ligand ratio of 1:1 only. All attempts made to prepare metal to ligand ratio of 1:2 resulted in the formation of 1:1 complexes only. Both complexes were obtained as orange solids and formulated as dichloro- (or dibromo) mono(2-benzoylpyridine) manganese(II). The 2-benzoylpyridine is found to be NO-co-ordinated in both complexes. The magnetic moments, in both cases, are consistent with high-spin manganese(II) complexes.

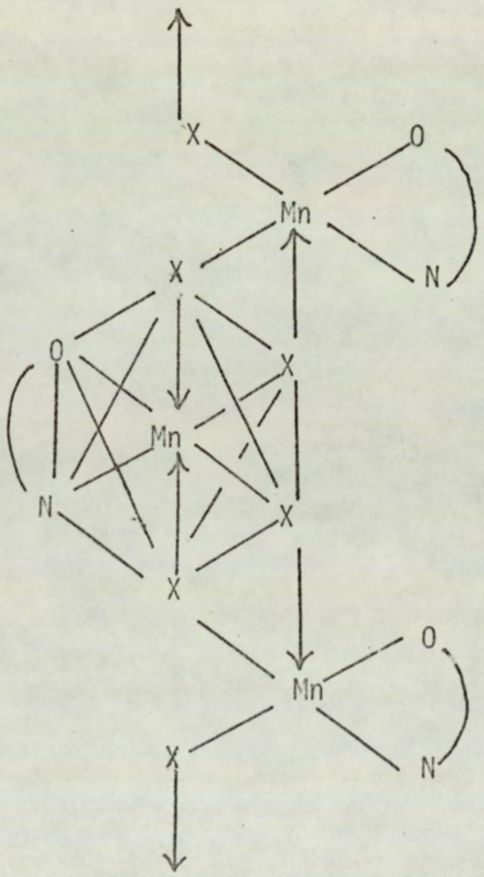
Goodgame et al.[55] found that most of the tetrahedral manganese(II) complexes fluoresce under ultraviolet light. (The state $^4T_{1g}$ (^4G) which is responsible for the fluorescence, is found in many manganous compounds)[56].

Since the dichloro- and dibromo-mono(2-benzoylpyridine) manganese(II) fail to fluoresce under ultraviolet light and since the position of the metal-halogen stretching frequency $\nu(MnCl)$ is too low for a four-co-ordinate species (the tetrahedral $[MnCl_4]^{2-}$ gives ν_3 at 284 cm^{-1} [57]), a polyme~~t~~ric structure for chloro- and bromo- complexes of manganese(II) in which manganese(II) is six co-ordinated, is likely. (fig.15(b)).

The extreme insolubility and the complexity of $\nu(MnCl)$ for the chloride are consistent with the polyme~~t~~ric structure of the dichloro-manganese(II) complex. Although soluble to the extent of *ca.*10^{-3}M in nitromethane, the bromide complex is believed to be similar.

4. Cadmium(II),Magnesium(II) and Zinc(II) complexes with 2-benzoylpyridine

Cd(II),Mg(II) and Zn(II) iodide compounds with 2-benzoylpyridine are isolated as *bis*-complexes and the metal ions are located in six-co-ordinate environments. The Cd(II) ($CdCl_2$) compound with 2-benzoylpyridine is isolated as monocomplex only. The position of carbonyl stretching frequency, $\nu(CO)$,indicated that 2-benzoylpyridine is N,O-co-ordinated in



(X = Cl, Br)

Fig. 15b. Polymeric (octahedral) structure for dihalo~~bis~~mono-(2-benzoylpyridine)manganese(II).

each of these halide complexes. With the exception of $Zn(PhCOpy)_2I_2$, it is observed that the carbonyl group interacts rather weakly with the metal ions in these halide complexes.

The x-Ray data (Table-10) suggests that the complexes $M(PhCOpy)_2I_2$ [(where M = Cd(II) and Zn(II))] are isomorphous with the complexes, $M(PhCOpy)_2I_2$ (where M = Co(II), Ni(II)) and also gives very similar photographs to $M(PhCOpy)_2Cl_2$ (where M = Co(II), Ni(II); green and yellow). The $Mg(PhCOpy)_2I_2.2H_2O$ has a very different x-Ray powder photograph and therefore is not isomorphous with any other complexes listed. Surprisingly, $Cd(PhCOpy)Cl_2$ gives a very similar photograph to $Ni(PhCOpy)_2Cl_2$ (Table 9). The complexes of the general formula, $M(PhCOpy)_2I_2$ (where M = Zn(II), Cd(II) and Mg(II) are non-electrolytes in nitromethane.

Since the position of the metal-halogen stretching vibration frequency, in $Cd(PhCOpy)Cl_2$, is too low for a four-co-ordinate species, a polymeric structure for dichloromono-(2-benzoylpyridine) cadmium(II) in which cadmium(II) is six-co-ordinated, is likely. The extreme insolubility of $Cd(PhCOpy)Cl_2$ in nitromethane and complexity of $\nu(CdCl)$ for the chloride are consistent with this view. From the insolubility in nitromethane and from far infrared data, it is seen that Cd(II) chloride complex of 2-benzoylpyridine is very similar to that of the manganese(II) chloride-2-benzoylpyridine complex.

CONCLUSIONS

The study of the complexes of 2-benzoylpyridine with first-row transition metal cations showed that 2-benzoylpyridine (PhCOpy) is a weak-field, bidentate (N,O co-ordination) ligand. With the exception of Mn(PhCOpy) X_2 (X = Cl or Br) and Cd(PhCOpy)Cl_2 all compounds isolated are shown to be bis-complexes with the metal ions located in six-co-ordinate environments in all cases.

PART II

Study of the compounds produced on the addition of iodine to some divalent first row transition metal complexes of the simpler pyridine bases

CHAPTER 4

INTRODUCTION

The ability of halide ions to associate with one another, with one or more halogen molecules or with an interhalogen molecule to form polyhalide ionic complexes has long been recognised [58a-60]. A few years ago, the polyhalides (also called perhalides) were defined as products of the additive combination of the metal halides or the halides of other radicles, which acting as Lewis bases, with the halogen or interhalogen molecule or molecules which act as Lewis acids[58a]. Recently however the positively charged polyhalide complex ions were isolated [58a]. Thus a polyhalide complex ion can be defined as an aggregate consisting of three or more halogen atoms and carrying either a positive or negative electric charge.

Polyhalide ions can be represented by a generalized formula, $X_m Y_n Z_p^{\pm}$, where X , Y and Z represent either an identical, two different or in the case of the anions, three different halogen atoms. The total number of halogen atoms, $m + n + p$ in such a complex is always odd, i.e. 3, 5, 7 or 9.

The property of forming polyhalides is connected with the volume of the cation. In order to form a polyhalide salt, the cation must have a large radius and a small charge. Caesium with the largest atomic volume of any metal, forms them most easily whereas other alkali metals form them to a less extent as the atomic volume decreases.

The general methods of preparation of crystalline polyhalide complexes in the solution has been reviewed by Chattaway and Hoyle[58], by Cremer and Duncan[59], and also by Popov and Buckles[60]. In the preparation of polyhalide complexes, the choice of an appropriate solvent as the reaction media, is of primary importance. The halogens and the polyhalides are highly reactive chemically and therefore the solvents which can easily be halogenated by polyhalogen compound or which effect solvolysis reaction are to be avoided. A large majority of polyhalide complexes can be prepared either in methanol or in ethanol solution. However, in the case of unstable polyhalides, a solvent which is more inert to halogenation has to be used such as acetic acid or 1,2-dichloroethane.

The stability of solid polyhalides depends on numerous factors such as the size and symmetry of the cation and the size, symmetry and the nature of the polyhalide ion and the chemical resistance of the compound to atmospheric moisture. The most stable polyhalide salts are formed when the ionic sizes of the cation and the anion are similar. In the alkali metal series, it is found that the stability of the polyhalides decreases in the order $Cs > Rb > NH_4 > K > Na$, which corresponds to the order of decrease in cationic size. All polyhalides decompose spontaneously into a halogen or interhalogen compound and a lower halide. It is found that many polyhalides dissociate at room temperature. The stability of crystalline polyhalides of caesium and rubidium has been determined by Ephraim[61] who measured the temperature at which the dissociation pressures of the polyhalides reached one atmosphere. From his results, it is found that the stability of a trihalide with respect to dissociation is greater when the cation is larger and more symmetrical. It is also evident that the centrosymmetric polyhalide ions are much more stable than those of asymmetric ones. (e.g. IBr_2^- is much more stable than the I_2Br^- ion. Cremer and Duncan[62] determined the relative stabilities of the polyhalide salts by suspending the solid polyhalide in carbon-tetrachloride solutions at 25°C. When the equilibrium was reached, they determined the concentration of halogen in the supernatent liquid. They made the same conclusion from their results that not only the size but also the symmetry of the cation is important in the overall stability of the polyhalides.

Most of the polyhalide complexes hydrolyze readily in the aqueous solutions. Cremer and Duncan[63] found that in the aqueous solutions, the triiodide ion was the most resistant one and that the extent of hydrolysis is increased with increasing replacement of iodine by more electronegative halogens. Because of its relative stability in aqueous solutions, the triiodide ion has been more thoroughly investigated than other polyhalides. Various physicochemical methods such as spectrophotometry (ultraviolet, visible and infrared), electrical conductance, potentiometry etc., have been used extensively in the studies of polyhalide ions in solutions. The spectrophotometric study for the reaction, $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$, in the solution of 10^{-5}M iodine and 10^{-4} - 10^{-3}M in the iodide ion has been made by Daniele[64]. The solutions were acidified with 10^{-3}M $HClO_4$ to supress the hydrolysis of iodine. It was found that the change of formation constant, Kf, with temperature gave the enthalpy of the reaction as -4760 ± 400 cal.mole^{-1} (-19915.84 ± 1673.6 joules.mol^{-1}) The value for the enthalpy of the I_3^- formation as -5100 ± 400 cal.mol^{-1} (-21338.4 ±1673.6 joules mol.$^{-1}$) in aqueous solution, has also been determined spectrophotometrically by Awtrey and Connick[65]. The measurement of the stability constant of the tribromide, Br_3^- and trichloride, Cl_3^- ion has been restricted due to their extreme instability in aqueous solution .

The spectrophotometric study of polyhalides in nonaqueous solvents was made by Buckles et al[66]. They studied the tetramethylammonium triiodide, pentaiodide and enneaiodide in 1,2-dichloroethane and showed that at solute concentration of about 2 x 10^{-5}M , only the triiodide ion exists in solution. The formation constant of the triiodide ion was determined from spectral measurements and was found to be 10^7 at 25°C. From their results, it is seen that the stability of triiodide, I_3^- in 1,2-dichloroethane is larger by several orders of magnitude than its stability in water. The conductivity measurements of the tetramethylammonium polyiodides in acetonitrile at 25°C, were made by Popov et al[67]. They indicated that the pentaiodide and the heptaiodide ions can only exist in more concentrated solutions. They also suggested that on dilution, the higher polyiodides undergo progressive dissociation as $I_n^- \rightleftharpoons I_{n-2}^- + I_2$ and at infinite dilution, the polyiodide ions dissociated completely to the stable triiodide, I_3^- and iodine. The dissociation of the tribromide ions, in water-methanol mixtures, has been studied spectrophotometrically by Dubois and Herzog[68]. From the data of the formation constant of Br_3^- ion in methanol and in water-methanol, they estimated the value for the enthalpy of the reaction $Br^- + Br_2 \rightarrow Br_3^-$ in methanol as -5790 ± 730 cal.mole^{-1}.(-24230 ± 3054 joules mol^{-1}).

The triiodides of the alkali metals have been investigated in more detail than the other polyiodides due to their relative stability in solution and in the solid state[58,60]. It is found that the alkali metal ions such as potassium, sodium and ammonium form hydrated (solvated) triiodides whereas alkali metal ions with large radii such as caesium and rubidium readily form anhydrous triiodide. Many alkali metal salts of triiodide anions have a tendency to form a variety of stable molecular complexes with some organic compounds. Martin[69] obtained the molecular complexes such as KI_3, $2C_6H_5CN$; $NaI_3.2C_6H_5CN$; and $LiI_3.4C_6H_5CN$, from alkaliiodide-iodine mixtures in benzonitrile. A similar 4:1 lithium complex was also obtained in o-toludine. The presence of such organic compounds or solvent molecules is essential for the stability of alkali-metal triiodides because the whole substance decomposes into a alkalimetal iodide and iodine when those organic compounds or solvent molecules are removed.

Many attempts have been made in the past to prepare the polyiodide salts of the polyvalent cations. It is believed that neither the alkaline earth metals nor the transition metals form such complexes in the solid state. However polyiodides can be formed when the size of the cation is increased by co-ordination. A number of polyiodides of transition metal ammines such as $Ni(NH_3)_4(I_7)_2$ and $Co(NH_3)_6(I_3)_3$ have been prepared by Ephraim and Mosimann[70]. Naldini[71,72] prepared some di-triiodides of iron(II) and Manganese(II) with triphenylphosphine and triphenylarsine (bulky organic ligands). The manganese(II) triiodides[72] were prepared by an addition of iodine to the mixture of MnL_2I_2(1 mole) and 2 moles of ligand where ligand, L = triphenylphosphine or triphenylarsine in dichloromethane. In the preparation of the triiodides, I_3^-, of iron(II)[71] having formula $FeL_4(I_3)_2$ (where L = triphenylphosphine or triphenylarsine) a stream of air has been passed constantly during an addition of iodine to the mixture of FeL_2I_2 (1 mole) and 2 moles of ligand in dichloromethane. These manganese(II) and iron(II)polyiodides are dark red solids, non-electrolytes in nitromethane at 25°C and are paramagnetic at room temperature. Recently Baranovskii and Belova[73] prepared the nickel(II) polyiodides $Ni(en)_2(I_3)_2$ and $Ni(en)_3I_4$ from the reaction of tris-(ethylenediamine) nickel(II) di-iodide and iodine in methanol. The compound, $Ni(en)_3I_4$, obtained in form of golden yellow plates, was found to be paramagnetic at room temperature while a black solid, $Ni(en)_2(I_3)_2$, was found to be diamagnetic at room temperature.

The crystal structure of the polyiodides of the alkali metals has been studied extensively by a number of investigators[74-76]. Mooney[74] has found that in ammonium triiodide the I_3^- group forms a linear ion within 3^{o} and is not centrosymmetrical. The I_3^- group has two different I-I bond distances, $2.82A^{o}$ and $3.10A^{o}$. The asymmetry of the triiodide ion, I_3^- was also found to hold in caesium triiodide. The I_3^- group has two I-I bond distances $2.83A^{o}$ and $3.03A^{o}$[75]. However in tetraphenylarsonium triiodide, Mooney and Slater[76] found that the triiodide ion, I_3^-, is symmetrical with the two I-I bond distances being $2.90 \pm 0.02A^{o}$ and the apex angle of 176.4^{o}.

The nature of bonding in the triiodide ion, I_3^-, was discussed by Pimentel[77], Hach and Rundle[78] who pointed out that the bonds in the triiodide ion, I_3^-, are the result of a delocalization of the 5p-electrons of the iodine atoms. The resonance forms of the triiodide ion ha~~s~~ve been shown as follows:

I^- I - I and I ----I I^-

They[77,78] also assumed that the resonance in the triiodide ion, I_3^-, results in a centrosymmetric system. The asymmetry of the triiodide is due to an asymmetric surrounding in the crystal, which disturbs the equivalence of the relatively weak bonds. Slater [79] however, expressed a different point of view namely that the symmetrical triiodide ion, I_3^-, is obtained only if a large positive ion exerts a pressure on the anion and forces it into symmetric configuration.

Mulliken[80] found that iodine in its violet solutions exists free but in its brown solutions it forms 1:1 molecular complexes. The stable molecular complex of iodine with pyridine, $Py.2I_2$, was first prepared by Prescott and Trowbridge[81]. Since then Chatelet[82], Mulliken[80,83], have reported that iodine forms stable complexes with pyridine and other related compounds. Chatelet [82] found that on evaporation of a concentrated solution of iodine in pyridine, long yellow transparent needles were formed, which largely converted to micro-crystals of iodine within five minutes. He studied the rates of evaporation of iodine-pyridine solution and from it, the composition $(C_5H_5N)_2.I_2$ was assigned to the crystals first deposited. The molecular complex formed between iodine and pyridine is regarded as charge-transfer complex[80]. Mulliken[80] suggested that when iodine is dissolved in pyridine, the following reactions should be considered as the primary reactions:

$$Py + I_2 \rightleftharpoons Py.I_2 \text{ "Outer complex"} \text{———————} (1)$$

$$Py.I_2 \rightleftharpoons (PyI)^+ \ I^- \text{ "Inner complex"} \text{—————} (2)$$

$$(PyI)^+ \ I^- \underset{\text{fast}}{\rightleftharpoons} PyI^+ + I^- \text{———————————} (3)$$

It was also suggested that in iodine solutions in pyridine, the pyridine was acting as an electron donor toward iodine in reaction (1) and was acting as a polar medium in assisting reaction (2) and (3).

The electric conductivity of iodine in pyridine as a function of concentration and time was investigated by Kortüm and Wilski[84]. They found that iodine in freshly prepared solutions in pure pyridine at a concentration of about 10^{-4} molar gives a very small conductivity. The concentration dependance of the very small initial conductivity of freshly prepared solutions indicates that the initial dissociation was:

$$Py.I_2 \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} (PyI)^+ + I^-$$

The subsequent rise in the conductivity of pyridine-iodine solution with time was found to be attributed to the formation of $(Py_2I)^+$ and I_3^-:

$$PyI_2 + (PyI)^+ + I^- \xrightarrow{slow} (Py_2I)^+ + I_3^-$$

Thus the results suggest that the conductivity of pyridine-iodine solution is mainly due to the formation of $(Py_2I)^+$ and I_3^- species. The net change in reaction was represented as

$$2PyI_2 \longrightarrow (Py_2I)^+ + I_3^-$$

The ultraviolet and visible absorption spectra of dilute solution of iodine and pyridine in heptane and in pyridine have been studied by Reid and Mulliken[83]. Their spectrophotometric study on the pyridine-iodine system in heptane indicated that at the equilibrium, $Py.I_2$ outer complex was formed. The visible iodine band and charge transfer band of PyI_2 were found at λmax, 422 nm (ε = 1320) and λmax 235 nm (ε = 50,000) respectively. (For free iodine, the iodine band is at 520 nm) Further spectrophotometric study[83] of the pyridine-iodine system in pyridine suggested that on addition of pyridine to the iodine solution in heptane, the iodine band of PyI_2, λmax, 422 nm shifted to lower wave number with increased intensity. At high concentration of pyridine (but not too dilute in iodine) the iodine band has reached about λmax = 389 nm (ε = 2620). These changes were found to be attributed to the increased polarity and stability[38], of the PyI_2 "outer complex" in the polar pyridine solvent than in heptane. Other interesting spectrophotometric changes have also been found by Reid and Mulliken[83] in which very dilute solutions of iodine in pyridine (10^{-4}M)were used. The two major bands were found to be shifted at λmax, 368 nm and λmax 287 nm respectively. These bands were due to the formation of triiodide, I_3^- ion in the solution. Buckles[66] et al. found that triiodide has two peaks, one at λmax, 385 nm and one of nearly double as great peak intensity at 295 nm . On further dilution of the iodine-pyridine solution below 10^{-5} molar suggests that the I_3^- band at ∿ max 365 nm has disappeared. This final change[83] may be attributed to redissociation of triiodide, I_3^-, ion in pyridine solution. The net change was represented as follows:

$$
\begin{array}{lcl}
Py.I_2 + I^- & \rightleftharpoons & I_3^- + Py \\
I_3^- + Py & \rightleftharpoons & (PyI)^+ + 2I^- \\
\end{array}
$$

$$
\left\{
\begin{array}{ll}
Py + PyI^+ & 2Py^+ + I^- \\
Py^+ + Py & Py^+ Py
\end{array}
\right\}
$$

The complexes of pyridine and its substituted derivatives with iodine both in the solid state and in solution have been studied by a number of investigators[85-90]. The spectrophotometric measurements of the pyridine-iodine system in heptane by Reid and Mulliken [83] gave the value of formation constant as ∿ 200M^{-1} at 25°C. McKinney et al.[86] determined the formation constants, (Kf) of the complexes of pyridine and substituted pyridines with iodine spectrophtometrically in carbon-tetrachloride at 25°C. Their results suggest that the plot of logKf vs pKa of the respective pyridines follows a linear relationship. However this linear relationship has not been observed[86] in the complexes of iodine with the sterically hindered pyridines. The influence of solvent properties on the formation of pyridine-iodine change-transfer complexes have been studied by McKinney and Pop~~a~~ov[87]. Their results of the formation constants of the pyridine-iodine complex in twelve different non-polar solvents at 25°C, suggests that the stability of pyridine-iodine complex increases with the increase in the dielectric constant of the reaction medium.

The infrared studies on pyridine-iodine and picolines-iodine systems by Glusker[85] et al, Glusker and Thomson[88], and Plyler and Mulliken[89] have revealed that the infrared spectra of pyridine and picolines are markedly altered by the addition of iodine. The spectral changes in the pyridine-iodine system were explained on the bases of the formation of a highly polarized "inner complex", $(IPy)^{+} I^{-}$. Plyler and Mulliken[89] suggests that when iodine and pyridine were dissolved together, the iodine fundamental vibration was absorbed strongly and the band shifted from its vapour value, 213 cm^{-1}* to 184 cm^{-1}* (in heptane) or 174 cm^{-1}* (in benzene). Moreover the pyridine iodine in benzene solution gives a very weak absorption band at 204 cm^{-1}*. Recently Ginn and Wood[90] studied the intermolecular vibration spectra of the pyridine-iodine complex and found that a solution of iodine in pyridine shows two absorption bands, one strong band at $\sim$ 167 cm^{-1}* and one weak band at 137 cm^{-1}*. Further study[90] on a solution containing 0.25 iodine in 10% pyridine plus 90% benzene V/V, shows only a single band at 171 cm^{-1}*. The n-heptane solution containing pyridine and iodine also gives a single band at 180 cm^{-1}*. Thus it was suggested[90] that the lower band was only observed in polar solvent, which was due to the formation of I_3^- ion in solution.

*(1×10^2 cm^{-1} = 1×10^5 nm)

The study of the paramagnetic susceptibility provides useful information on the stereochemistry, structure, bonding and an oxidation state of transition elements in co-ordination compounds[91]. In co-ordination compounds the metal ions, which are responsible for paramagnetic effect, are kept separated from each other by a bulk of magnetically inert ligand atoms. The magnetic interaction between neighbouring dipoles reduces greatly and hence the co-ordination compounds are usually magnetically dilute. However many paramagnetic substances show magnetically concentrated behaviour to some extent at temperature near absolute zero[92(a)].

It is found that the ideal paramagnetic substance obeys the Curie law, which states that paramagnetic susceptibilities depend inversely on temperature:

$$\chi = \frac{C}{T}$$

where C = Curie constant; T = absolute temperature.

The magnetic properties of complexes are usually described in terms of magnetic moment, μ_{eff}, rather than of the susceptibility, χ_A. The following equation shows the relation between magnetic moment and magnetic susceptibility at the given temperature:

$$\mu_{eff} = (3k/N\beta^2)^{\frac{1}{2}} \ (\chi_A T)^{\frac{1}{2}}$$

where N is Avogadro's number = 6.023×10^{23} molecules mol^{-1}.

β is the Bohr magneton = 0.9273×10^{-20} erg/gauss

k is Boltzmann's constant = 1.381×10^{-16} erg/deg.

T is the temperature in ^oK,

therefore

$$\mu_{eff} = 2.83 \ (\chi_A T)^{\frac{1}{2}} \text{ Bohr magnetons}$$

The modification[92(b)] of the Curie law, describing the behaviour of the magnetic susceptibility as a function of temperature, is known as the Curie-Weiss law:

$$\chi_A = \frac{C}{T + \theta}$$

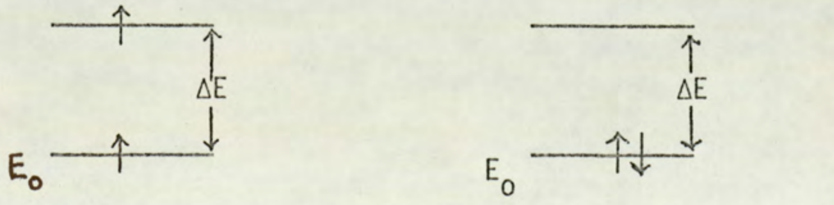
θ is known as the Weiss constant. According to the Curie-Weiss law, the susceptibility should be linearly related to the reciprocal of the absolute temperature, T.

$$\mu_{eff} = 2.83 \ \{\chi_A \ (T + \theta)\}^{\frac{1}{2}}$$

The Weiss constant θ can be determined as a finite intercept in a plot of $\frac{1}{\chi_A}$ against T.

It is of interest to understand the magnetic properties of a transition metal complex in terms of the orbital splitting [93(a)]. According to Hund's rule of maximum multiplicity, a group of 'n' or less electrons occupy a set of 'n' degenerate orbitals, they spread out among the orbitals and give 'n' unpaired spins so the process of pairing of electrons requires energy to make it occur. Moreover additional energy is required for the electrons to be placed in the same orbital, i.e. paired.

Let us consider a hypothetical molecule in which two orbitals have been separated by an energy ΔE and that two electrons are to be placed in these orbitals. It is seen from the figure-16, that if one electron is to be placed in each orbital, their spin would remain unpaired and their combined energy would be $2E_0 + \Delta E$. (where E_0 = energy of the lower state and ΔE = the energy separating between lower state and excited state). If these two electrons are to be placed in the lower orbital, their spins will have to be coupled to satisfy the Pauli exclusion principal. The total energy at this time is $(2E_0 + P)$ where 'P' denotes the energy required to cause pairing of two electrons in the same orbital. So there are two possibilities, either (a) or (b) (figure -16) for its ground state and this depends on whether ΔE is greater or less than the pairing energy,P. If $\Delta E < P$, the triplet state (a) would be more stable and if $\Delta E > P$, the singlet state(b) would be the more stable.



$E = E_0 + (E_0+\Delta_E) = 2E_0+\Delta E$

(a)

$E = E_0 + E_0 + P = 2E_0 + P$

(b)

Fig. 16 A hypothetical two-orbital system which shows two possible distribution of two electrons.

The above argument is now considered for transition metal ions. It has been seen previously (page 1) how crystal field theory describes the effect of the ligand field on transition metal ions. The splitting of the five degenerate d-levels of a transition metal ion into two or more separate sets of levels depends on the symmetry of the field. For fields of O_h symmetry, the e_g and t_{2g} levels are produced. The e_g level exists as an upper doublet (the dx^2-y^2 and dz^2 orbitals) and the t_{2g} as a lower triplet (the dxy, dxz and dyz orbitals). This is shown in figure 17 .

The spin state of any transition metal ion in an octahedral electrostatic field depends upon whether the splitting energy Δ_o is greater or less than the mean pairing energy P[93(b)]. For a particular ion of d^4, d^5, d^6 or d^7 type in a strong crystal field, a more stable configuration will be obtained because the electrons will occupy the more stable t_{2g} orbitals. On the other hand, for weak crystal fields, where $P > \Delta_o$, the electrons will spread themselves out among the set of d orbitals. In such cases the spin multiplicity will be the maximum. Thus for d^4, d^5, d^6 or d^7 in O_h symmetry the spin state is dependent on the strength of the ligand field. For ions d^1, d^2, d^3, d^8, d^9 and d^{10}, it is found that the number of unpaired electron is fixed at the free ion value regardless of how strong the crystal field is[93(b)].

The effect of distortions of the co-ordination polyhedron upon the magnetic properties is best seen in the d^8 ion in O_h symmetry where the low spin state does not exist. All regular octahedral complexes of nickel(II) show a paramagnetism due to the presence of two unpaired spins. However, this situation changes whenever an octahedral environment is subjected to an axial distortion. Such distortion lowers the symmetry from O_h to D_{4h} and this results in

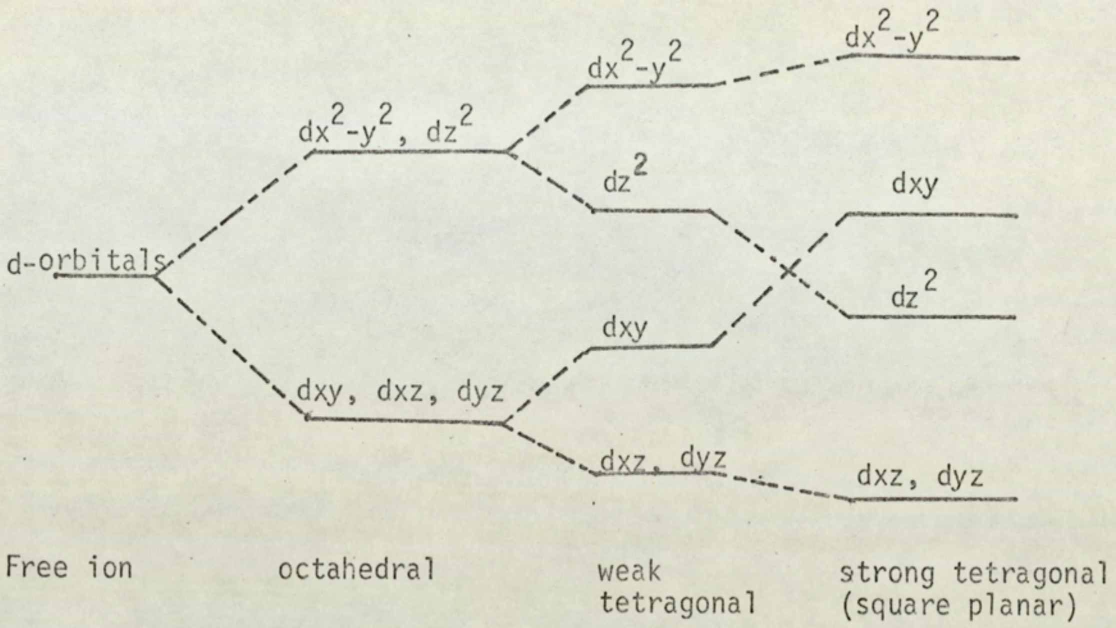


Fig.17: Splitting of orbitals in octahedral, tetragonal and square planar ligand fields.

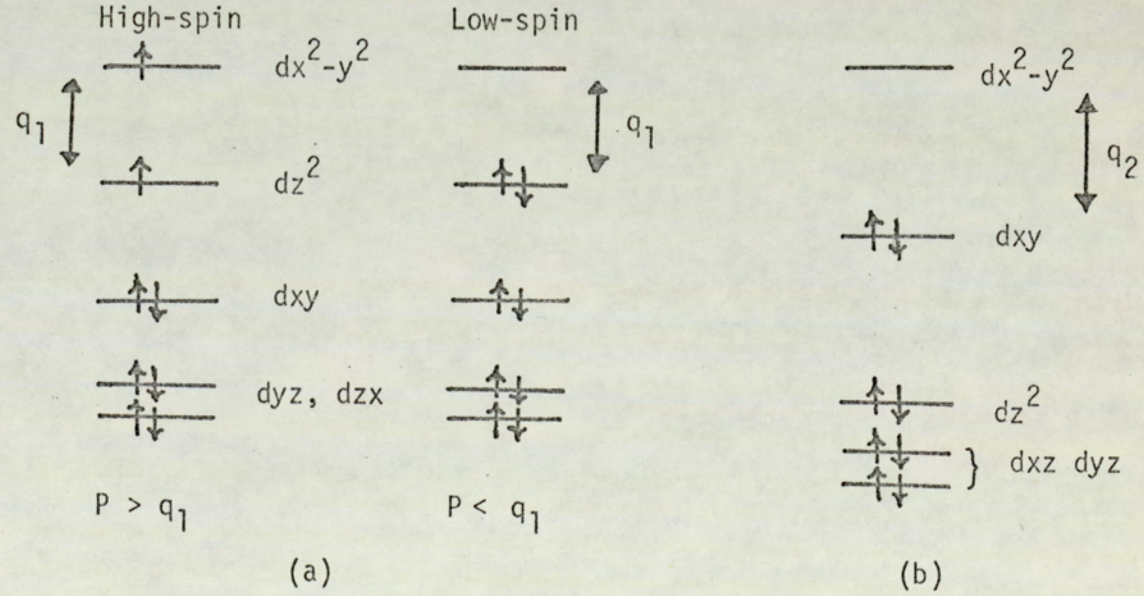


Fig.18: The high-spin and low-spin ground states for d^8 system (Ni(II) ion) in a tetragonally distorted octahedral field.

(a) weak tetragonal distortion (b) strong distortion or square field.

further loss of degeneracy of the d-orbitals. Figure -18(a) shows the situation as to whether a tetragonally distorted d^8 complex will have high spin or low spin. This is simply depends upon whether the pairing energy,P, is greater or less than the separation energy,q_1 (fig.-18(a)). When the tetragonal distortion is large, the energy separation between the dx^2-y^2 and dz^2 orbitals,(q_1) or between dx^2-y^2 and dxy orbitals (q_2) may increase the electron pairing energy. (fig.-18(a) and (b)). It is clear that large tetragonal distortion leads to square planarity. The dz^2 orbital may fall below the dxy orbital (fig.-18(b) and fig.-17). Thus in such case there will be a change in magnetic moment from ca 3.0 B.M. to zero.

The measurement of magnetic susceptibility below room temperature provides valuable information concerning the origin of anomalous magnetic behaviour[91,94]. In D_{4h} symmetry nickel(II) ion may undergo a singlet-triplet spin state isomerism. The magnetic cross-over was found in a series of tetragonal nickel(II) complexes. This cross-over occured due to a small change in the nature of the axial ligands[94]. Goodgame and Venanzi[95] studied a series of N,N'-diethylethylenediamine complexes of the type, Ni(diamine)X_2, where X was univalent anion Two types of complexes, a diamagnetic and paramagnetic were found to exist. The cross-over in ground states have been found between X = Br(diamagnetic) and X=Cl (μ_{eff} = 3.29 BM .). Brubaker and Busch[96] observed a similar result for complexes of nickel(II) with the planar quadri-dentate ligand, S,S'-O-xylyl-2,3-pentanedione-bis(mercaptoethylimine). They found that perchlorate and iodide complexes of Ni(II) were diamagnetic while the chloride, azide and thiocyanate were paramagnetic (μ_{eff}= 3.1, - 3.2 B.M.) A sharp change in magnetic cross-over has also been found for complexes of 1, 4, 8, 11-tetra-azacyclotetradecane (cyclam) with nickel(II) ion[97]. The chloride and bromide complexes of nickel(II) cyclam were paramagnetic and the iodide was diamagnetic. In all of the complexes seen above, the room temperature magnetic bahaviour is consistent with either the singlet or triplet ground state.

Certain systems can be understood on the basis of equilibria between co-existing singlet and triplet states whose energy separation is comparable with thermal energies. In such cases the distribution between the two states can be described by Maxwell-Boltzmann statistics if there would be no change in structure other than the alteration in spin-state[94]. For such systems, the magnetic susceptibility is calculated by the following equation:

$$\chi_A = \frac{2g^2N\beta^2}{3kT} \left[1 + \frac{1}{3} \exp \frac{\Delta E}{kT} \right]^{-1} + N\alpha$$

Where g is the Lande' splitting factor, N is Avogadro's number, β is the Bohr magneton, k is the Boltzmann constant, T is the absolute temperature, ΔE is the energy separation between singlet and triplet states and $N\alpha$ is the temperature independent paramagnetism. This equation suggests that the magnetic susceptibility will increase with temperature. However this could not be possible where $\Delta << kT$.

Spin-state isomerism (singlet- triplet) in a crystalline nickel(II) complexes has been reported by several workers[98-100]. Holt et al.[98] reported that dichlorotetrakis (N,N'-diethylthiourea)nickel(II) is found to be spin-paired at temperatures lower than ca 194°K, but partial paramagnetism is obtained on raising the temperature. The corresponding N,N'-diethylthiourea complexes of nickel(II) bromide and iodide are found to be diamagnetic at room temperature, but the bromide complex becomes weakly paramagnetic at 373°K. Melson and Busch[99] studied a series of nickel(II) complexes with the planar quadridentate macrocyclic ligand, tetrakis-anhydroaminobenzaldehyde (TAAB).

The chloro and bromo complexes exhibit anomalous room temperature moments and the measurements of the variation of magnetic susceptibility as a function of temperature give non-Curie-Weiss plots. An interesting series of nickel(II) complexes with benzimidazole has been studied by Goodgame et al[100]. Several of these compounds show unusual magnetic behaviour. The blue form of $NiL_4Cl_2S_2$ (where L = benzimidazole and S = acetone of solvation) is magnetically normal. The green form with the same stoichiometry had a room-temperature magnetic moment of 3.06 B.M., but the temperature dependence of the susceptibility of same compound indicated antiferromagnetic interaction.

The normal magnetic moments of 6-co-ordinate Co(II) complexes fall in the range of <u>ca</u> 1.8 B.M. to <u>ca</u> 5.2 B.M. At sufficiently high ligand fields, the ^2E_g (^2G) state crosses the $^4T_{1g}$ (^4F) state and in this region, a thermal distribution between spin states could exist. A study of the temperature-dependence of the magnetic susceptibility by Stoufer et al[101] showed that the moment for the complex <u>bis</u>-(2,6-pyridinedialdehyde dihydrazone) cobalt(II) iodide varies from 1.9 B.M. at 80°K to 3.7 B.M. at 337°K. Stoufer,Smith et al[102] also reported temperature-dependence studies on the magnetic properties of six cobalt(II) complexes. These compounds, containing ligands with unsaturated nitrogen donors{(e.g. pyridine-2-aldehyde methylimine,PMI, biacetyl-<u>bis</u>(methylimine),BMI, etc.)}exhibit anomalous magnetic behaviour and they give non-linear Curie-Weiss plots. They[101,102] found that an equilibrium between a doublet and quartet state exists for these cobalt (II) complexes with PMI, BMI and pyridine-2,6-dialdehyde dihydrazone. An enthalpy calculation on linear portion of the susceptibility curves[102] indicates that the ^2E_g (^2G) state is the one of lower energy. This suggests that the ligand field is not strong enough to cause complete spin pairing.

CHAPTER 5

EXPERIMENTAL

(A) CHEMICALS

Reagent grade pyridine, β-picoline and γ-picoline were purified by drying over sodium hydroxide pellets and redistilled before use. The resublimed grade of iodine was used. Other chemicals such as silver nitrate, sodium thiosulphate and potassium thiocyanate used were A.R.grade. The metal iodides e.g. $NiI_2, 6H_2O$; $CoI_2,6H_2O$ and $MnI_2, 4H_2O$; were synthesised in the laboratory. General procedure for the synthesis of metal iodides is described as follows:

An equivalent amount of metal carbonate ($NiCO_3$, $CoCO_3$ or $MnCO_3$) was dissolved in a minimum quantity of the hydroiodic acid. After evolution of carbon dioxide ceased, the iodide solution boiled for a few minutes and filtered in a conical flask. Fine metal wire or metal powder was added to the iodide solution and corked. The flask was fitted with a bunsen valve. The solution was boiled gently. Thus excess of the iodine was taken up by the metal and any excess of hydroiodic acid was evaporated by prolonged boiling of the solution. When the volume of the solution was suitably reduced, the metal iodide crystals were separated on cooling. They were filtered off and dried between filter-paper pads.

(B) SOLVENTS

All solvents were reagent grade and were purified by standard methods [50,66,104]. The procedure for purification and drying of each solvent were adopted as follows:

Methanol:

Anhydrous calcium sulphate was added to methanol and was kept for a couple of days. The methanol was then decanted from the calcium sulphate and filtered. Then it was distilled under reduced pressure. For keeping dry, it was kept over the molecular sieves, type 3A.

Dichloromethane:

The dichloromethane was dried over anhydrous calcium sulphate for a couple of days. Then it was decanted from the calcium sulphate, filtered and distilled under reduced pressure. For keeping dry, it was kept over molecular sieves. The boiling point of dry dichoromethane was checked as 40-41^{o}C at 760 m.m. pressure.

Nitromethane:

The nitromethane was kept over phosphorus pentoxide for a couple of days. Then it was decanted from the phosporous pentoxide and centrifuged to remove any trace of solid phosphorus pentoxide. Finally it was distilled under reduced pressure. The boiling point of distilled nitromethane was checked as 101^{o}-102^{o}C at 760 m.m.pressure.

1,2-Dichloroethane:

Commercial 1,2-dichloroethane was shaken with concentrated sulphuric acid, followed by two or three portions of water. The material was dried over anhydrous calcium chloride and then heated with barium oxide under reflux. After that it was distilled through a fractionating column packed with glass helices. The distillation product of 1,2-dichloroethane gave a b.p. 83^{o}C at 760 m.m. pressure.

Dimethyl Sulphoxide:

Dimethyl sulphoxide was refluxed for several hours in contact with calcium oxide and then was distilled through a fractionating column under reduced pressure.

(C) SPECTRA:

(i) Diffuse Reflectance Spectra:

Diffuse reflectance spectra (30000 - 4000 . cm^{-1})* were recorded for finely powdered specimens against a lithium fluoride reference using a "UNICAM, SP 700" spectrophotometer with diffuse reflectance attachments, "SP 735". Several compounds were decomposed on grinding in open air. They were sensitive to moisture. As a precaution all compounds were powdered in a dry box.

(ii) Infrared Spectra: (4000 - 250 cm^{-1})

A "Perkin Elmer" spectrophotometer "PE-457" was used to record spectra for paraffin oil mulls. Great care was taken with very unstable compounds. The paraffin mulls were prepared in dry box in the case of compounds which readily decompose in the open air.

(iii) Solution Spectra: (50000 - 14000 cm^{-1})

Solution spectra were measured using a "Perkin Elmer" spectrophotometer PE-137 with 1 cm matched silica cells. The 1,2-dichloroethane[66], acetonitrile and nitromethane which were used for solution spectra, were purified, dried and redistilled. Fresh stock solutions were prepared for each series of spectra.

(D) X-Ray Powder Photography:

X-Ray powder photographs were taken using Mo $K\alpha$ radiation. The "SOLUS-SCHALL" London generator and "PHILLIPS" camera and X-Ray tubes were used.

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* (1×10^6 cm^{-1} = 10 nm)

(E) CONDUCTIVITY

Molar conductivities of freshly prepared solutions (10^{-3}M) in purified nitromethane and in some cases, in dimethylsulphoxide were determined with a Mullard conductivity bridge, using standard conductivity cell type E 7591/B and cell constant 1.36.

Theoretical Consideration:

The determination of conductivity for co-ordination compounds and the interpretation of the results obtained in terms of possible structures was first carried out eighty years ago[103].

The majority of people have calculated molar conductivity, Λ_M of solution at a single concentration (i.e. 10^{-3}M) and have compared this value with previous work to judge the nature of a given electrolyte type.

The specific conductivity, k, of a solution can be determined by measuring the resistance, R, in an experimental cell of known cell constant. The cell thus formed one arm of a Wheatstone bridge circuit. Then k, specific conductivity calculated from the following expression :

$$k = \text{cell constant}/R$$

{ The resistance, R, of any uniform conductor varies directly as its length (ℓ cm) and inversely as its area of the cross section (a sq.cm) }

Inorganic chemists have widely used molar conductivity, Λ_M for comparisons of the conductivity of electrolytes. The following expression gives the relation between the specific conductivity and the molar conductivity of a solution:

$$\Lambda_M = kV_M \text{ and } \Lambda_M = k/C_M$$

where V_M is the volume of mole of solute and C_M is the concentration of solute expressed in mole.cm^{-3}.

Solvent Consideration in conductivity measurement of the metal complexes:

The selection of a solvent for conductivity determination on metal complexes depends on its dielectric constant, viscosity, specific conductivity, easiness in purification and donor properties towards metal ions. So in practice, a solvent with a high dielectric constant and low viscosity would be preferred for the conductivity study. Thus nitromethane, acetonitrile and methanol may be selected for conductivity measurement. The data of dielectric constant, viscosity and specific conductance for selected solvents were tabulated as follows[103].

Solvent	Dielectric constant at 25^{0}C	Viscosity ($g^{-1}.sec^{-1}$) at 30^{0}C	Specific conductance Ohm^{-1} cm^{-1} at 25^{0}C
Nitromethane	35.9	0.595	6.56×10^{-7}
Methanol	32.6	0.545	1.50×10^{-9}
Acetonitrile	36.2	0.325	5.9×10^{-8}
Dimethyl-sulphoxide	46.6	1.960	3.0×10^{-8}

The use of methanol suffers from its high toxicity and difficulty in purification. Acetonitrile has high toxicity and strong donor property. The use of dimethylsulphoxide is also avoided due to its high viscosity and strong donor capacity. The donor capacity of the common organic solvents for metal ions is roughly in order of dimethylsulphoxide > dimethylformamide > acetonitrile > nitromethane[103].

Thus from the above data it is seen that nitromethane has become the most widely used solvent for the determination of molar conductivity of the metal complexes. The molar conductivity of the tetramethylammonium iodide was measured at 22^{o}C which had value 90.2 ohm^{-1}.cm^{2}.mol^{-1}. This value agrees with the literature value as 91.5 ohm^{-1}.cm^{2}.mol^{-1} at 25^{o}C.[103]. The average values for complexes of unidentate ligands were found to be 88.5 ohm^{-1}.cm^{2}.mol^{-1} for 1:1 electrolytes and 167 ohm^{-1}.cm^{2}.mol^{-1}. for 2:1 electrolytes. The molar conductivity of tetramethylammonium iodide was measured in dimethylsulphoxide as 31.0 ohm^{-1}.cm^{2}.mol^{-1}. at 22^{o}C and agrees with the literature values[104]. The values of molar conductance of metal complexes in dimethylsulphoxide give low results due to its high viscosity.

(F) ANALYSIS:

Microanalysis for carbon, hydrogen and nitrogen were carried out by Mrs. Taylor, Microanalytical laboratory, this department; Dr.F.Strauss, Microanalytical laboratory, 10 Carlton Road, Oxford, and also by A. Bernhardt, 5251 Elbach Über Engelskirchen, West Germany. The analysis of carbon, hydrogen and nitrogen which was carried out in this department, were done on F & M Scientific Instrument, Model "185" C,H & N autoanalyser. In "F & M" machine the carbon, hydrogen and nitrogen were analysed by combustion of a sample on combustion bar (with cavity at the end) and the gas produced, followed by gas-liquid chromatographic analysis. Some compounds (mainly triiodide,I_3^- complexes) were found to give low carbon values, when analysed on the F & M machine. This was due to the presence of an excess iodine in the compound and on combustion of such a compound, the iodine inhibited the oxidation of carbon monoxide to carbon dioxide ($CO \rightarrow CO_2$) thus leading to a low carbon value.

Analysis of "metal" and iodide(I^-) in the complexes having formula "ML_4I_2": (where M = Ni(II),Co(II), Mn(II), Fe(II) and Cd(II),L = pyridine, β-picoline and γ-picoline:

Analysis of "Metal":

Sample (0.3g) was weighed into a conical flask and dissolved in 25 ml. of distilled water.

Soldium hydroxide pellets (0.3 - 0.5g) were added to the solution. The solution was boiled for 20-25 minutes to remove the heterocyclic base (pyridine or β-picoline or γ-picoline). The solution was cooled and diluted further with 25 ml. of distilled water, and then it was acidified with a few drops of dilute hydrochloric acid. This solution was used for respective metal analysis, e.g. nickel(II) was determined gravimetrically as nickel(II) dimethylglyoximate [51(a)], cobalt(II) was determined as $Co(Py)_4(SCN)_2$[51(b)].

Analysis of iodide (I^-) by Volhard's method[51(c)]

The iodide (I^-) was determined volumetrically by Volhard's method.

Procedure:

Sample (0.1g) was weighed in a conical flask and dissolved in 25 ml. of distilled water. Sodium hydroxide pellets (0.1g) were then added to the solution. The solution was boiled for 20-25 minutes to boil off the heterocyclic base (pyridine or β-picoline or γ-picoline) It was cooled and acidified with a few drops of 6N nitric acid. A measured, excess volume of standard (0.05N) silver nitrate solution was added. The iodide present in the sample was precipitated as AgI and excess of silver nitrate ($AgNO_3$) which remained in the solution was then back titrated with standard (0.05N) potassium thiocyanate solution using ferric alum solution as an indicator (For each titration 1 ml of an indicator was used).

From the titration reading, the iodide content was determined as follows:

(a) Total $AgNO_3$(0.05 N) Sol^n. added = A ml.

(b) In back titration, 0.05N KSCN solution used = B ml.

Therefore, (m.moles of I^- in sample) = (Total m.moles of Ag^+ added to the sample solution) - (m.moles of KSCN used for back titration)

= (0.05 x A) - (0.05 x B) = 'C'

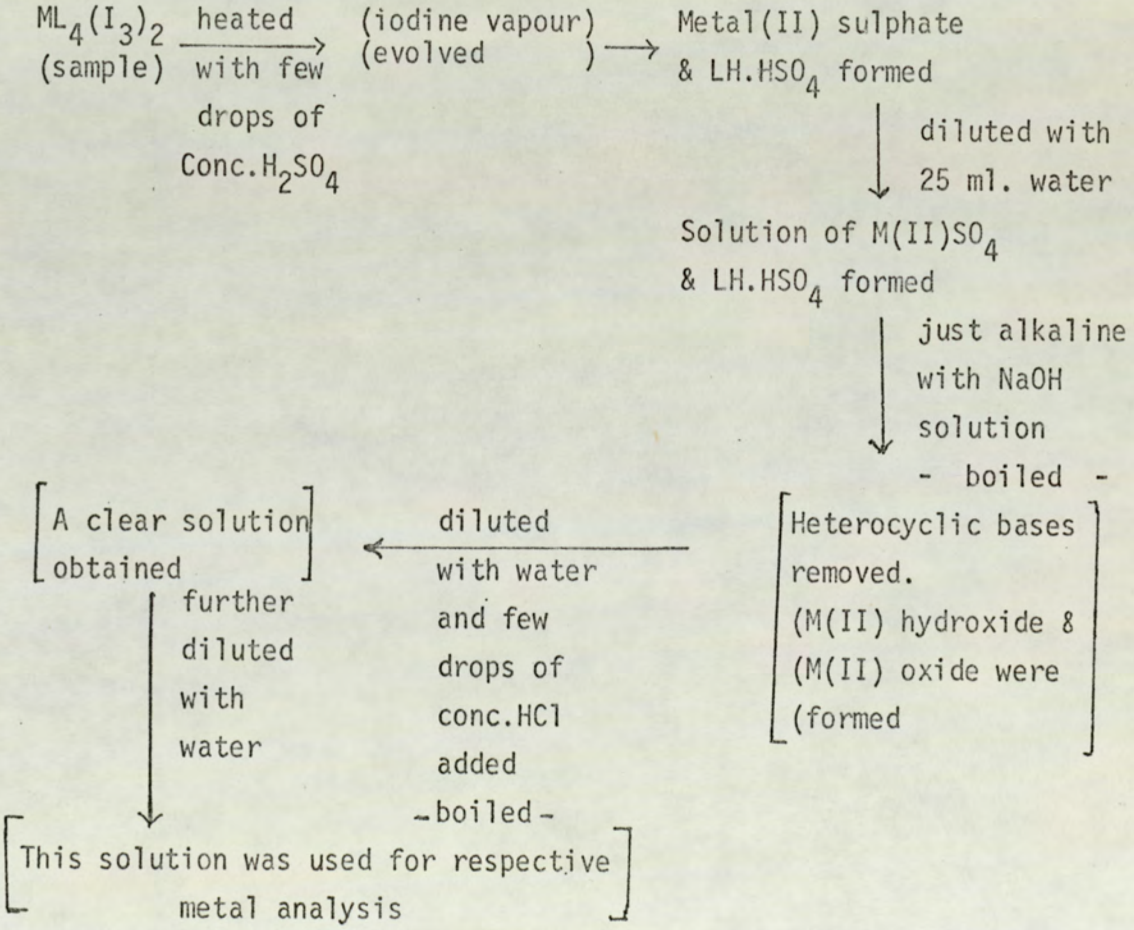
$$\text{hence the \% of } I^- \text{ in the sample} = \text{'C'} \times 126.90 \times \frac{100}{\text{wt of sample (in mg)}} = D\%$$

Analysis of "metal", "added iodine" and "total iodine" in the compound having formula $ML_4(I_3)_2$ (where M = Ni, Co, Mn, Cd and Fe; L = pyridine, β-picoline, γ-picoline)

Analysis of "Metal":

Sample (0.3g) was weighed into a 250 ml. beaker. A few drops of concentrated sulphuric acid were added carefully with the use of glass-rod. The beaker was covered with a clock-glass. The mixture was heated gently with micro-burner flame. The iodine was evolved as a violet vapour. The beaker was removed from the heat and cooled. Again a few drops of concentrated sulphuric acid were added and the mixture was heated gently to remove all remaining traces of iodine. After evolution of violet vapour (iodine) ceased, the mixture was heated further for a few minutes and then cooled. The metal was converted to its sulphate ($M(II)SO_4$) and the heterocyclic base to their cation-sulphate, $LH.HSO_4$ (where L = pyridine or β-picoline or γ-picoline). Distilled water (25 ml.) was added to dissolve the solid-mixture. The solution was then made alkaline with concentrated sodium hydroxide solution and was boiled for 20-25 minutes to remove the heterocyclic base. At this stage the metal ions were converted to metal(II) hydroxide and formed metal(II) oxide on further heating of the alkaline solution. The solution was cooled and a few drops of concentrated hydrochloric acid were added to dissolve metal(II) hydroxide and metal(II) oxide. When the solution became clear it was further diluted with 30 ml. of distilled water This diluted solution was finally used for the respective metal analysis, e.g. nickel was determined gravimetrically as nickel(II)-dimethylglyoximate, cobalt was determined gravimetrically as $Co(Py)_4(SCN)_2$ and so on.

The summary of the reactions involved in removing iodine and the heterocyclic base (pyridine, β-picoline or γ-picoline) is described as follows:



(e.g. Nickel was determined as Ni-dimethylglyoximate, gravimetrically using NH_3-ammonium acetate buffers at pH, 7.5±.1)

Analysis of "added iodine" in $ML_4(I_3)_2$ compounds

The added iodine was determined volumetrically by titrating with a standard (0.1N) sodium thiosulphate solution using iodine as self-indicator. The colour of the triiodide, I_3^-, solution before titration, was reddish-brown. It became yellow on addition of $Na_2S_2O_3$ solution and at the end point it was found colourless.

In order to obtain an accurate titration result, all "added iodine" should be liberated completely from the triiodide(I_3^-) complexes. The triiodide (I_3^-) complexes, $ML_4(I_3)_2$, were not soluble in water. They were found to be dissolved easily in many polar organic solvents such as methanol, ethanol, acetonitrile and acetone, which were missible with water, but in most cases, the iodine-starch reaction was rather faint[60]. The best results were obtained by dissolving the triiodide $ML_4(I_3)_2$ (where L = pyridine, β -picoline or γ-picoline; M = Ni(II), Co(II), Mn(II), Fe(II), or Cd(II),) in a small amount of glacial acetic acid, diluted with water and titrated immediately with standard (0.1N) sodium-thiosulphate solution. The presence of an acetic acid does not seem to influence the starch-iodine reaction. However, it was found that using iodine as self-indicator the error was practically nil. (or $< 0.1\%$).

Procedure for the determination of "added iodine" from the triiodide (I_3^-) complexes is described as follows:

A sample (0.1g) of triiodide complex was weighed into an iodine-flask and dissolved in a minimum of glacial acetic acid. The solution was diluted at once with distilled water (25 ml.) and the flask stoppered. The solution was stirred for a while and the liberated iodine was then titrated with standard (0.1N) sodium thiosulphate solution using iodine as self-indicator. The colour of the triiodide

(I_3^-) solution before titration was reddish-brown, then became yellow on addition of sodium thiosulphate solution, and was found colourless at the end point of the titration. The "added iodine" was determined as:

$$1\ \text{ml. N}\ Na_2S_2O_3 \equiv 0.1269_g.I.$$

The overall reaction which occured rapidly and stoichiometrically under the experimental condition (pH < 5) was: [51(e)]

$$2\ S_2O_3^{--} + I_2 = S_4O_6^{--} + 2I^-$$

$$\text{also}\ \ I_2 + I^- \rightleftharpoons I_3^-$$

$$2\ S_2O_3^{--} + I_3^- = S_4O_6^{--} + 3I^-$$

The colourless intermediate $S_2O_3I^-$ was formed by the reversible reaction:

$$S_2O_3^{--} + I_2 \rightleftharpoons S_2O_3I^- + I^- \ ;$$

This, $S_2O_3I^-$, intermediate was reacted with thiosulphate ion to produce the main course of overall reaction:

$$S_2O_3I^- + S_2O_3^{--} = S_4O_6^{--} + I^-$$

The intermediate $S_2O_3I^-$ was also reacted with iodide ion:

$$2\ S_2O_3I^- + I^- = S_4O_6^{--} + I_3^-$$

This explained the appearance of iodine near the end point in the titration of very dilute iodine solution by thiosulphate.

Analysis of the "total iodine" in the compound having formula $ML_4(I_3)_2$ (Where M = Ni,Co,Mn,Fe or Cd and L = pyridine,β -picoline or γ-picoline

Procedure:

A sample (0.3g) was weighed and transferred into a narrow mouthed conical flask and dissolved in 20-25 ml. of glacial acetic acid. The solution was diluted with 25-30 ml. of distilled water. The iodine liberated in the solution was reduced by passing sulphur dioxide (SO_2) gas into the solution for a few seconds. The solution became colourless as iodine was reduced to iodide. The excess of sulphur dioxide which remained in the iodide solution, was removed or minimised by adding a few drops of concentrated potassium permanganate solution. After removal of an excess sulphur dioxide, the iodide solution was boiled for 5 - 10 minutes, and acidified with a few drops of dilute nitric acid. The solution was transferred to a beaker and iodide was precipitated as silver iodide by adding an excess of dilute silver nitrate solution. The solution containing AgI precipitate, was boiled for 5 minutes and cooled. The precipitate was filtered off through a sintered glass crucible (Por-4) washed with cold dilute nitric acid and finally three times with hot distilled water. Prolonged contact of the precipitate (AgI) with nitric acid, was avoided as the iodide would be attacked through oxidation.

The precipitate was dried at 140°C for about one hour and weighed as silver iodide. It was further dried for 10-15 minutes to check the constant weight of AgI. From the precipitate's weight, iodine was determined as;

$$\mathrm{AgI} \equiv \mathrm{I}$$

$$234.7 \equiv 126.9$$

Gravimetric Factor = 0.5405

If the weight of ppte. of AgI = 'x'g and weight of sample taken, was 0.3g then percentage of iodine is,

$$= 'x' \times 0.5405 \times \frac{100}{0.3} = 'y' \%$$

(G) MAGNETISM

(i) Magnetic susceptibility measurement at room temperature:

Magnetic susceptibilities were determined by the Gouy method at room temperature.

The Gouy method is the most simple and frequently employed method for the measurement of the magnetic susceptibility of a given compound. The technique in this method consists of the measurement of the difference in the force developed on application and removal of the magnetic field, H. The apparatus used in the Gouy method is shown in figure 19(a).

Specimens:

The Gouy tube which was made of glass, was used for holding the powdered sample. The tube was constructed with a diaphram across its middle. It was suspended in a collar as illustrated. In figure-19(b) diagram of a Gouy tube and its method of suspension is given. The length and internal diameter of the tube are 20.0 cm and 0.3 cm respectively. The specimen length (up to a reference mark) is 10 cm . Uniform packing of the powder into the Gouy tube is necessary to avoid error in the measurement of susceptibility of a compound. A small quantity of the powdered sample was introduced into the tube and the bottom of the tube tapped firmly on a wooden surface a number of times to pack the powder uniformly. The process of a small addition of the powder and tapping of the tube continued until the tube was filled up to the mark (i.e. 10 cm mark).

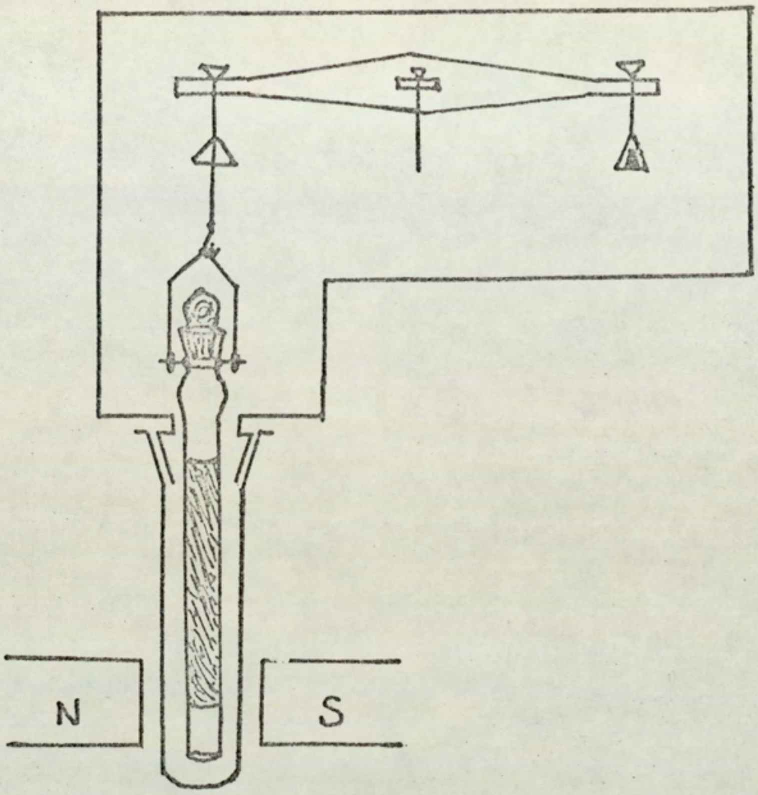


Fig. 19(a) Apparatus for the Gouy method

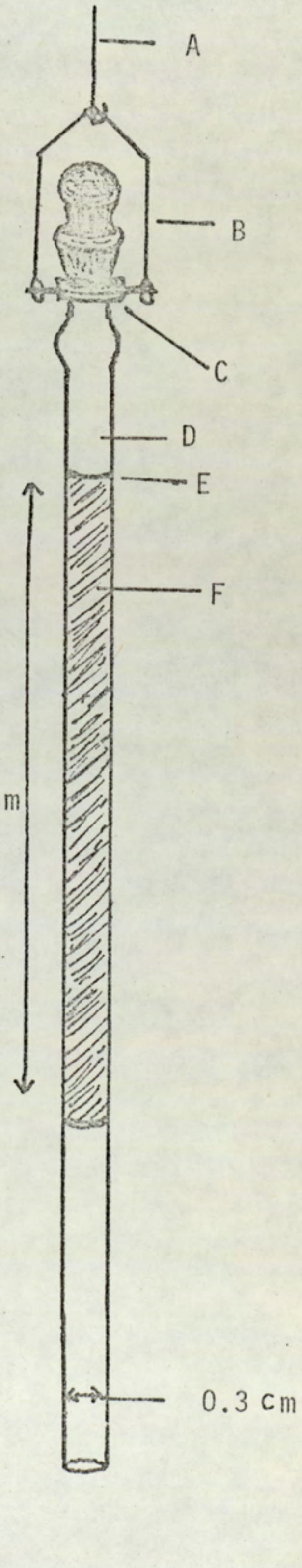


Fig. 19(b) The Gouy tube

A = suspension from balance

B = wire loop

C = collar

D = Gouy tube

E = reference mark

F = sample (powdered)

The magnet power supply type D 104 (Newport Instrument) was used to produce the magnetic field. A Stanton Instrument Ltd. balance, model SM-12 was used for the measurement of the difference in the force developed in the absence and presence of the magnetic field.

The Gouy tube alone was placed in the magnetic field to obtain the force developed on an empty tube. This force was negative because it is composed of a diamagnetic material. It usually denoted by 'δ'. In order to obtain the force on the sample alone (F'), the force on the empty Gouy tube, 'δ', has to be subtracted from the force (F) on the tube with sample.

Thus force on the sample alone, $F' = F-(-\delta) = F + \delta$ (here F, F' and δ in milligram). The following expression was used to determine the magnetic susceptibility of a given compound,

$$10^6 \chi = \frac{\alpha+\beta F'}{w} \qquad (1)$$

where α= a constant allowing for the displaced air and is equal to 0.029 x specimen volume. (The specimen volume in cm^3 was measured on 100 mm. length of the sample packing); β = the tube "calibration constant"; w = the weight of the sample (in gram).

Two very good solid calibrants are $HgCo(CNS)_4$ and $Ni(en)_2S_2O_3$. They are easily prepared pure, do not decompose or absorb moisture, and pack well. Their susceptibilities at 20^0C are 16.44×10^{-6} and 11.03×10^{-6} c.g.s. units, decreasing by 0.05×10^{-6} and 0.04×10^{-6} per degree temperature rise respectively, near room temperature. The cobalt compound, besides having the higher susceptibility, also packs rather densely and is suitable for calibrating low fields while the nickel compound with lower susceptibility and density is suitable for higher fields[53A].

The tube calibration constant, β, was determined as follows:

Mercury$^{(II)}$ tetrathiocyanato-cobaltate(II) was used for the determination of the Gouy tube calibration constant β. The magnetic susceptibility of $Hg[Co(CNS)_4]$ had been previously determined by Figgis and Nyholm$^{52(a)}$ as $\chi_g = 16.44 \times 10^{-6}$ cg.s units at 20°C. Taking this real value of χ_g for $Hg[Co(CNS)_4]$, the tube calibration constant,β was determined by observing the force on Gouy tube filled with finely powdered $Hg[Co(CNS)_4]$.

Determination of the tube calibration constant 'β'

Weight of empty Gouy tube, magnet 'off' = 8.53991 g.

Weight of empty Gouy tube, magnet 'on' = 8.53942 g.

Temperature = 20.0°C

Weight of Gouy tube filled with $Hg[Co(CNS)_4]$ magnet 'off' = 9.65378 g.

Weight of Gouy tube + $Hg[Co(CNS)_4]$, magnet 'on' = 9.72550 g

Specimen volume 'V' (at 10.0cm height) = 0.6027 ml.

(Water was used to measure 'V')

α = constant allowing for the displaced air $= 0.029 \times V$

$= 0.0175$

'δ' = Force on empty Gouy tube = - 0.49 mg

F' = Force on the sample $= F - (-\delta)$

$= 71.82 + 0.49 = 72.21$ mg

(where F being the observed force on specimen + tube

W = Weight of $Hg[Co(CNS)_4]$ only = 1.1138 g

Using the above data, the tube calibration constant, β was determined using the above equation (1),on Page 96.

The χ_g for $Hg(Co(CNS)_4)$ was taken as 16.44×10^{-6} at 20°C. Putting values for w, α, β in equation (1) then;

$$10^6\{16.44 \times 10^{-6}\} = \frac{0.0175 + \beta(72.21)}{1.1138}$$

$$\beta = \frac{18.25}{72.21} = 0{\cdot}253$$

The magnetic susceptibility of $Ni(en)_2S_2O_3$ was determined by using the above 'β' value. The susceptibility, χ_g was obtained as $10.60 \pm 0.1 \times 10^{-6}$ c.g.s. units at 19°C. This value agrees satisfactorily with the literature values[53B], and so confirms the value obtained for β.

The detailed observation and calculation for the determination of the magnetic susceptibility of the compound, diiodo-tetrakis(pyridine)nickel(II), is illustrated as follows:

(a) <u>Determination of Magnetic Susceptibility of $Ni(Py)_4I_2$</u>

Weight of empty Gouy tube, magnet 'off' = 8.53991 g

Weight of empty Gouy tube, magnet 'on' = 8.53942 g

Temperature = 20.5°C

Weight of Gouy tube filled with powdered $Ni(Py)_4I_2$, magnet 'off' = 9.32083 g

Weight of Gouy tube + $Ni(Py)_4I_2$, magnet 'on' = 9.33985

Specimen volume 'V' (at 10cm height) = 0.6027 ml

$\alpha = 0.029 \times 0.6027 = 0.0175$

'δ', observed force on the Gouy tube only = - 0.49 mg

Force on the specimen = $F - (-\delta) = F + \delta = 19.51$ mg

(where F being the observed force on the sample + tube = 19.02 mg)

Weight of sample, $Ni(Py)_4I_2$ only = w_g = 0.7809 g.

Using above experimental values for 'α', 'β', 'w' and F', the magnetic susceptibility of $Ni(Py)_4I_2$ was determined as follows:

$$10^6\,\chi_g = \frac{\alpha+\beta F'}{w} = \frac{0.0175 + 0.253\ (19.51)}{0.7809}$$

$$\chi_g = 6.34 \times 10^{-6} \text{ c.g.s. units.}$$

The molecular weight of $Ni(Py)_4I_2$ is 628.9

$$\chi_M = \{628.9 \times 6.34\} \times 10^{-6} = 3987.0 \times 10^{-6} \text{ c.g.s. units}$$

(b) <u>Determination of magnetic moment, μ_{eff}, of the $Ni(Py)_4I_2$</u>

χ_g for $Ni(Py)_4I_2$ = 6.34×10^{-6} c.g.s. units

Molar susceptibility χ_M for $Ni(Py)_4I_2$ = 3987.0×10^{-6} c.g.s.units

The diamagnetic correction for the pyridine, iodine etc. was made from Pascal's constants as listed by Figgis and Lewis[52(b)]. It was

Ni: $1 \times 12.8 = 12.80 \times 10^{-6}$

C: $20 \times 6.0 = 120.00 \times 10^{-6}$

H: $20 \times 2.93 = 58.60 \times 10^{-6}$

N: $4 \times 4.61 = 18.44 \times 10^{-6}$

I: $2 \times 44.60 = 89.20 \times 10^{-6}$

double bonds: $12\times(-8.2) = -98.4 \times 10^{-6}$

$\underline{200.6 \times 10^{-6}}$

Thus

$$\begin{aligned} \chi'_M &= \{\chi_M + (\text{diamagnetic correction})\} \times 10^{-6} \\ &= (3987 + 200.6) \times 10^{-6} \\ &= 4187.6 \times 10^{-6} \text{ c.g.s. units.} \end{aligned}$$

and hence magnetic moment, μ_{eff}, was determined using the following expression:

$$\mu_{eff} = 2.84 \{T \chi'_M\}^{\frac{1}{2}} \quad \text{B.M.} \qquad (2)$$

(where T = room temperature + 273.0 = 293.5)

putting the value of T and χ'_M in the above equation (2);

$$\mu_{eff} = 2.84 \{293.5 \times 4187.6 \times 10^{-6}\}^{\frac{1}{2}}$$

$$= 3.184 \text{ B.M.}$$

This value, 3.148 B.M. i.e. 3.15 B.M. for $Ni(Py)_4I_2$ agrees satisfactorily with literature values[105]. (The value of μ_{eff} for $Ni(Py)_4I_2$ obtained by Belova et al.[105] was 3.15 B.M. at 20°C)

(ii) Magnetic Susceptibility Measurements down to Liquid Nitrogen Temperatures: (Ref: 120)

The method employed for the magnetic susceptibility measurements at low temperature was basically the same as that for room temperature measurement. However the low temperature measurements need a cryostat to maintain low environmental temperatures of the specimen. The Newport Instrument, with variable-temperature Gouy balance system, was used to perform the susceptibility measurements at low temperature. A diagram of the general arrangement of the balance and cryostat is shown in Figure-20. The liquid nitrogen inlet is shown in Figure -21.

The Basic Equipment

1. Magnet and Power Supply

A Newport 4 in. Electromagnet Type A was used. A field strength of about 6000 gauss was used. The power supply will provide continuous variable current from zero up to 20 amps.

2. The Balance

A Stanton semi-micro balance, Type SM12S, was used.

3. The Cryostat:

The cryostat consists of three major components; an inner copper cylindrical chamber of high thermal inertia, an inner glass dewar with controllable vacuum surrounding the chamber and an outer glass dewar. The specimen was suspended inside the copper chamber which was heated electrically by a coil wound in a groove around the outside of the chamber. The copper chamber was 7 inches long with an outer diameter of 7/8 inches and an internal diameter of 1/2 inch. The inner dewar separates the chamber and specimen from the liquid nitrogen. So, by connecting a vacuum pump to the outlet of the vacuum space, the heat leak to the liquid nitrogen can be controlled. The inner dewar was suspended inside the outer dewar with the copper chamber vertical. The stepped outer dewar was used to contain the liquid nitrogen coolant.

4. Specimen Temperature Measurement and Control

The temperature control was performed by using the unbalance voltage of the resistance bridge to switch a heater current on and off. A large diameter variable resistance was calibrated accurately in terms of temperature and was used to set the temperature value required.

5. Specimen and Suspension

The specimen was powdered and packed into a Gouy tube. The Gouy tube was made of silica-glass and was found to be purely diamagnetic. The specimen length of 10 cm was chosen. The suspension of the specimen tube is shown in Figure(20).

Experimental Procedure:

The glass draught excluding tube (Fig. 20) was removed and the inside of the inner dewar was flushed with nitrogen to remove the air. This was achieved by placing a ground glass stopper over the top of the dewar and connecting the vacuum pump to it. The dewar was then switched from the vacuum line to an input of dry nitrogen.

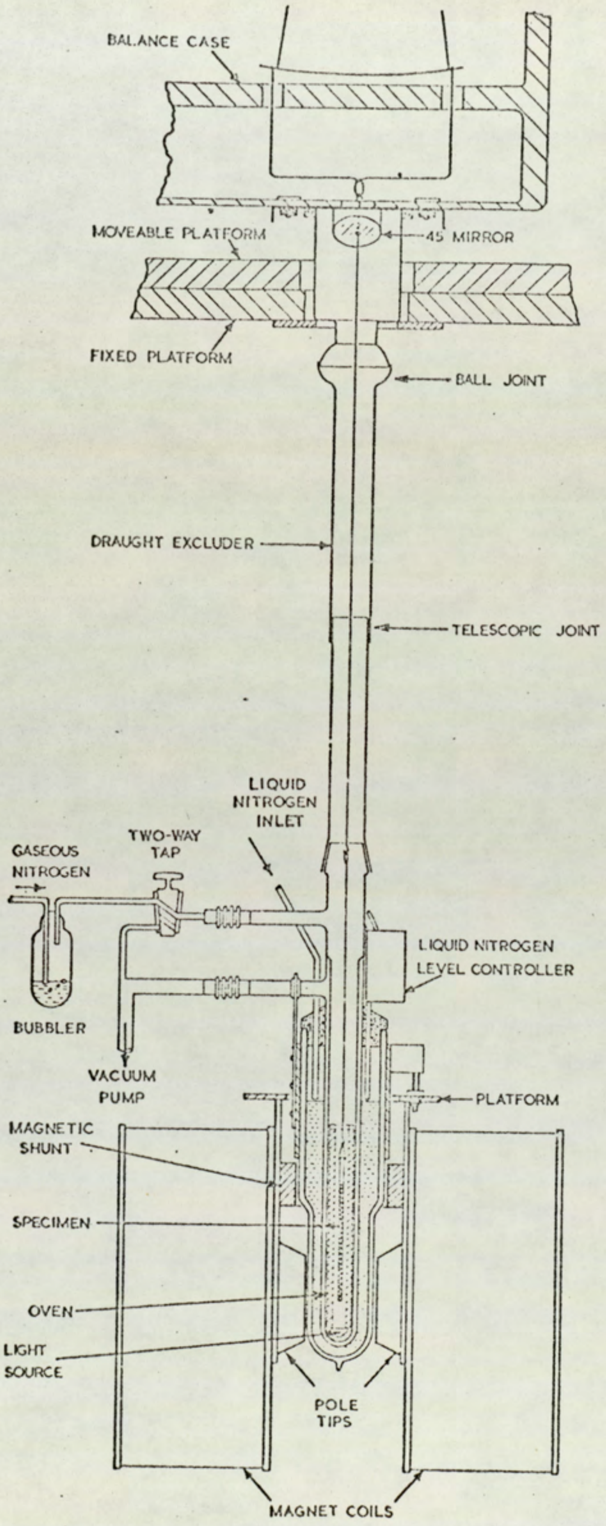


Fig. 20 A diagram of the general arrangement of the balance and cryostat. (Ref: 120)

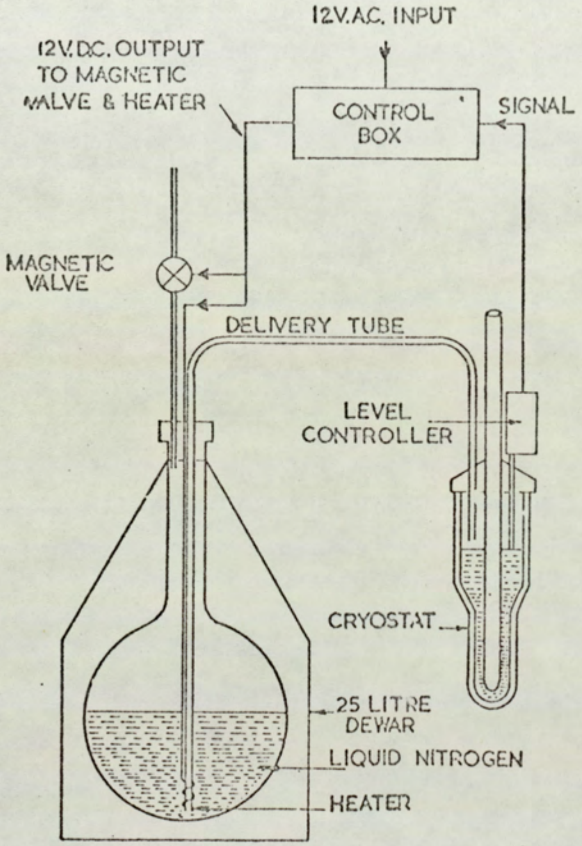


Fig. 21 The liquid Nitrogen inlet system. (Ref: 120)

After the flushing, the Gouy sample tube, containing the finely powdered sample was hooked onto the suspension, lowered into the chamber and the glassware replaced. The temperature was set at room temperature ($20^{\circ}C$) and after 15-20 minutes the Gouy sample tube was weighed with and without the magnetic field. Then the temperature control was set at $-180^{\circ}C$ and, with the vacuum applied between the walls of the inner dewar, the liquid nitrogen supply was switched on. When the required temperature ($-180^{\circ}C$) was reached, the heating current was switched on. (heater supply dial set at $\sim 8^{\circ}c$). After complete equilibrium attained, the Gouy sample tube was weighed with and without the magnetic field. For the measurements at higher temperature (above $-180^{\circ}c$) again the temperature control was set at required temperature, with heater supply switched on. (set the heater supply dial at $10-15^{\circ}C$). Once the thermostat has begun to function, half an hour was sufficient for equilibrium to be attained and then weighing with and without the magnetic field were repeated.

The diamagnetic correction for the Gouy tube was made by measuring the weight of empty tube in the same way as was done with the sample (i.e. at $-180^{\circ}C$, and other different temperatures). Mercury(II)-tetra-thiocyanato-cobaltate(II) was used for the determination of the Gouy tube calibration constant, β .

The results are usually presented in the form of a graph of reciprocal susceptibility (after diamagnetic correction) against temperature, T(K) which, if the Curie-Weiss Law is obeyed, will be a straight line intersecting the temperature axis at θK, the law being:

$$\chi = \frac{C}{T + \theta}$$

CHAPTER 6

The compounds produced on the addition of iodine to some first row transition metal complexes of the simpler pyridine bases

In this chapter the preparations, characterisations, spectroscopic and magnetic properties are presented for the following new complexes of the types $ML_4(I_3)_2$ and $M'L_4(NCSI_2)_2$. (where M = Ni(II), Co(II), Fe(II), Mn(II) and Cd(II), L = pyridine, β-picoline or γ-picoline and M' = Ni(II) only-). The reaction between CdI_2, iodine and γ-picoline is also described.

Complex	Preparations	Solid state & solution data	Discussion
Ni(pyridine)$_4$(I$_3$)$_2$	p 109	Tables 11,12,18, 19 & 20.	p 154
Ni(β-picoline)$_4$(I$_3$)$_2$	p 109	"	p 154
Ni(γ-picoline)$_4$(I$_3$)$_2$	p 110	" "	p 154
Ni(pyridine)$_4$(NCSI$_2$)$_2$	p 112	Tables 11,13,18, 19 & 20.	p 160
Ni(β-picoline)$_4$(NCSI$_2$)$_2$	p 113	" "	p 160
Ni(γ-picoline)$_4$(NCSI$_2$)$_2$	p 113	" "	p 160
Co(pyridine)$_4$(I$_3$)$_2$	p 116	Tables 15,17,18 & 19.	p 170
Co(β-picoline)$_4$(I$_3$)$_2$2(CH$_3$CN)	p 117	" "	p 170
Co(γ-picoline)$_4$(I$_3$)$_2$2(CH$_3$CN)	p 118	" "	p 170
Fe(pyridine)$_4$(I$_3$)$_2$	p 131	Tables 14,16,17, 18 & 19.	p 170
Fe(~~β~~γ-picoline)$_4$(I$_3$)$_2$	p 131	"	p 170
Fe(γ-picoline)$_4$(I$_3$)$_2$ 2(CH$_3$CN)	p 132	" "	p 170

Complex	Preparation	Solid state & solution data	Discussion
Mn(γ-picoline)$_4$(I_3)$_2$ 2(CH_3CN)	p 120	Tables 16,17,18 & 19.	p 170
Cd(pyridine)$_4$(I_3)$_2$	p 121	" 14,16,18 & 19	p 172
Cd(γ-picoline)$_4$(I_3)$_2$ 2(CH_3CN)	p 123	" "	p 172

PREPARATIONS

The preparation of the triiodide (I_3^-) complexes, $ML_4(I_3)_2$, involved a two step process. The first step is the preparation of the parent compounds of the stiochiometry, ML_4I_2 and the second step is the preparation of the triiodide (I_3^-) compounds of the stoichiometry $ML_4(I_3)_2$ from their respective diiodides. (Where M = divalent cations and L = pyridine, β-picoline and γ-picoline). Similarly the iodine addition compounds of nickel(II) thiocyanate with pyridine, β-picoline and γ-picoline are prepared from their parent compounds $NiL_4(NCS)_2$.

1. Nickel(II) compounds with pyridine, β-picoline and γ-picoline

(A) Preparation of nickel(II) iodide compounds of the stoichiometry, NiL_4I_2; (where L = pyridine, β-picoline, and γ-picoline)

A hot ethanolic solution of nickel(II) iodide hexahydrate (10m.moles, 4.2g) was added dropwise with constant stirring to a hot ethanolic solution of the appropriate ligand (Py or picolines). A pale green crystalline product formed immediately on cooling, which was filtered off and dried between filter-paper pads. It was further dried over sodium hydroxide pellets for an hour in a desiccator at an atmospheric pressure. The washing and recrystallisation of a pale-green product was restricted due to the loss of the ligand molecules (pyridine bases).

The following pure complexes were isolated using above general method.

(i) Diiodotetrakis-(pyridine)nickel(II)

A pale-green solid was obtained. Yield, 6.5g. It was fairly stable in the open air but decomposed on prolonged exposure to air.

(Found: C,38.21; H,3.3; N,8.78; I,40.30%

$C_{20}H_{20}I_2N_4Ni$;requires:C,38.19; H,3.21; N,8.90;I,40.7%)

(ii) Diiodotetrakis-(β-picoline)nickel(II)

A pale-green solid was obtained. Yield 6.8g.

(Found: C,42.2; H,4.02; N,8.00; I,37.0%

$C_{24}H_{28}I_2N_4Ni$; requires:C,42.1; H,4.12; N,8.17; I,37.10%)

This compound was very sensitive to moisture and turned to sky-blue in open air within a few minutes. The analysis of the sky-blue solid suggested the formula,($Ni(H_2O)_2(\beta\text{-pic})_4I_2$).

(Found: C,39.89; H,4.51; N,7.71; I,35.2%

$C_{24}H_{32}I_2N_4NiO_2$:requires:C,39.96; H,4.48; N,7.76; I,35.05%)

The infrared spectrum of a sky-blue, ($Ni(H_2O)_2(\beta\text{-pic})_4I_2$), suggested the presence of water molecules and ν(OH) was found at ~ 3400cm^{-1}, while infrared spectrum of freshly prepared green compound, $Ni(\beta\text{-pic})_4I_2$, the water band at ~ 3400 cm^{-1} was absent. Therefore freshly prepared compound, $Ni(\beta\text{-pic})_4I_2$ was kept in a sealed ampoule for future use. It was stable for many months in a sealed ampoule.

(iii) Diiodotetrakis-(γ-picoline)nickel(II)

A pale-green solid was obtained. Yield, 7.0g.

(Found: C,42.25; H,4.20; N,7.95; I,36.98%

$C_{24}H_{28}I_2N_4Ni$: requires; C,42.1; H,4.12; N,8.17; I,37.1%)

This compound was moderately sensitive to moisture and decomposed on prolonged exposure to air. Therefore it was kept in a sealed ampoule for future use.

(B) Preparation of the triiodide (I_3^-) complexes of nickel(II) with pyridine, β -picoline and γ-picoline.

The general methods of preparation of crystalline polyhalide complexes in the solution have been reviewed by Chattaway and Hoyle[58], and by Cremer and Duncan[59]. They studied principally the tetraalkylammonium salts of polyhalide ions. In the preparation of triiodide,(I_3^-) complexes in solid state, the choice of an appropriate solvent as the reaction medium is of primary importance. The iodine and triiodides (I_3^-) are highly reactive chemically and therefore the solvents which can easily be halogenated by triiodide compounds or which effect hydrolysis reactions were avoided. The large majority of tetraalkylammonium-polyhalide compounds were prepared either in methanol or in ethanol solution. However in the preparation of triiodide (I_3^-) complexes, solvents which are more inert to halogenation or hydrolysis such as 1,2-dichloroethane, dichloromethane have been used. The preference was given to dichloromethane owing to its low boiling point (40°C) (very volatile in nature). The triiodide,I_3^-, complexes were very unstable in the open air and they decomposed into free iodine and iodide, $I_3^- \rightleftharpoons I_2 + I^-$. Therefore all complexes were prepared in a closed system at room temperature. The quick-fit flask, water-condenser and other glass equipments which were used in the preparation of complexes, were carefully dried before use. The dichloromethane was dried and purified (page 83) before use as a solvent in the reaction.

The following nickel(II)-triiodide complexes having the composition $NiL_4(I_3)_2$, were prepared(where L = pyridine, β-picoline or γ-picoline). The diiodide complexes of nickel(II) with pyridine, β-picoline and γ-picoline were used as starting material in the respective preparations.

(i) Di-triiodotetrakis(pyridine)nickel(II)

The diiodotetrakis(pyridine)nickel(II) (5 m.moles,3.15g) was weighed in a dry 50 ml. quick-fit flask. Iodine (10 m.moles; 2.53g) was added to the flask. Both solids were mixed together and the flask stoppered immediately. The solid mixture swirled for a minute. Then 20-25 ml. of dichloromethane was added at once. The flask was attached to a water-condenser which in turn was fitted with an anhydrous calcium chloride guard tube. The solution was then stirred with a magnetic stirrer without heating for 10-15 minutes. Reddish-brown sparkling crystals formed in the solution which were filtered off and dried over sodium hydroxide pellets for half an hour in a desiccator at atmospheric pressure. The crystalline product was then sealed in a dry ampoule. Yield of reddish-brown solid, 4.5g.

(Found: C,21.2; H,2.1; N,4.8; added iodine,45.2;
total iodine,66.95; Ni,4.89%,
$C_{20}H_{20}I_6N_4Ni$ requires: C,20.15; H,1.8; N,4.9; added iodine,44.7;
total iodine,67.0; Ni,5.15%)

(ii) Di-triiodotetrakis(β-picoline)nickel(II):

This compound was prepared in the same way as the above ditriiodotetrakis(pyridine)nickel(II). A reddish-brown crystalline product was obtained on slow evaporation of the solution (which contained 10 m.moles of $Ni(\beta\text{-pic})_4I_2$ and 20 m.moles of iodine in dichloromethane) in a vacuum desiccator at room-temperature. The product was dried over sodium hydroxide pellets in a desiccator at atmospheric pressure. This compound was very sensitive to moisture and turned to a black oily mass in the open air within a few minutes. Therefore it was sealed in a dry ampoule for future use. In a sealed ampoule however it remained unchanged for many months. Yield of a reddish-brown solid, 5.1g.

(Found: C,24.5; H,2.6; N,4.55; added iodine,43.0,
total iodine,63.90; Ni,4.95%.
$C_{24}H_{28}I_6N_4Ni$ requires: C,24.18;H,2.40;N,4.79; added iodine,42.5;
total iodine,63.84; Ni,4.92%)

(iii) Di-triiodotetrakis-(γ-picoline)nickel(II)

This compound was prepared as in the procedure outlined for the preparation di-triiodotetrakis(pyridine)nickel(II). A reddish-brown crystalline product was obtained. Yield,5.45g. The product was kept in a dry ampoule for future use.

(Found: C,23.3; H,2.8; N,4.4; added iodine,42.2,
total iodine,63.73; Ni,4.86%.
$C_{24}H_{28}I_6N_4Ni$ requires: C,24.18; H,2.40; N,4.79; added iodine,42.5;
total iodine,63.84; Ni,4.92%)

(C). Ni(II)-thiocyanate compounds with pyridine, β-picoline and γ-picoline

The complexes, $NiL_4(NCS)_2$ where L = Py, β-pic, or γ-pic) were prepared by the following procedure:

Ethanolic solutions of nickel(II) nitrate hexahydrate (10 m.moles, 2.9g) and potassium isothiocyanate (20 m.moles,1.94g) were mixed and precipitated potassium nitrate removed by filtration. The solution (which contained NCS^- and Ni^{++} ions) was warmed gently for a 3-5 minutes and filtered again. This hot solution was then mixed with a hot ethanolic solution of an appropriate ligand(L) (45m.moles)(where L = Py. or β-pic or γ-pic). Sky-blue crystals formed immediately on cooling, were filtered off &washed with a small amount of alcohol containing 5% of the appropriate ligand (Py,β-pic or γ-pic). The crystalline solid was then dried over sodium hydroxide pellets for an hour in a desiccator at atmospheric pressure.

The following compounds having the composition, $NiL_4(NCS)_2$ (where L = Py, or β-pic or γ-pic) were isolated using the above general methods:

(i) Di-thiocyanato-tetrakis(pyridine)nickel(II)

A sky-blue crystalline solid was obtained. Yield, 4.9g.

(Found: C,53.68; H,4.07; N,16.95%

$C_{22}H_{20}N_6NiS_2$ requires: C,53.79; H,4.11; N,17.12%)

(ii) Di-thiocyanato-tetrakis(β-picoline)nickel(II)

A pale-blue crystalline solid was obtained. Yield, 5.31g.

(Found: C,56.92; H,4.98; N,15.27%

$C_{26}H_{28}N_6NiS_2$ requires: C,57.0; H,5.1; N,15.40%)

(iii) Di-thiocyanato-tetrakis-(γ-picoline)nickel(II)

A sky-blue crystalline solid was obtained. Yield,5.4g.

(Found: C,56.95; H,5.06; N,15.36%

$C_{26}H_{28}N_6NiS_2$ requires: C,57.0; H,5.10; N,15.40%)

These thiocyanato complexes of nickel(II) with pyridine, β-picoline and γ-picoline were fairly stable in the open air but decomposed on prolonged exposure. Therefore they were kept in a sealed ampoule for future use.

(D). Iodine addition compounds with $NiL_4(NCS)_2$ (where L = Py. β-pic or γ-pic)

The iodine addition compounds with $ML_4(NCS)_2$ (where M = Co(II), and Ni(II), L = py) were first prepared by Pfeiffer and Tilgner[106]. The same compounds were also prepared and studied spectroscopically by Foster and Goodgame[107]. Both authors have used ethanol as solvent for the reaction. The following procedure was used by Pfeiffer and Tilgner[106] for the preparation of iodine adduct with di-thiocyanato-tetrakis(pyridine)nickel(II).

4.9g of $Ni(Py)_4(SCN)_2$ was dissolved in 15 ml. of ethanol and 7.6g of iodine was added to it. The solution was warmed on a water-bath for two hours with reflux~~ed~~ condenser. The ethanol was then evaporated to small bulk. Dark crystals were formed in the solution on cooling. The crystalline product was re-crystallised from chloroform.

In the present work, however, a different procedure was used for the preparation of the iodine addition compounds with $NiL_4(SCN)_2$ (where L = Py, β-pic or γ-pic). They were prepared as follows:

(i) Iodine adduct of dithiocyanato-tetrakis(pyridine)nickel(II)

Dithiocyanato-tetrakis(pyridine)nickel(II) (5 m.moles 4.90g) was weighed in a dry 50 ml quick-fit flask. Iodine (10 m.moles,2.53g) was added to the flask. Both solids were mixed together and the flask stoppered immediately. The solid mixture swirled for a minute. Then 20-25ml of dichloromethane was added at once. The flask was attached to a water-condenser which in turn was fitted with an anhydrous calcium chloride guard tube. The solution was then stirred with a magnetic stirrer without heating for 10-15 minutes. Dark-brown crystals were formed on slow evaporation of the solution in a vacuum desiccator at room-temperature. The crystals were collected and recrystallised from chloroform. The product was dried over sodium hydroxide pellets for about an hour in a desiccator at atmospheric pressure. This compound was moderately sensitive to moisture and decomposed on prolonged exposure to air.Therefore the dark-brown solid was stored in a sealed dry ampoule. Yield of the solid, 6.5g.

(Found: C,26.7; H,2.4; N,8.2; I,50.78; Ni,5.82%
$C_{22}H_{20}I_4N_6NiS_2$ requires:C,26.46;H,2.02; N,8.4;I,50.83; Ni,5.87%)

(II) Iodine adduct of dithiocyanato-tetrakis(β-picoline)nickel(II)

This compound was prepared in the same way as the above iodine adduct of di-thiocyanato-tatrakis(pyridine)nickel(II). Dark-brown crystalline product was obtained. Yield of product, 6.7g. This compound was very sensitive to moisture and decomposed to a dark oily mass on exposure to air. Therefore it was stored in a sealed dry ampoule.

(Found: C,29.2; H,2.80; N,7.61; I,48.2; Ni,5.72%
$C_{26}H_{28}I_4NiS_2$ requires: C,29.6; H,2.70; N,7.9; I,48.1; Ni,5.5%)

(iii) Iodine adduct of dithiocyanato-tetrakis(γ-picoline)nickel(II)

This compound was prepared in the same way as the above iodine adduct of dithiocyanato-tetrakis(pyridine)nickel(II).A dark -brown crystalline product was obtained. Yield 6.81g. It was very sensitive to moisture and decomposed to a dark oily mass on exposure to air. Therefore it was stored in a sealed dry ampoule.

(Found: C,29.2; H,2.8; N,7.7; I,48.3; Ni,5.8%
$C_{26}H_{28}I_4N_6NiS_2$ requires:C,29.6;H,2.7; N,7.9; I,48.1; Ni,5.5%)

2. Cobalt(II) complexes with pyridine,β-picoline and γ-picoline

(A) Preparation of cobalt(II) iodide complexes of pyridine, β-picoline and γ-picoline

The cobalt(II) complexes having the formula CoL_4I_2 (where L = py, β-pic or γ-pic) were prepared in the same way as the diiodo-tetrakis-(pyridine)nickel(II) (page106). The following compounds were isolated in the solid state.

(i) Diiodo-tetrakis(pyridine)cobalt(II)

A pink crystalline product was obtained. Yield, 6.2g.

(Found: C,38.3; H,3.1; N,8.76; I,40.4; Co,9.2%
$C_{20}H_{20}CoI_2N_4$ requires: C,38.2; H,3.21; N,8.9; I,40.7; Co,9.37%)

(ii) Diiodotetrakis(β-picoline)cobalt(II)

A brownish-pink crystalline product was obtained. Yield of product, 6.42 g.

(Found: C,42.2; H,4.3; N,8.2; I,37.2; Co,9.1%
$C_{24}H_{28}CoI_2N_4$ requires: C,42.06;H,4.12;N,8.2; I,37.1; Co,9.2%)

(iii) Diiodotetrakis(γ-picoline)cobalt(II)

A greyish-pink crystalline product was obtained. Yield of product, 6.90g.

(Found: C,42.3; H,4.2; N,8.18; I,36.97; Co,9.3%
$C_{24}H_{28}CoI_2N_4$ requires: C,42.06;H,4.12;N,8.20, I,37.1; Co,9.2%)

The above cobalt(II) compounds, CoL_4I_2 (where L = py,β-pic or γ-pic) were found to be very sensitive to moisture and decomposed in a few minutes on exposure to air. The decomposition of CoL_4I_2 was seen by the colour changing from pink to bluish-green. A bluish-green compound was found as CoL_2I_2, a tetrahedral species. Thus the compound, CoL_4I_2, was carefully prepared, dried and sealed immediately in a dry ampoule for future use.

(B) Preparation of the triiodide(I_3^-) complexes of cobalt(II) with pyridine, β-picoline and γ-picoline

The triiodide (I_3^-) complexes of cobalt(II) with pyridine, β-picoline and γ-picoline were prepared in the same way as the triiodide(I_3^-) complexes of nickel(II) with pyridine, β-picoline and γ-picoline (page 109). However in the preparation of the triiodide(I_3^-) compounds of cobalt(II), there was only an oily mass formed instead of a crystalline product when dichloromethane was used as the reaction solvent. Other solvents such as 1,2-dichloroethane, chloroform and methanol were found to be useless and gave the same results as the dichloromethane. On the other hand solvents which induce crystallisation e.g. benzene, diethylether, carbontetrachloride, were added separately to the oily mass (dark brown) of the triiodide-cobalt(II) complexes in dichloromethane, but a crystalline product was not obtained.

Martin[69] had prepared some alkali metal salts of triiodide anions and found that a variety of stable molecular complexes could be isolated in the presence of an organic compound or solvent molecule of crystallisation. The presence of such organic compound or solvent molecules were essential for the stability of metal-triiodides because in their absence, the triiodide(I_3^-) compound decomposed into metal iodide and free iodine.

The above idea[69] was applied in the preparation of triiodide(I_3^-) complexes of cobalt(II) with β-picoline and γ-picoline. Acetonitrile was subsequently found to be a good solvent in the preparation of cobalt(II) triiodide complexes. The diiodide-complexes of cobalt(II) with pyridine, β-picoline and γ-picoline were used as starting material in the following preparations.

(i) Di-triiodotetrakis(pyridine)cobalt(II);

Diiodotetrakis(Pyridine)cobalt(II) (5 m.moles,3.15g) was weighed in a dry 50 ml.quick fit flask.Iodine (10 m.moles 2.53g) was added to the flask. Both solids were mixed together and the flask stoppered immediately. Then 20-25 ml of dichloromethane was added at once. The flask was attached to a water-condenser which in turn was fitted with an anhydrous calcium chloride guard-tube. The solution was stirred with a magnetic stirrer, without heating for 20-25 minutes. Dark-brown oily mass was formed on slow evaporation of solvent in a vacuum desiccator at room-temperature. A small amount of this oily mass was treated separately with benzene, diethylether and carbontetrachloride to induce crystallisation but a solid stable product was not obtained. The dark-brown oily mass which formed in dichloromethane was then kept in a desiccator over sodium hydroxide pellets at atmospheric pressure. A dark-brown crystalline product was obtained from the oily mass after 10 days keeping in a desiccator at atmospheric pressure. The product was further dried over sodium hydroxide pellets in a desiccator. Yield of product,5.2g. This compound was found to be sensitive to moisture and decomposed to a dark oily mass on exposure to air. Therefore it was kept in a sealed ampoule.

(Found: C,21.5; H,2.2; N,4.8; added iodine,44.31;
total iodine,66.91; Co,5.03%

$C_{20}H_{20}CoI_6N_4$ requires: C,21.14; H,1.80; N,4.9; added iodine,44.7;
total iodine,67.0; Co,5.16%)

(ii) Preparation of di-triiodo-(β-picoline) and di-triiodo-(γ-picoline)cobalt(II) using acetonitrile as the reaction solvent:

(a) Di-triiodotetrakis(β-picoline)cobalt(II) diacetonitrile

Diiodotetrakis(β-picoline)cobalt(II) (5 m.moles,3.42g) was weighed in a dry 50 ml. quick-fit flask. Iodine (10 m.moles,2.53g) was added to the flask. Both solids were mixed together and the flask stoppered. Then 20-25 ml. of acetonitrile was added at once. The flask was attached to a water-condenser which in turn was fitted with an anhydrous calcium chloride guard tube. The solution was then stirred with a magnetic stirrer without heating for 20-25 minutes. Reddish-brown sparkling crystals separated on slow evaporation of solution in a vacuum desiccator. The crystalline product was then dried over sodium hydroxide pellets for about an hour in a desiccator at atmospheric pressure. Yield of product, 5.6g. This compound was very sensitive to moisture and decomposed to a dark-brown oily mass on exposure to air. Therefore it was kept sealed in a dry ampoule. The infrared spectrum of this compound supported the presence of the acetonitrile molecules and also suggested that the cyanide group (CN^-) was not co-ordinated{(ν(CN)}for compound found at ~2303 and 2279 cm^{-1} and for free acetonitrile, ν(CN) is at 2283 cm^{-1}). The analysis of this compound also suggested the presence of two molecules of acetonitrile.

(Found: C,26.29; H,2.81; N,6.49; added iodine,39.77;
total iodine, 59.70; Co,4.64%

$C_{28}H_{34}CoI_6N_6$ requires: C,26.37; H,2.69; N,6.59; added iodine,39.84;
total iodine, 59.75; Co,4.62%)

(b) Di-triiodotetrakis(γ-picoline)cobalt(II)di-acetonitrile

This compound was prepared in the same way as the above di-triiodotetrakis(β-picoline)cobalt(II) diacetonitrile. A reddish-brown crystalline product was obtained. Yield of product, 5.63g. The infrared evidence supported the presence of acetonitrile molecules in the compound, and also suggested that the cyanide (CN^-) group was not co-ordinated{(ν(CN)}found at 2305 and 2278 cm^{-1}; for CH_3CN,ν(CN) is at 2283 cm^{-1}). This compound was less sensitive to moisture than the above cobalt(II)-β-picoline compound. However on long exposure to air, it decomposed to a dark-brown oily mass. Therefore it was stored in a sealed ampoule.

(Found: C,26.35; H,2.90; N,6.44; added iodine,
39.80;total iodine,59.70; Co,4.65%
$C_{28}H_{34}CoI_6N_6$ requires: C,26.37; H,2.69; N,6.59; added iodine
39.84;total iodine,59.75; Co,4.62%)

3. Manganese(II) compounds of pyridine,β-picoline and γ-picoline

(A) Preparation of Manganese(II)iodide complexes of pyridine, β-picoline and γ-picoline

The manganese(II) compounds having the formula MnL_4I_2 (where L = py, β-pic. or γ-pic) were prepared in the same way as the nickel(II) iodide complexes of pyridine and picolines (Page 106). Pink-white coloured crystals were obtained which were dried over sodium hydroxide pellets in a desiccator at atmospheric pressure. These compounds were very sensitive to moisture and decomposed on prolonged exposure to air.

The following solid compounds of manganese(II) iodide with pyridine, β-picoline and γ-picoline were isolated in a pure state.

(i) Diiodotetrakis(pyridine)manganese(II)

Straw coloured crystals were obtained. Yield of product, 5.7g.

(Found: C,38.1; H,3.2; N,8.8; I,40.4%,

$C_{20}H_{20}I_2MnN_4$ requires: C,38.3; H,3.4; N,9.0; I,40.5%)

(ii) Diiodotetrakis(β-picoline)manganese(II)

Pale-pink crystals were obtained. Yield of product, 5.3g.

(Found: C,42.05; H,4.40; N,7.99; I,35.05%

$C_{24}H_{28}I_2MnN_4$ requires: C,42.3; H,4.15; N,8.22; I,35.2%)

(iii) Diiodotetrakis(γ-picoline)manganese(II)

Straw coloured crystals were obtained. Yield of product,6.0g.

(Found: C,42.1; H,4.30; N,8.0; I,35.1%

$C_{24}H_{28}I_2MnN_4$ requires: C,42.3; H,4.15; N,8.22;I,35.2%)

(B) Preparation of the triiodide(I_3^-) compounds of manganese(II) with pyridine, β-picoline and γ-picoline

The triiodide(I_3^-) complexes of manganese(II) with pyridine and β-picoline were not isolated in the solid state. The use of both dichloromethane and acetonitrile gave a dark-brown oily mass. Other solvents such as 1,2-dichloro~~m~~ethane, chloroform and methanol gave the same result as the dichloromethane and acetonitrile. Solvents which induce crystallisation e.g. benzene, diethylether, carbontetrachloride were added separately to an oily mass (dark brown) of the triiodide-manganese complexes with pyridine and β-picoline (in dichloromethane and in acetonitrile) but in both cases no crystalline solid was obtained. All experiments were done in a dry nitrogen atmosphere in a dry-box.

Preparation of the triiodide(I_3^-) compound of manganese(II) with γ-picoline

The preparation of triiodide-manganese(II) compound of γ-picoline in dichloromethane gave a dark-brown oily mass. The use of other solvents such as 1,2-dichloroethane, chloroform and methanol were found to be useless, and gave the same result as dichloromethane. Acetonitrile on the other hand, was found to be a good solvent in the preparation of manganese(II)-triiodide compound of γ-picoline. The diiodotetrakis (γ-picoline) manganese(II) was used as starting material in the following preparation:

Di-triiodotetrakis(γ-picoline)manganese(II)diacetonitrile

This compound was prepared in the same way as the di-triiodotetrakis(β-picoline)cobalt(II)diacetonitrile(Page 117).A reddish-brown crystalline product was obtained. Yield of product,5.7g. The infrared evidence supported the presence of the acetonitrile molecules in this compound and also suggested that the cyanide group (CN^-) was not co-ordinated. (ν(CN) in the compound found at 2302 and ~ 2279 cm^{-1}; (ν(CN) in CH_3CN is at ~2283 cm^{-1}). The analysis of this compound also suggested the presence of two molecules of acetonitrile. This compound was sensitive to moisture and decomposed to a dark-brown oily mass on exposure to air. Therefore it was stored in a sealed ampoule.

(Found: C,26.21; H,2.8; N,6.41; added iodine,39.76
total iodine,59.73; Mn,4.80%
$C_{28}H_{34}I_6MnN_6$ requires: C,26.4; H,2.70; N,6.6; added iodine,39.94;
total iodine,59.90; Mn,4.85%)

4. Cadmium(II) compounds with pyridine, β-picoline and γ-picoline

(A) Preparation of cadmium(II)iodide complexes of pyridine, β-picoline and γ-picoline

The cadmium(II) compounds having formula CdL_4I_2 (where L = pyridine β-picoline and γ-picoline) were prepared in the same way as the nickel(II) iodide compounds of pyridine, β-picoline and γ-picoline (Page106).A white crystalline product was obtained in each preparation. The product was dried over sodium hydroxide pellets in a desiccator at atmospheric pressure. These compounds were not particularly sensitive to moisture.

The following solid compounds of cadmium(II)iodide with pyridine, β-picoline and γ-picoline were isolated in a pure state.

(i) Diiodotetrakis(pyridine)cadmium(II)

A white crystalline product was obtained. Yield of product 6.0g.

(Found: C,34.90; H,3.1; N,7.90; I,37.11; Cd,16.30%

$C_{20}H_{20}CdI_2N_4$ requires: C,35.1; H,2.9; N,8.2; I,37.2; Cd,16.46%)

(ii) Diiodotetrakis(β-picoline)cadmium(II)

A white crystalline product was obtained. Yield of product, 6.1g.

(Found: C,39.12; H,3.1; N,7.30; I,34.30; Cd,15.01%

$C_{24}H_{28}CdI_2N_4$ requires: C,39.01; H,3.02;N,7.50; I,34.35; Cd,15.21%)

(iii) Diiodotetrakis(γ-picoline)cadmium(II)

White crystals were obtained. Yield of product, 6.4%.

(Found: C,38.39; H,3.00; N,7.33; I,34.29; Cd,15.13%

$C_{24}H_{28}CdI_2N_4$ requires: C,39.01; H,3.02; N,7.50; I,34.35; Cd,15.21%)

(B) Preparation of the triiodide(I_3^-)compounds of cadmium(II) with pyridine, β-picoline and γ-picoline

(i) Di-triiodotetrakis(pyridine)cadmium(II)

This compound was prepared in the same way as the di-triiodonickel(II) compound of pyridine (Page 109). A dark-brown crystalline product was obtained. Yield of product, 5.7g. This compound was moderately sensitive to moisture and decomposed on prolonged exposure to air. Therefore it was stored in a sealed ampoule.

(Found: C,19.89; H,1.80; N,4.54; added iodine,42.51;
total iodine,63.86; Cd,9.37%
$C_{20}H_{20}CdI_6N_4$ requires: C,20.1; H,1.70; N,4.70; added iodine,42.66;
total iodine,63.98; Cd,9.44%)

The compound, ditriiod~~ide~~o-tetrakis(β-picoline)cadmium(II) could not be isolated in solid state. The reaction between di-iodotetrakis (β-picoline)cadmium(II)(1 mole) and iodine (2 mole) in dichloromethane and in acetonitrile gave a dark-brown oily mass. Addition of di-ethyl ether, benzene and carbon tetrachloride to the dark-brown oily mass did not induce crystallisation. Other solvents such as chloroform, methanol, 1,2-dichloroethane gave the same results as the dichloromethane and acetonitrile. The oily mass obtained in dichloromethane and in acetonitrile, were kept separately in a desiccator over sodium hydroxide pellets for a long time but in both cases no crystalline solid was obtained.

(ii) Reaction of di-iodotetrakis(γpicoline)cadmium(II) and iodine in dichloromethane

This experiment was performed in a dry nitrogen atmosphere in a dry box at room temperature. Di-iodotetrakis(γ-picoline)cadmium(II) (1 mole) was weighed in a dry 50 ml. Quick-fit flask. Iodine (2 mole) was added to the flask. Both solids were mixed together. Then 20-25 ml. of dichloromethane was added at once. The solution was stirred for 15 minutes and then evaporated slowly on a clock-glass. Reddish-brown crystals were separated on a clock-glass. They were collected and dried between filter paper-pads. The crystalline solid was then sealed immediately in a dry ampoule. The solid was found to be decomposed within half an hour in a sealed ampoule. A dark-brown oily mass formed which was unreactive to the sodium thiosulphate in glacial acetic acid and found insoluble in common organic solvents e.g.chloroform, acetone, carbon tetrachloride etc. However, the freshly prepared solid was found to be soluble in all common organic solvents and also reactive to sodium thiosulphate in glacial acetic acid. The analysis of freshly prepared reddish-brown solid suggested that the di-triiodotetrakis(γ-picoline)cadmium(II) compound was formed. This compound remained unchanged at freezing temperature in a sealed ampoule for a long period.

(iii) Reaction of di-iodotetrakis(γ-picoline)cadmium(II) (1 mole) and iodine (2 mole) in acetonitrile

The reaction between diiodotetrakis(γ-picoline) Cd(II) (1 mole) and iodine(2 moles) in acetonitrile gave the same result as in dichloromethane. Reddish-brown sparkling crystals were formed which were dried between filter-paper pads. The analysis of the freshly prepared red-brown solid suggested that di-triiodotetrakis(γ-picoline) cadmium(II)-di-acetonitrile was the compound formed. The infrared evidence also supported the presence of acetonitrile molecules and suggested that the cyanide group,CN^-, was not co-ordinated. Although this compound was sealed immediately in a dry ampoule, it was decomposed into a dark-brown oily mass within half an hour. The dark brown oily mass was found to be insoluble in common organic solvents e.g.chloroform acetone, carbon tetrachloride etc. and found unreactive to sodium thiosulphate in glacial acetic acid. The freshly prepared compound, however remained unchanged at freezing temperature in a sealed ampoule for a long period.

(C) Alkyl-pyridine Polymerisation reactions: .

(i) Reaction between cadmium(II)iodide, γ-picoline and iodine at 60-80^{0}C

Cadmium(II)iodide (1 mole) was weighed in a 50 ml dry Quick-fit flask, γ-picoline (4 moles)was added to the flask. Then, after 2-3 minutes, iodine (2 moles) was added. Heat was produced when the iodine mixed with the γ-picoline-cadmium iodide mixture. The flask was then attached to a water-condenser which in turn was fitted with an anhydrous calcium chloride guard tube. The solid mixture formed in the flask, was heated for a couple of hours on water-bath at a temperature of 60-80^{0}C. A dark-brown viscous oil was formed in the flask. The vapour of this oily mass was tested with litmus paper which suggested that hydroiodic acid was not produced. The flask was cooled and a dark-brown oily mass which smelt like γ-picoline was collected. This viscous oil was kept over sodium hydroxide pellets in a desiccator. The dark-brown oil was found to be insoluble in common organic solvents, e.g. chloroform, acetone, carbontetrachloride etc. and also found unreactive to sodium thiosulphate in glacial acetic acid.

(ii) Treatment of the above dark-brown oil with 50% hydrochloric acid

The dark-brown viscous oil was refluxed with 1:1 hydrochloric acid-water mixture for about two and a half hours. The viscous oil was dissolved in boiling hydrochloric-water mixture. A yellow-brown clear solution was formed.A yellow-brown i.e. sandy microcrystalline substance was deposited on cooling the orange-brown clear solution. The crystalline solid was filtered off and washed three times with cold 1:1 hydrochloric acid-water solution and finally with cold water. The yellow-brown solid was then dried over sodium hydroxide pellets in a vacuum desiccator.

The filtrate (mother liquor) of yellow-brown solid was exposed to a limited supply of air at room temperature. Dark-brown crystals were deposited in the form of flat needles. This compound was soluble in, and decomposed by water. It was filtered off and dried over sodium hydroxide pellets in a desiccator. The analysis of this compound suggested that it contained much iodine but no cadmium. The infrared spectra suggested the presence of organic molecules in the compound. A fresh crop of the dark-brown compound was produced on re-exposing the mother liquor to the atmosphere.

(iii) Action of slow direct heat to the dark-brown viscous oil

The dark-brown viscous oil was heated gently in a sublimation apparatus. A yellow vapour was evolved which was turned to a brown solid mass on cooling. This dark-brown compound deposited on the cold finger of the sublimation apparatus and was collected. It was found to be very sensitive to moisture. The brown compound was recrystallised from petrolium-ether. The pale straw coloured plates were obtained on recrystallisation. The analysis of pale-straw crystals suggested the presence of cadmium and iodine.

This crystalline product was treated with aquous sodium hydroxide. The organic compound was then separated by ether extraction. The ether-extract was distilled slowly on water-bath. Off-yellow liquid smelling like γ-picoline was obtained at the end of distillation and dried over sodium hydroxide pellets in a desiccator. The molecular weight of this yellow-liquid was found as 93.0 using mass-spectra. (Picolines have a molecular weight of 93.13). The picrate derivative of this yellow-liquid was prepared. The melting point of this derivative was found as 163°C(The picrate derivative of γ-picoline has a melting point of 164°C). Therefore it was believed that the yellow liquid obtained from ether extraction was nothing but only γ-picoline.

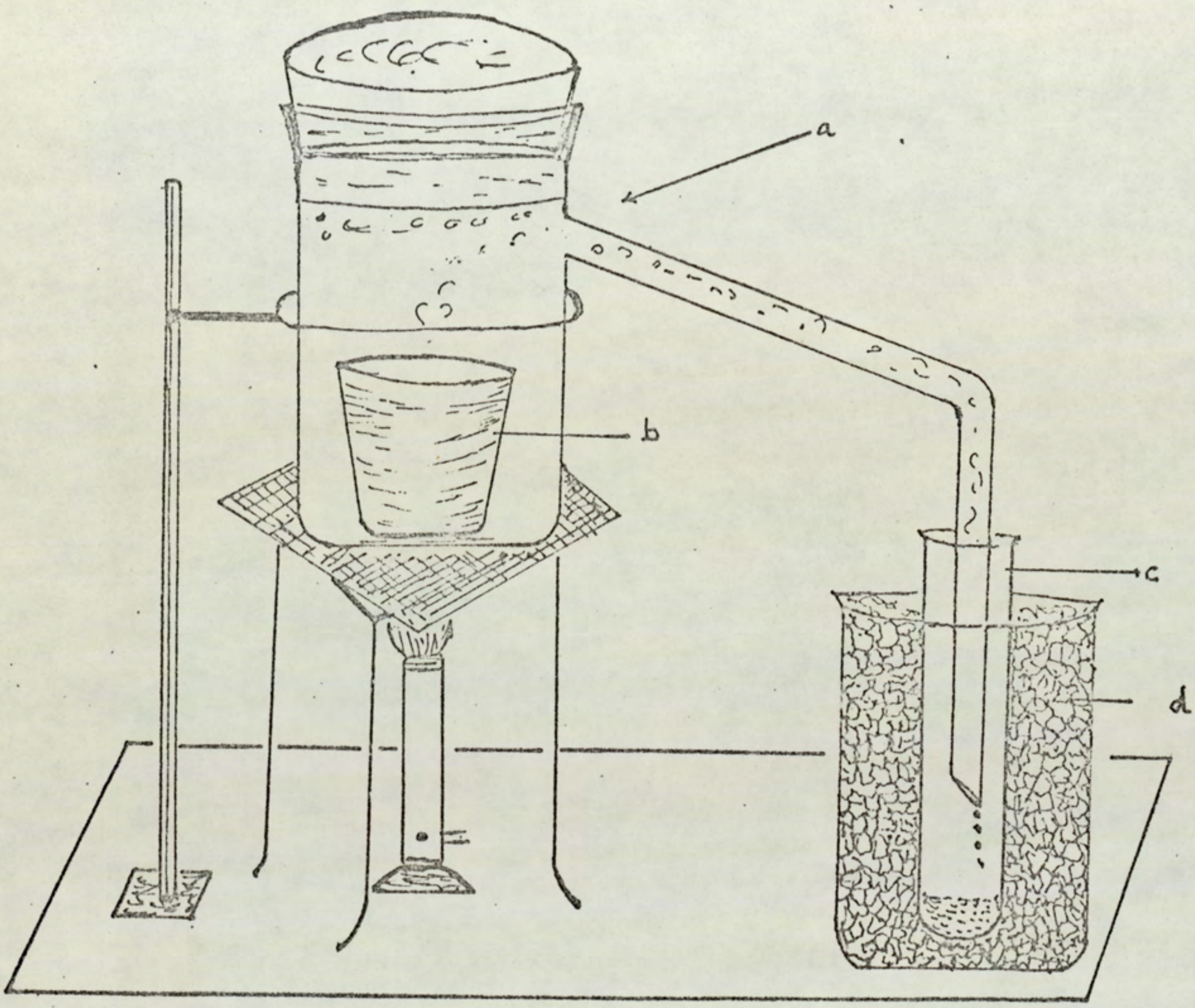


Fig.22. Simple glass apparatus for the separation of the complex organic ligand from an orange cadmium (II) compound.

a. Glass apparatus with narrow side tube.

b. Nickel-crucible containing orange-brown compound and powdered sodium hydroxide mixture.

c. Glass test tube for collecting yellow liquid.

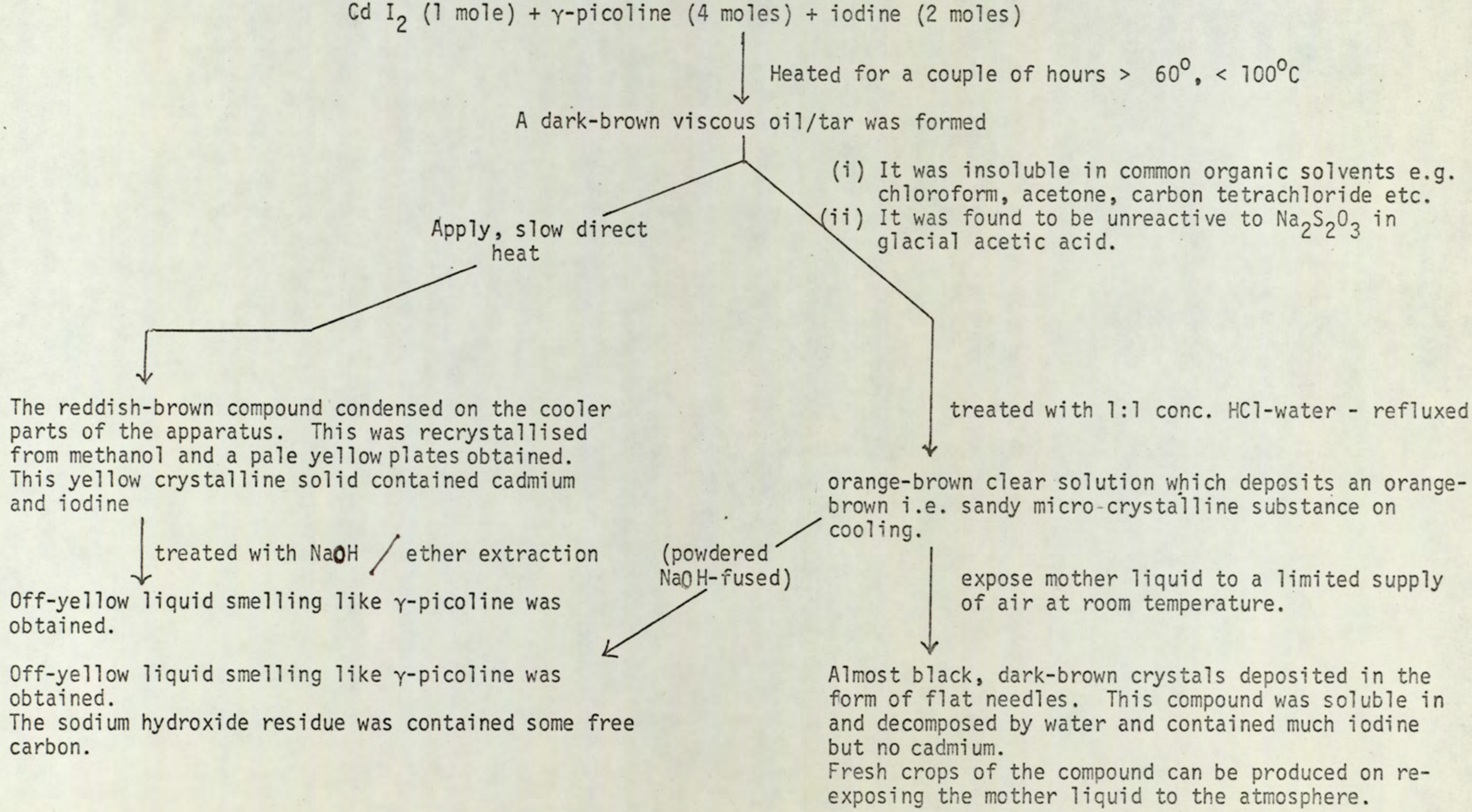
d. Ice bath for cooling vapour which had not condensed.

(iv) An attempt to liberate the ligand from the orange-brown (sandy microcrystalline)compound

The orange-brown compound was mixed with powdered sodium hydroxide. The solid mixture was put into a nickel-crucible. The crucible was then placed in a simple glass apparatus (Shown in fig.22). The solid mixture in the crucible was fused by applying direct heat to the glass-apparatus. The yellow-vapour was evolved which was condensed in the side-tube of the apparatus. The condensate was collected in the test-tube which was dipped in an ice-bath. The yellow vapour was turned to a yellow liquid on cooling. This off-yellow liquid smelt like γ-picoline and it contained much water. It was then dried over sodium hydroxide pellets. Finally it was distilled at 143-145°C from a micro-distillation flask to remove water and excess of γ-picoline. However it was found that the liquid boiled at 143°-145°C leaving no residue in the distillation flask. The picrate derivative of the above distillate was prepared and its melting point was found as 164°C.. (The picrate derivative of γ-picoline has a melting point of 164°C) Therefore it was believed that the yellow liquid separated from fusing of orange-compound was nothing but γ-picoline only.

The summary of the above cadmium(II)iodide-γ-picoline-iodine reaction and the products obtained from it, are described in the chart (page 128).

Alkyl-pyridine "polymerisation" reactions



Cd I_2 (1 mole) + γ-picoline (4 moles) + iodine (2 moles)

Heated for a couple of hours > 60^o, < 100^oC

A dark-brown viscous oil/tar was formed

(i) It was insoluble in common organic solvents e.g. chloroform, acetone, carbon tetrachloride etc.
(ii) It was found to be unreactive to $Na_2S_2O_3$ in glacial acetic acid.

Apply, slow direct heat

The reddish-brown compound condensed on the cooler parts of the apparatus. This was recrystallised from methanol and a pale yellow plates obtained.
This yellow crystalline solid contained cadmium and iodine

treated with NaOH / ether extraction

Off-yellow liquid smelling like γ-picoline was obtained.

treated with 1:1 conc. HCl-water - refluxed

orange-brown clear solution which deposits an orange-brown i.e. sandy micro-crystalline substance on cooling.

(powdered NaOH-fused)

Off-yellow liquid smelling like γ-picoline was obtained.
The sodium hydroxide residue was contained some free carbon.

expose mother liquid to a limited supply of air at room temperature.

Almost black, dark-brown crystals deposited in the form of flat needles. This compound was soluble in and decomposed by water and contained much iodine but no cadmium.
Fresh crops of the compound can be produced on re-exposing the mother liquid to the atmosphere.

6. Iron(II)compounds of pyridine, β-picoline and γ-picoline

(A) Preparation of iron(II)-iodide complexes of pyridine, β-picoline and γ -picoline

The iron(II) complexes having formula FeL_4I_2 where L = pyridine, β-picoline, or γ-picoline were prepared in the same way as that used by Golding et al.[108] for the preparation of diiodotetrakis(pyridine) iron (II) compound.

The following procedure was adopted for the preparation of FeL_4I_2 complexes (where L, pyridine, β-picoline or γ-picoline). Finely divided iodine (7 g) was gradually added to 2 g of pure iron powder in 20 ml. of methanol. The solution was stirred and then filtered into a flask containing 50 ml. of the appropriate ligand - (pyridine, β-picoline or γ-picoline). The mixture was allowed to stand for a few hours in a nitrogen atmosphere over the sulphuric acid (as a drying agent) in a desiccator. The stream of nitrogen gas was passed over the solution continuously to avoid an oxidation of iron(II) solution. Bright yellow crystals were obtained which were filtered quickly and dried over sulphuric acid in a dry nitrogen atmosphere in a desiccator at atmospheric pressure.

The following pure complexes were isolated using the above general method.

(i) Diiodotetrakis-(pyridine)iron(II):

Bright yellow crystals were obtained. Yield of the crystalline solid, 7.1g. It was kept in a sealed ampoule for future use.

(Found: C,38.2; H,3.2; N,8.6; I.40.23; Fe,8.78%

$C_{20}H_{20}FeI_2N_4$ required: C,38.4; H,3.33;N,8.9; I,40.55; Fe,8.90%)

This compound was moderately sensitive to moisture. It was unstable to atmospheric oxidation and became brown on standing.

(ii) Diiodotetrakis(β-picoline)iron(II):

A bright yellow crystalline solid was obtained. This compound was found to be very sensitive to moisture and also very unstable to atmospheric oxidation and became brown even though it was stored in a sealed ampoule. The analysis of freshly prepared yellow solid suggested that the diiodotetrakis-(β-picoline)iron(II) compound was formed.

(Found: C,42.0; H,4.20; N,8.13; I,35.05; Fe,8.5%
$C_{24}H_{28}FeI_2N_4$ required: C,42.15; H,4.31;N,8.21; I,35.18; Fe,8.67%)

(III) Diiodotetrakis(γ-picoline)iron(II):

Bright yellow microcrystalline solid was obtained. This compound was moderately sensitive to moisture but unstable to atmospheric oxidation and became brown on standing. Therefore it was kept sealed in a dry ampoule for future use.

(Found: C,42.1; H,4.25; N,8.18; I,35.10; Fe,8.60%
$C_{24}H_{28}FeI_2N_4$ required: C,42.1; H.4.31; N,8.21; I,35.18; Fe,8.60%)

(B) Preparation of triodide(I_3^-) complexes of iron(II) with pyridine, β-picoline and γ-picoline

These iron(II) compounds were prepared in a dry nitrogen atmosphere in a dry box. Only two compounds, the di-triiodotetrakis (pyridine) and ditriiodotetrakis(γ-picoline)Fe(II) were isolated in a pure solid state. The di-triiodo-tetrakis-(β-picoline)iron(II) could not be isolated in the solid state, because the starting material diiodotetrakis(β-picoline)iron(II) was very unstable to atmospheric oxidation and sensitive to moisture.

The preparation of di-triiodotetrakis(pyridine) and di-triiodotetrakis (γ-picoline)iron(II) using dichloromethane as the reaction medium(solvent) gave a good result. The diiodide complexes of iron(II) with pyridine and γ-picoline were used as starting material in the respective preparations.

The following iron(II)-triiodide complexes having composition, $FeL_4(I_3)_2$, were prepared (where L, = pyridine or γ-picoline).

(i) Di-triiodotetrakis(pyridine)iron(II)

This compound was prepared in the same way as the di-triiodonickel(II) compound of pyridine(page 109). Reddish-brown crystals were obtained on slow evaporation of the solution in a vacuum desiccator. The solid was then dried over sodium hydroxide pellets in a nitrogen atmosphere in a desiccator. This compound was very unstable in the open air and decomposed on standing. Therefore it was kept sealed in a dry ampoule.

(Found: C,20.10; H,1.70; N,4.68; added iodine,44.72;
Fe,4.90; total iodine,67.0%
$C_{20}H_{20}FeI_6N_4$ required: C,21.2; H,1.78; N,4.90; added iodine,44.80
Fe,4.90; total iodine,67.20%)

(ii) Di-triiodotetrakis(γ-picoline)iron(II)

This compound was prepared in the same way as the procedure outlined previously (Page 109) for the preparation of di-triiodotetrakis (pyridine)nickel(II). Reddish-brown crystals were obtained on slow evaporation of the solution in a vacuum desiccator at room temperature. This compound was sensitive to moisture and decomposed on exposure to air. Therefore it was stored in a sealed ampoule.

(Found: C,24.36; H,2.60; N,4.60; added iodine,42.60%
Fe,4.58; total iodine,62.80%
$C_{24}H_{28}FeI_6N_4$ required: C,24.24; H,2.40; N,4.70; added iodine,42.69%
Fe,4.69; total iodine,63.04%)

The same iron(II)-di-triiodide compound of γ-picoline was prepared using acetonitrile as the reaction medium (solvent) but the compound (red-brown) obtained, contained two molecules of acetonitrile as solvent of crystallisation. The analysis of this compound suggested the presence of two molecules of acetonitrile. The infrared evidence of this compound also supported the presence of acetonitrile molecules and suggested that the cyanide group (CN^-) was not co-ordinated,($\nu(CN^-)$ in the compound was found at 2298 cm^{-1}, 2283 cm^{-1}). The analysis of the acetonitrile adduct was as follows:

(Found: C,26.20; H,2.51; N,6.48; added iodine,39.76%
Fe,4.28; total iodine,59.64%
$C_{28}H_{34}FeI_6N_6$ required: C,26.4; H,2.7; N,6.61; added iodine 39.90%
Fe,4.40;total iodine,59.85%)

RESULTS

Solid state data for complexes of nickel (II) with pyridine, β-picoline and γ-picoline are described in Tables 11, 12, 13 and 20. Solid state data for the complexes of manganese (II), cobalt (II), iron (II) and cadmium (II) with pyridine, β-picoline and γ-picoline are described in Tables 14, 15, 16 and 17. The conductivity data of the above complexes are given in Table 18. The absorption spectral data for the triiodide (I_3^-) complexes of nickel (II), cobalt (II), manganese (II), iron (II) and cadmium (II) are given in Table 19.

Figure 22 shows a simple glass-apparatus used in the attempted separation of the complex organic ligand from an orange-cadmium compound. Figure 23 (a) and (b) and Figure 25 (a) and (b) show the infrared spectra of nickel (II) complexes, $Ni(py)_4X_2$ ($X = I^-$ or I_3^-) and $Ni(py)_4X_2$ ($X = NCS^-$ or $NCS\text{-}I_2^-$) respectively. Figure 24 and Figure 26 show the diffuse reflectance spectra of $Ni(py)_4X_2$ ($X = I^-$ or I_3^-) and $Ni(py)_4X_2$ ($X = NCS^-$ or $NCS\text{-}I_2^-$) respectively. Figure 27 describes the magnetic behaviour of the complexes, $NiL_4(NCS\text{-}I_2)_2$ (where L = pyridine, β-picoline or γ-picoline) at various temperatures.

The x-ray powder photographs of some nickel(II), cobalt(II) and cadmium(II) complexes are given on pages 149 & 150.

TABLE 11

Solid State data of nickel(II)complexes of pyridine, β -picoline and γ-picoline

¶Complex	Colour	†Magnetic moment		Diffuse Reflectance spectra (maxima in cm^{-1})§
		μ_{eff} B.M.	Temp. ^{o}C.	
$Ni(py)_4I_2$	Yellow-green	3.15	20.5	$25,600$; $19,600_{sh}$; $15,700$ $12,400_w$; $10,800_w$; $7,400_w$
$Ni(py)_4(I_3)_2$	Reddish-brown	Dia-magnetic	17.5	$27,200$; $23,900_{(br,sh)}$, $18,900_{(br,sh)}$ $11,800_w$;$8,700_w$
$Ni(\beta\text{-pic})_4I_2$	Yellow-green	3.14	21.0	$25,200$; $19,600$; $16,000$; $13,200_w$; $7,800_w$.
$Ni(\beta\text{-pic})_4(I_3)_2$	Reddish-brown	2.82	19.0	$26,400$; $23,000_{(w,sh)}$ $19,700_{sh}$.
$Ni(\gamma\text{-pic})_4I_2$	Yellow-green	3.21	18.0	$25,400$; $19,300_{sh}$;$15,900$; $10,700_{sh}$; $7,800_w$.
$Ni(\gamma\text{-pic})_4(I_3)_2$	Reddish-brown	Dia-magnetic	16.0	$26,800$; $23,800_{(w,sh)}$; $19,100_{sh}$.
$Ni(py)_4(NCS)_2$	Sky-blue	3.15	16.0	$27,400$; $23,100_{sh}$; $16,950$ $12,800_{sh}$; $10,200$.
$Ni(py)_4(NCS\text{-}I_2)_2$	Dark-brown	3.06	20.0	$27,200$; $23,800_{(w,sh)}$ $18,900_{sh}$; $10,500$.
$Ni(\beta\text{-pic})_4(NCS)_2$	Blue	3.11	18.2	$27,300_{sh}$; $17,200$; $12,400_{sh}$ $10,400$.
$Ni(\beta\text{-pic})_4(NCS\text{-}I_2)_2$	Dark-brown	3.22	19.5	Compound decomposed to dark-brown oily mass.
$Ni(\gamma\text{-pic})_4(NCS)_2$	Sky-blue	3.10	18.0	$27,900$; $25,400_{sh}$; $23,500_{sh}$ $17,100$; $12,700_{sh}$; $10,400$.
$Ni(\gamma\text{-pic})_4(NCS\text{-}I_2)_2$	Dark-brown	3.18	20.0	$26,800$; $22,900_{(w,sh)}$ $18.700_{(w,sh)}$ $10,600$.

§ 1×10^6 cm^{-1} = 10 nm
w - weak, sh - shoulder, br - broad.; ¶ py - pyridine. pic - picoline.
† Positive values of μ are obtained for paramagnetic substances.

TABLE 12

Infrared Spectra of Nickel(II) complexes of pyridine, β-picoline and γ-picoline

Pyridine (Liquid film)	$Ni(py)_4I_2$	$Ni(py)_4(I_3)_2$	β-picoline (Liquid film)	$Ni(\beta\text{-pic})_4I_2$	$Ni(\beta\text{-pic})_4(I_3)_2$	γ-picoline (Liquid film)	$Ni(\gamma\text{-pic})_4I_2$	$Ni(\gamma\text{-pic})_4(I_3)_2$
*1598	1603	1605	1594	1605	1615 1605	1605	1617	1617
1583	1597	-	1579	1582	1582_{w}	1560	-	-
1483	1483_{vw}	1487	1479	1480_{w}	1480_{sh}	1495	1504	1505
1439	1448	1448	1450 1413	1460 1420	1460 1420_{sh}	1447_{sh} 1413	1460 -	1460 1435
1375_{vw}	1377	1379 1359	1383 -	1378 1338	1378 1364_{sh}	1381 1364_{sh}	1377 -	1378 1333
1218	1224 1214	1242 1212	1228	1242	1240	1285	-	1254
1148	1158	1155	1190	1195	1198	1214 1211	1232 1212	1208 1208
1069 - -	1082 1073 1061	1074 1066 -	1125 1106 -	1133 1112 -	1110	1090_{sh}	1110	1123

TABLE 12 continued

Pyridine (Liquid film)	Ni(py)$_4$I$_2$	Ni(py)$_4$(I$_3$)$_2$	β-picoline (Liquid film)	Ni(β-pic)$_4$I$_2$	Ni(βpic)$_4$(I$_3$)$_2$	γ-picoline (Liquid film)	Ni(γ-pic)$_4$ I$_2$	Ni(γ-pic)$_4$(I$_3$)$_2$
*1031	1040	1045	1043	1053	1058	1072	1070	1069
991	1012	1020	1030	1038	1015	1042	1020	1050
940_{vw}		940	-	987_{vw}	995_{vw}			
745	762	760	790	815	817	997	980	975
	752			795	794	972		
700	707	-	715	705	708			
-	698	698	-	-	-	873	-	862
602	632	635	630	648	670	800	812	812
					652	730	725	721
-	-	417	535	538	570	672	-	-
405	435	435	457	480	482	516	540	577
-	-	-	-	420	435	485	499	510
-	-	-	-	360_{w}	410	-		

* Frequency of absorption bands in cm^{-1} (1×10^{4}cm^{-1}=1000nm and 1×10^{2}cm^{-1}=1×10^{5}nm)
py-pyridine; pic-picoline; v - very; w - weak; sh - shoulder

TABLE - 13

Infrared Spectra of the di-thiocyanato-nickel(II)complexes of pyridine, β-picoline, γ-picoline and its Iodine adducts

Band Assign-ments	§ $NiL_4(NCS)_2$	$NiL_4(NCS\text{-}I_2)_2$	$NiL'_4(NCS)_2$	$NiL'_4(NCS\text{-}I_2)_2$	$NiL''_4(NCS)_2$	$NiL''_4(NCS\text{-}I_2)_2$
¶ ν(C-N)	{2080}	{2127}	{2080}	{2110}	{2070}	{2125}
	1600	1600	1607	1610	1618	1620
	1573	1571	1585	1585	1560 1504	1558 1505
	1488 1483	1483	1485	-	-	-
	1460	1460	1460	1460	1460	1460
	1443	1441	1420	1425_{sh}	1422	1420
	1378	1378	1380	1380	1378	1378
	1357	-	1336_{vw}	1338	-	1335_{vw}
	1235	1235	1245 1235_{sh}	1245 -	1230 -	1232 -
	1219 1215	1218 1214	1213_{sh} -	1215_{vw} -	1214 -	1211 -
	1150 -	1150 -	1198 1185_{sh}	1199 1185_{sh}	- 1160	- -
	1120	-	1135 1115	1135 1115	1125 -	- -
	1070	1069	1070_{sh} 1057	1060 -	1071 -	1072 -
	1045 1040	1041 -	1040 -	1040 -	1040_{w}	-
	1010	1010	1021_{sh}	-	1024	1023
	997_{vw}	-	992_{vw}	995_{w}	985	-

CONTINUED..

TABLE - 13 continued

Band Assign-ments	§ $NiL_4(NCS)_2$	$NiL_4(NCS\text{-}I_2)_2$	$NiL'_4(NCS)_2$	$NiL'_4(NCS\text{-}I_2)_2$	$NiL''_4(NCS)_2$	$NiL''_4(NCS\text{-}I_2)_2$
¶ 2δ(NCS)	{970_w}	{955_{vw}}	{965_{vw}}	{947_{vw}}	{965}	-
	950	932_{vw}	923_{vw}	920_w	870	870
	884	880_{vw}	817	818	815	818 812
ν(C-S)	{802}	{775}*	{802}*	{802}*	{805}*	{775}
	770	-	790	773	728	740
	760	759	--	760		
	715	722	710	710	-	-
	702	703	-	-	-	-
	655	-	652	652	-	-
	630	630	538	538_w	540	540
	-	-	497	497	500	498
δ(NCS)	{485}	{465}	{481}	{472}	{483_{sh}}	{477}
(bending mode)	440	433	419	420	-	-
	435 404	-	358	362	360_w	-
ν(M-NCS)	{285}	{280_w}	{275}	{269_{sh}}	{272}	{270w}

v - very; w - weak; sh - shoulder

§ L = pyridine; L' = β -picoline; L" = γ -picoline.

¶ Frequency of absorption bands in cm^{-1};

($1 \times 10^4\ cm^{-1} = 1000$nm and $1 \times 10^2\ cm^{-1} = 1 \times 10^5$ nm)

* Partly obscured by ligand bands.

TABLE - 14

Infrared Spectra of Iron(II) and cadmium (II) iodide and di-triiodide compounds of pyridine

Pyridine (liquid film)	$Fe(py)_4I_2$	$Fe(py)_4(I_3)_2$	$Cd(py)_4I_2$	$Cd(py)_4(I_3)_2$
* 1598	1600	1602	1603	1598
1583	1582_{w}	1589	1593) 1583)	1570
1483	1485	1517	1484	1484
-	1460	1460	1460	1460
1439	1445	-	1445	1443
$1375_{v.w.}$	1377	1377	1378	1378
1218	1222	1228	1216	1215
-	1213	-	1210	-
1148	1155	1154	1152	1150
1069	1078) 1072)	1065	1065	1065
1031	1038	1042	1038	1035
991	1009	1026	1013	1008
-	-	-	993	-
$940_{w.}$	974	975	-	943_{w}
745	758	$753_{v.w.}$	758	753
	751	775	-	-
700	704_{sh}	698	705	698
-	697	-	694_{sh}	-
602	628	632	632	627
405	422	430_{sh}	421	418
-	-	-	415_{sh}	412_{sh}

*Frequency of absorption bands in cm^{-1} (1x10^{4}cm^{-1}=1000nm & 1x10^{2}cm^{-1} =1x10^{5}nm)
py - pyridine, v - very, w - weak, sh - shoulder.

TABLE - 15

Infrared spectra of cobalt(II) complexes of pyridine, β-picoline and γ-picoline

Pyridine (Liquid film)	$Co(py)_4I_2$	$Co(py)_4(I_3)_2$	β-picoline (Liquid film)	$Co(\beta\text{-pic})_4I_2$	$Co(\beta\text{-pic})_4(I_3)_2$ $2CH_3CN$	γ-picoline (Liquid film)	$Co(\gamma\text{-pic})_4I_2$	$Co(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$
					$\nu(CN)$(2303 (2278			2305) 2278) $\nu(CN)$
*1598	1602	1598	1594	1605	1605	1605	1616	1619
1583	1590	-	1579	1581	1580	1560	1554	-
1483	1485	1485_{sh}	1479	1480	1482	1495	1503	1502
1439	1440	1440	1450) 1413)	1460) 1420)	1460) 1416)	1447) 1413)	1460 1420	1460 1420
$1375_{v.w.}$	1377	1375	1383	1378 1337	1378 1360	1381 1364_{sh}	1376	1376
1218	1217 1210	1232 1216	1228 -	1242 -	1240 -	1285 -	-	-
1148	1150	1150	1190	1195	1197	1224 1211	1230 1213	1231 1208
1069	1072_{sh} 1068	1065 -	1125 1106	1131 1110	1130 1110	1090_{sh}	-	-

TABLE - 15 continued

Pyridine (Liquid film)	$Co(py)_4I_2$	$Co(py)_4(I_3)_2$	β-picoline (Liquid film)	$Co(\beta\text{-pic})_4I_2$	$Co(\beta\text{-pic})_4(I_3)_2$ $2CH_3CN$	γ-picoline (Liquid film)	$Co(\gamma\text{-pic})_4I_2$	$Co(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$
* 1031	1040 1035	1040 1035	1043	1062 1054	1058	1072	1072	1067
991	1012 1005	1009	1030	1038	1035_{sh}	1042	1040 1020	1038 $1023^{v.w.}$
$940_{v.w.}$	-	-	-	997	-	997	$992_{v.w.}$	-
745	763 752_{sh}	755 750^{sh}	790	815 806	815 -	972 873	982 865_{sh}	- $870_{v.w.}$
				797	798			
700	700	700	715	707	712 705	800 -	814 -	817 811^{sh}
602	643 622	630	630	660 650	650	730	728	724
-	-	-	535	537	537	672	$670_{v.w.}$	-
405	428	428	457	475	475	516	535	542
-	-	-	402	417	417	485	497	495
-	-	-	-	355	357	-	-	-

*Frequency of absorption bands in cm ($1 \times 10^4 cm^{-1} = 1000$ nm and $1 \times 10^2 cm^{-1} = 1 \times 10^5$nm)
py - pyridine, pic - picoline, v - very, w - weak , sh - shoulder

TABLE - 16

Infrared Spectra of Manganese(II), Iron(II) and Cadmium(II) iodide and di-triiodide compounds of γ-picoline

γ-picoline (liquid film)	$Fe(\gamma\text{-pic})_4I_2$	$Fe(\gamma\text{-pic})_4(I_3)_2$	$Fe(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$	$Mn(\gamma\text{-pic})_4I_2$	$Mn(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$	$Cd(\gamma\text{-pic})_4I_2$	$Cd(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$
-	-	-	2305) 2275) ν(C-N)	-	2300) 2270) ν(C-N)	-	2295) 2265) ν(C-N)
* 1605	1615	1618	1618 1590	1615	1618	1615	1618
1560	1550_w	-	1560	-	-	-	1562
1495	1503	1500	1500	1504	1503_{sh}	1504	1503
1447_{sh}	1457	1460	1460	1460	1460	1460	1460
1413	1420_{sh}	-	1420_{sh}	-	1420_{sh}	-	1
1381	1377	1375	1378	1378	1376	1378	1378
1285	1300	-	-	1300_{sh}	1300_{sh}	1300_{sh}	-
1224 1211	1230 1212	1230_w 1210_w	1233 1210	1232 1214	1232 1218	1228 1213	1230 1206_{sh}
1090_{sh}	1160_w	$1150_{w,sh}$	1195	1160_{sh}	1150	-	1115_{sh}
	-	-	-	1120_w	-	-	-

TABLE - 16 continued

γ-picoline (liquid film)	Fe(γ-pic)$_4$I$_2$	Fe(γ-pic)$_4$(I$_3$)$_2$	Fe(γ-pic)$_4$(I$_3$)$_2$ 2CH$_3$CN	Mn(γ-pic)$_4$I$_2$	Mn(γ-pic)$_4$(I$_3$)$_2$ 2CH$_3$CN	Cd(γ-pic)$_4$I$_2$	Cd(γ-pic)$_4$(I$_3$)$_2$ 2CH$_3$CN
* 1072	1070	1068	1067	1070	1066	1072	1067 1060$_{sh}$
1042	1040$_w$	1040$_{sh}$	1038$_w$	1043	1035$_w$	1043	1036$_w$
997	1018	1024	1021	1016	1018	1016	1022$_{sh}$ 1015
972	982	970	975	982	970$_w$	980	972$_w$
873	-		869	-	890	-	867
800	813	803 797	806 798	815 -	816 807	814 -	815 802
730	726	720	724	728	723	726	721
672	-	632	-	-	-	-	-
516	538	542	542	534	536	532	538
485	493	492$_{sh}$	493	492	490	489	495$_{sh}$ 485
-	395$_{v.w.}$	477	478	392$_w$	393$_w$		387$_w$

* Frequency of absorption bands in cm^{-1} (1 x 10^{4}cm^{-1} = 1000 nm and 1 x 10^{2}cm^{-1} = 1 x 10^5 nm)
pic - picoline, v - very, w - weak, sh - shoulder

TABLE 17

Solid State data of Cobalt (II), Manganese (II) and Iron (II) complexes of pyridine, β-picoline and γ-picoline

¶ Complex	Colour	†Magnetic moment		Diffuse Reflectance spectra (maxima in cm^{-1})§
		μ_{eff} B.M.	Temp. ^{o}C	
$Co(py)_4I_2$	Pink	4.95	18.5	24,700; 20,800; $18,800_{sh}$ $17,600_{sh}$; 8,800
$Co(py)_4(I_3)_2$	Dark-brown	4.70	20.5	$25;900_{w}$; $24,000_{sh,br}$; $8,800_{w}$
$Co(\beta\text{-}pic)_4I_2$	Pink-brown	5.00	21.0	26,500; $21,800_{sh}$; $18,400_{sh}$ $15,800_{sh}$; 8,700
$Co(\beta\text{-}pic)_4(I_3)_2$ $2CH_3CN$	Red-brown	4.84	18.0	$26,500_{w}$; $23,400_{sh}$; $19,100_{sh}$; 10,000
$Co(\gamma\text{-}pic)_4I_2$	Grey-pink	4.98	19.0	25,200; $21,500_{sh}$; 17,300; $15,300_{sh}$; 8,600
$Co(\gamma\text{-}pic)_4(I_3)_2$ $2CH_3CN$	Red-brown	4.80	17.7	$26,800_{w}$; $24,000_{sh}$; $19,100_{sh}$ 10,100
$Mn(\gamma\text{-}pic)_4I_2$	Straw	5.83	18.7	$27,800_{sh,w}$; $21,300_{v.w}$; $17,600_{w,sh}$
$Mn(\gamma\text{-}pic)_4(I_3)_2$ $2CH_3CN$	Red-brown	5.82	18.5	**Not observed
$Fe(py)_4I_2$	Yellow	5.91	19.5	
$Fe(py)_4(I_3)_2$	Red-brown	5.80	19.1	
$Fe(\gamma\text{-}pic)_4I_2$	Yellow	5.60	18.5	
$Fe(\gamma\text{-}pic)_4(I_3)_2$	Red-brown	5.41	19.8	
$Fe(\gamma\text{-}pic)_4(I_3)_2$ $2CH_3CN$	Red-brown	5.33	20.0	

¶ py - pyridine; pic - picoline; w - weak; sh - shoulder; v - very; br - broad

† Positive values of μ are obtained for paramagnetic substances

**Compounds were decomposed to dark-oily mass

§ $1 \times 10^{4} cm^{-1} = 1,000$ nm

TABLE 18

Conductivity data of Nickel (II), Cobalt (II), Cadmium (II), Manganese (II) and Iron (II) complexes of pyridine, β-picoline and γ-picoline

¶ Complex	Solvent	Temperature °C	Molar Conductivity † Λ_M (in 10^{-3}M solution)
$Ni(py)_4I_2$	Nitromethane	22	121.0
$Ni(py)_4(I_3)_2$	"	23	175.0
$Ni(\beta\text{-pic})_4I_2$	"	22	124.0
$Ni(\beta\text{-pic})_4(I_3)_2$	"	24	185.0
$Ni(\gamma\text{-pic})_4I_2$	"	22	127.0
$Ni(\gamma\text{-pic})_4(I_3)_2$	"	24	213.0
$Ni(py)_4(NCS)_2$	"	22	42.0
$Ni(\beta\text{-pic})_4(NCS)_2$	"	22	40.0
$Ni(\gamma\text{-pic})_4(NCS)_2$	"	22	43.0
$Ni(py)_4(NCS\text{-}I_2)_2$	Dimethyl-sulphoxide	24	86.0
$Ni(\beta\text{-pic})_4(NCS\text{-}I_2)_2$	"	24	85.0
$Ni(\gamma\text{-pic})_4(NCS\text{-}I_2)_2$	"	24	86.0
$Co(py)_4I_2$	Nitromethane	24	119.0
$Co(py)_4(I_3)_2$	"	23	155.0

TABLE 18 (CONTINUED)

¶ Complex	Solvent	Temperature ^{o}C	Molar Conductivity †Λ_M (in 10^{-3}M solution)
$Co(\beta\text{-pic})_4I_2$	Nitromethane	24	108.0
$Co(\beta\text{-pic})_4(I_3)_2$ $2CH_3CN$	"	23	165.0
$Co(\gamma\text{-pic})_4I_2$	"	24	106.0
$Co(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$	"	25	163.0
$Cd(py)_4I_2$	Dimethyl-sulphoxide	23	38.0
$Cd(py)_4(I_3)_2$	"	23	80.0
$Mn(\gamma\text{-pic})_4I_2$	"	25	40.0
$Mn(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$	"	25	72.0
$Fe(py)_4I_2$	"	24	34.0
$Fe(py)_4(I_3)_2$	"	22	80.0
$Fe(\gamma\text{-pic})_4I_2$	"	25	35.0
$Fe(\gamma\text{-pic})_4(I_3)_2$	"	24	72.0
$Fe(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$	"	24	75.0

¶ py - pyridine; pic - picoline

†Λ_M = Molar Conductivity = $Ohm^{-1}.\ mol^{-1}.\ cm^2$.

TABLE 19

Absorption Characteristics of Triiodide (I_3^-) Complexes of Ni (II), Co (II), Mn (II), Fe (II) and and Cd (II) with Pyridine Bases in 1,2-Dichloroethane and in Acetonitrile

¶Complex	Dichloroethane λmax (nm) & ε (lit $mol^{-1}cm^{-1}$) §				Acetonitrile λmax (nm) & ε (lit $mol^{-1}cm^{-1}$) §			
	λmax_1	ε_1	λmax_2	ε_2	λmax_1	ε_1	λmax_2	ε_2
$Ni(py)_4(I_3)_2$	365	36,500	297	61,500	363	13,000	291	27,500
$Ni(\beta\text{-pic})_4(I_3)_2$	365	36,000	297	62,000	363	13,200	292	39,000
$Ni(\gamma\text{-pic})_4(I_3)_2$	365	32,500	298	61,000	363	13,500	291	40,000
$Co(py)_4(I_3)_2$	365	18,000	296	34,000	363	13,000	291	28,000
$Co\ (\beta\text{-pic})_4(I_3)_2 \cdot 2CH_3CN$	366	28,000	297	49,000	363	12,000	290	26,000
$Co(\gamma\text{-pic})_4(I_3)_2 \cdot 2CH_3CN$	365	25,000	296	45,500	363	13,000	290	33,500
$Cd(py)_4(I_3)_2$	365	7,000	296	13,250	363	2,200	290	4,800
$Fe(py)_4(I_3)_2$	364	35,500	297	55,000	364	13,500	291	39,700
$Fe(\gamma\text{-pic})_4(I_3)_2$	365	36,000	298	55,500	362	13,000	291	39,500
$Fe(\gamma\text{-pic})_4(I_3)_2 \cdot 2CH_3CN$	366	36,000	298	60,000	360	13,400	292	40,000
$Mn(\gamma\text{-pic})_4(I_3)_2 \cdot 2CH_3CN$	Insoluble in dichloroethane				358	13,000	296	24,500
{Tetramethyl- } {ammonium triiodide}	362	25,000	292	45,800	360	25,000	291	48,000

¶ py - pyridine; pic - picoline ; § ε = molar extinction coefficient.

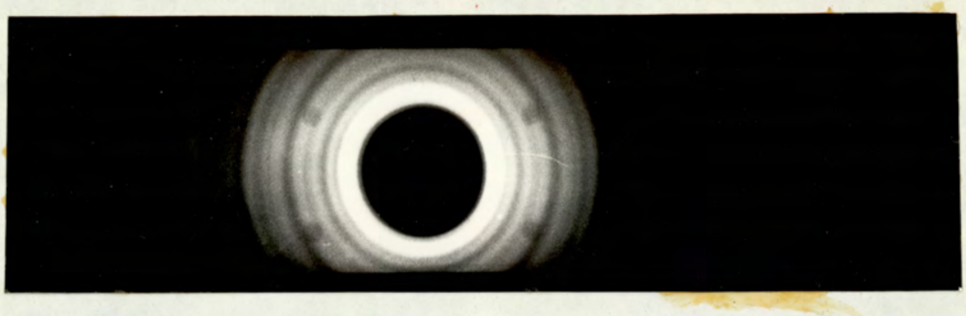
TABLE 20

The magnetic data of Nickel(II) complexes at various temperatures

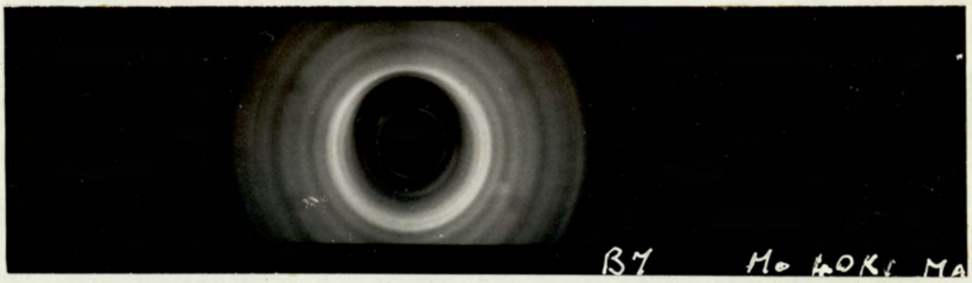
†Compound	Temperature (K)	$10^6 \times \chi'_M$ * (c.g.s.units)	μ_{eff} B.M.
$Ni(py)_4(I_3)_2$	291	-	dimagnetic
$Ni(\gamma\text{-pic})_4(I_3)_2$	289	-	diamagnetic
$Ni(\beta\text{-pic})_4(I_3)_2$	293	3441	2.85
	193	-	diamagnetic
	93	-	diamagnetic
$Ni(py)_4(NCS\text{-}I_2)_2$	293	3992	3.07
	193	6066	3.07
	93	12432	3.05
$Ni(\beta\text{-pic})_4(NCS\text{-}I_2)_2$	293	3900	3.01
	193	5984	3.01
	93	12000	2.91
$Ni(\gamma\text{-pic})_4(NCS\text{-}I_2)_2$	293	4188	3.14
	193	6067	3.07
	93	12080	3.00

† py - pyridine; pic - picoline

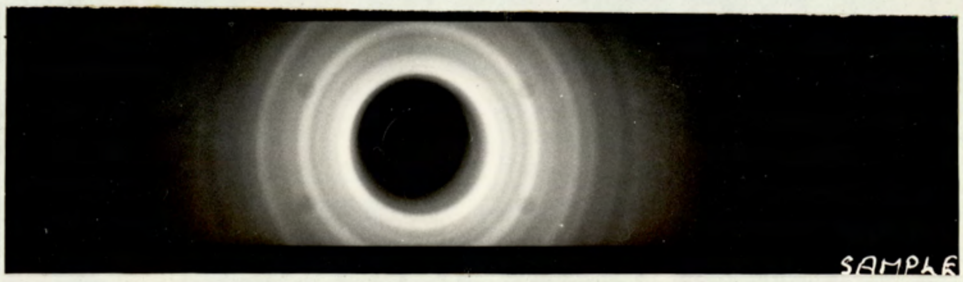
* Molar susceptibilities, χ'_M reported after diamagnetic corrections.



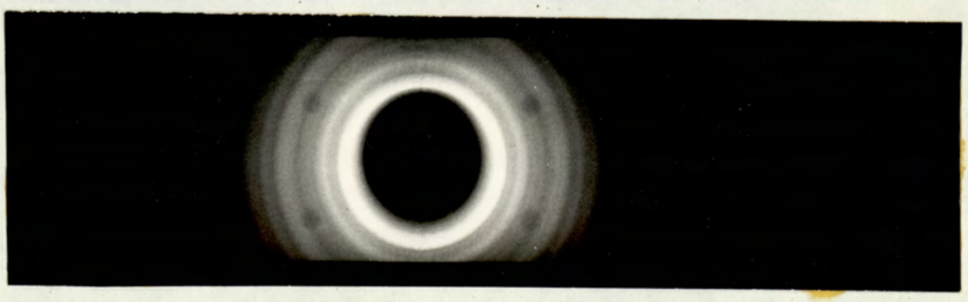
Iodine adduct of dithiocyanatotetrakis(pyridine)nickel(II)



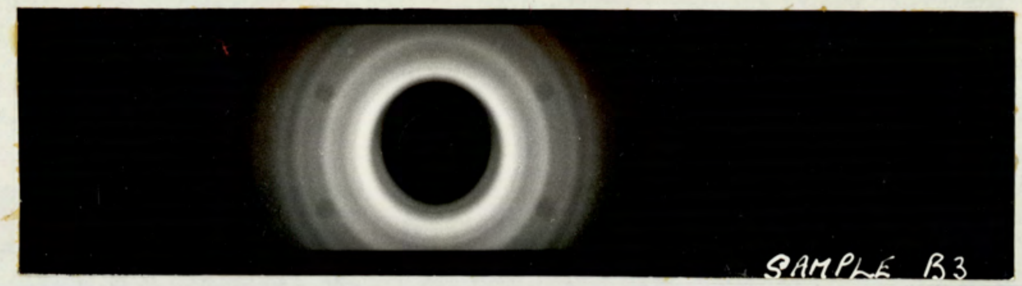
Di-triiodotetrakis(pyridine)cobalt(II)



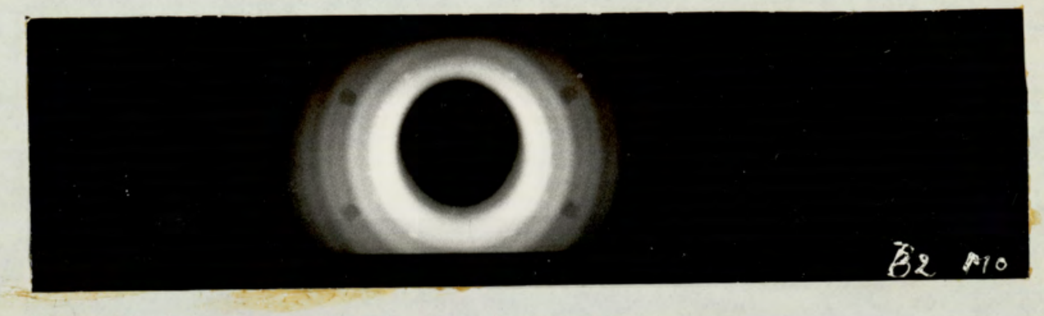
Di-triiodotetrakis(pyridine)cadmium(II)



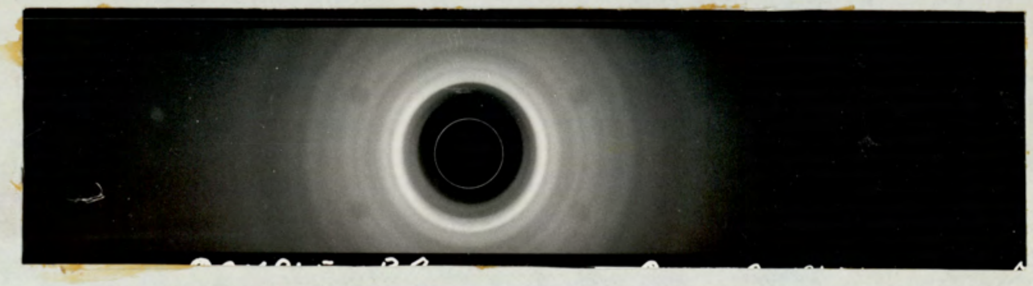
Di-triiodotetrakis(pyridine)mickel(II)



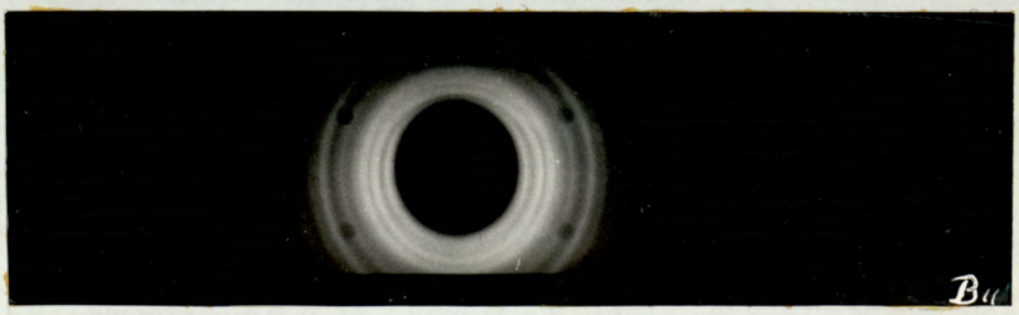
Di-triiodotetrakis(β-picoline)nickel(II)



Di-triiodotetrakis(γ-picoline)nickel(II)



Di-triiodotetrakis(γ-picoline)cobalt(II)-diacetonitrile



Di-triiodotetrakis(γ-picoline)manganese(II)-diacetonitrile

DISCUSSION

The compounds investigated have all been of one or the other of two types, namely

$$(\text{pyridine base})_4\ (M)^{2+}(X_3^-)_2$$

where X was iodine, and M was a divalent 1st row Transition Metal or

$$(\text{pyridine base})_4(M')^{2+}(CNS.I_2)_2$$

where M' = Nickel(II) only.

Some triiodide,I_3^-, compounds of iron(II), manganese(II), cobalt(II) and cadmium(II) with pyridine bases were crystallised from acetonitrile. The infrared evidence of these compounds pointed strongly to the acetonitrile being held as a lattice component unco-ordinated to the metal ion. These compounds are: $CoL_4(I_3)_2.2CH_3CN$, where L = β-picoline or γ-picoline; $ML_4(I_3)_2.2CH_3CN$, where M = Mn(II), Fe(II) and Cd(II), and L = γ-picoline only. The triiodide,I_3^-, complexes of Mn(II), Fe(II) and Cd(II) with β-picoline could not be isolated in the solid state, i.e. they could not be crystallised.

The ion I_3^- is known to be linear within 3^o [74]. The crystallographic data of the ion $(CNS.I_2)^-$ is not known but it is believed that the ion $(CNS.I_2)^-$ could not remain linear. Both of the anions will be highly polarisable and also very bulky. The triiodide ion I_3^- has an overall length of about $5.92A^o$. The ion $(NCS.I_2)^-$ will probably be bonded as $M\text{-}NCS\text{-}I_2$. The bonding of iodine to sulphur of the NCS group and bonding of metal ion to $(NCS.I_2)$ group through nitrogen is explained by the spectroscopic evidence (page 164). Again the pyridine bases have a 'rigid' well defined shape and are known to interact strongly with halogens [81-89]. The detailed nature of this interaction will be very much a function of temperature since the position of the equilibrium $I_3^- \rightleftharpoons I_2^0 + I^-$ will lie more and more over towards the righthand side as the temperature is raised. It was expected that in a number of instances that the interaction of the pyridine base and the complex anion would be sufficiently strong to impose an unusual 'geometry' on some of the metal ions and that this would be detectable using the ordinary physical methods.

The pyridine bases used in this work were limited to three, namely pyridine, 3-methylpyridine (β-picoline) and 4-methylpyridine (γ-picoline). The ligand 2-methylpyridine (α-picoline) was excluded from the series owing to the considerable steric hindrance experienced at the nitrogen owing to the presence of the adjacent methyl group. Again another reason why 2-methylpyridine (α-picoline) was excluded, was because, it is electronically analogous to 4-methylpyridine(γ-picoline), that is 3- and 4-methylpyridines by themselves illustrated the principle effects of alkyl substitution in the pyridine ring on the availability of the lone pair on the nitrogen atom.

In the normal course of events the electronic spectrum of a compound will give one a very good guide to the stereochemical environment of a first row transition metal ion contained therein, however, in the compounds under investigation it was found that even at liquid nitrogen temperatures the absorption spectrum due to I_3^- was both so broad and intense that in general the d↔d bands of the compounds under examination were completely obscured and so no information concerning the electronic structure of the compound was available from this source. It was found that in the following limited series of compounds, namely $ML_4(I_3)_2$, where M =Ni(II),Co(II), Fe(II) and Cd(II) & L = pyridine; $NiL_4(I_3)_2$, where L = β-picoline or γ-picoline; $NiL_4(NCS.I_2)_2$ where L = pyridine, β-picoline or γ-picoline and also $ML_4(I_3)_2.2CH_3CN$, where M = Co(II), Mn(II), Fe(II) and Cd(II), L = γ-picoline, that at liquid nitrogen temperature they changed in colour from very dark reddish-brown or black to a bright orange-red. However, in few cases of nickel(II), it was observed that the compounds were diamagnetic at room temperature and therefore planar and so expected to be red or orange-yellow and so once again the electronic spectrum was found to be uniformative.

Overall it was found that the most informative data was derived from the measurement of the magnetic susceptibilities of these compounds- when in general no evidence of unusual or unexpected stereochemistry was found except in the case of the following nickel(II) compounds, $Ni(pyridine)_4(I_3)_2$ and $Ni(\gamma\text{-picoline})_4(I_3)_2$ which were found to be diamagnetic at room temperature. The conclusion drawn from this was that at least in the case of nickel(II) it has been found possible to prepare compounds which were either 'planar' or 'tetragonally distorted octahedral' compounds with one of the octahedral diagonal axis greatly elongated.

The effect of distortion of the coordination polyhedron upon the magnetic properties is best seen in the nickel(II) ion in O_h symmetry where the low-spin state does not exist. All regular octahedral nickel(II) compounds show a paramagnetism due to the presence of the two unpaired spins. This situation, however, changes whenever an octahedral environment is subjected to an axial distortion. Such geometrical distortion lowers the symmetry from O_h to D_{4h} and this results in further loss of degeneracy of the d-orbitals. The tetragonally distorted d^8 complexes will have high-spin or low-spin depending upon whether the pairing energy, 'P', is greater or less than the separation energy, 'q_1'. (Fig.18(a), page 78). When the tetragonal distortion is large, the energy separation between the $dx^2 - y^2$ and dz^2 orbitals (q_1) or between $dx^2 - y^2$ and dxy orbitals (q_2) may increase the electron pairing energy (Fig.18(a) and 18(b), page 78). It is seen from the figure-17, (page 78), that a strong tetragonal distortion leads to square planarity. In such case the dz^2 orbital may fall below the dxy orbital (fig.18(b) and 17, page 78) and there will be a change in magnetic moment from ca 3.0 B.M. to zero.

1. Nickel(II) complexes of pyridine,β-picoline and γ-picoline

A. The triiodide,I_3^- complexes of nickel(II) with pyridine, β-picoline and γ-picoline:

The preparation of the triiodide,I_3^-,complexes of nickel(II) of the stoichiometry, $NiL_4(I_3)_2$ (where L = pyridine,β-picoline or γ-picoline) involved a two step process. The first step is the preparation of the parent compound of the formula, NiL_4I_2 and the second step is the preparation of the triiodide,I_3^- complexes of the stoichiometry,$NiL_4(I_3)_2$ from their respective diiodide compounds.

The study of the infrared spectra of nickel(II) iodide and triiodide (I_3^-) complexes with pyridine bases showed that the vibrational bands of the ligands were little changed on co-ordination with nickel(II) ion. Gill et al.[16] found that the pyridine vibrational bands in the high frequency region (above 650 cm^{-1}) show very little shift upon complex formation while bands at 602 cm^{-1} (in-plane ring deformation) and 405 cm^{-1} (out-of-plane ring deformation) were shifted to higher frequencies upon co-ordination to metal ions. From the infrared spectrum of $Ni(py)_4I_2$, it is found that the vibrational bands at 602 and 405 cm^{-1} of free pyridine are shifted to 632 and 435 cm^{-1} respectively. A band at 745 cm^{-1} (C-H out of plane deformation) of free pyridine splits into two bands which are shifted to 762 and 752 cm^{-1} in the complex,$Ni(py)_4I_2$. In the triiodide compound, $Ni(py)_4(I_3)_2$ these bands (at 602 , 405 and 745 cm^{-1}) of free pyridine are shifted to the same position as found in the compound, $Ni(py)_4I_2$. In addition, a new band found at 477 cm^{-1} in the dz^2 orbital may fall below the dxy orbital (fig.18(b) and 17, page 78) and there will be a change in magnetic moment from ca 3.0 B.M. to zero.

1. Nickel(II) complexes of pyridine, β-picoline and γ-picoline

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The preparation of the triiodide, I_3^-, complexes of nickel(II) of the stoichiometry, $NiL_4(I_3)_2$ (where L = pyridine, β-picoline or γ-picoline) involved a two step process. The first step is the preparation of the parent compound of the formula, NiL_4I_2 and the second step is the preparation of the triiodide, I_3^- complexes of the stoichiometry, $NiL_4(I_3)_2$ from their respective diiodide compounds.

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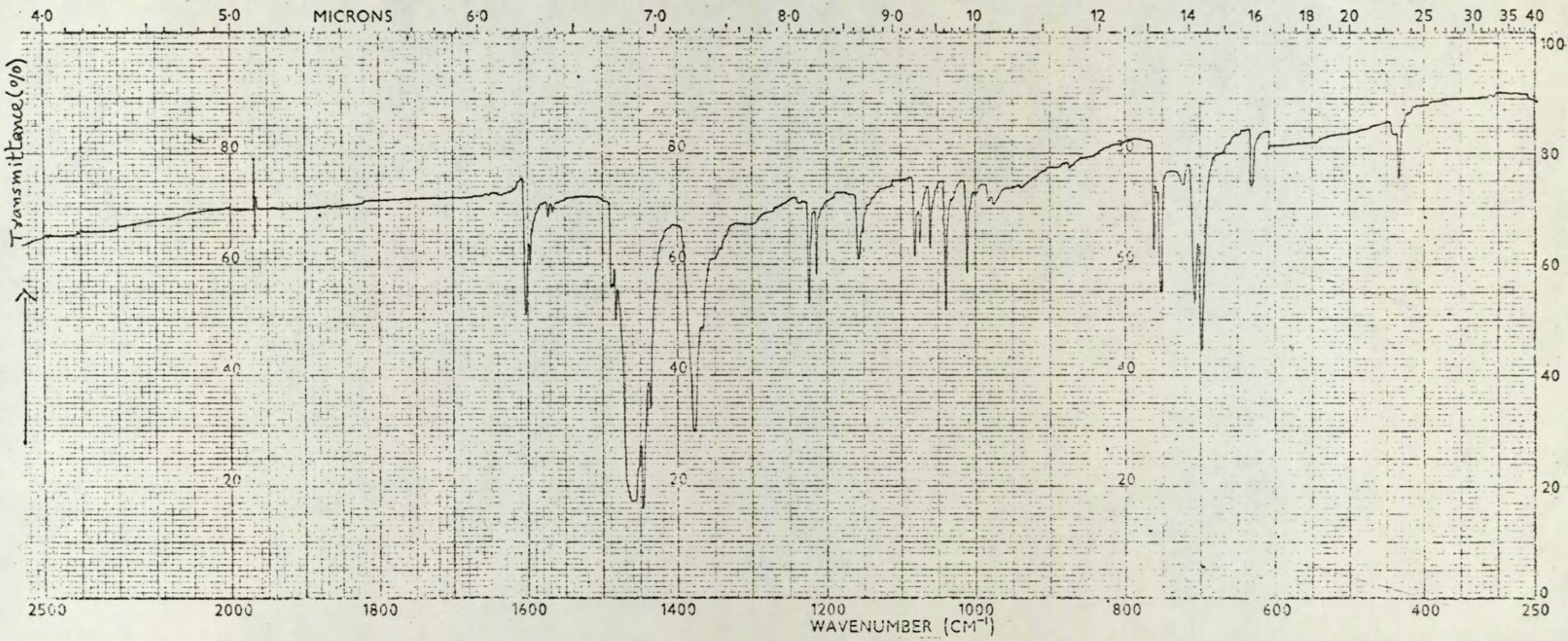

Fig.23(a). Infrared spectrum of Diiodo<u>tetrakis</u>-(pyridine) nickel (II)

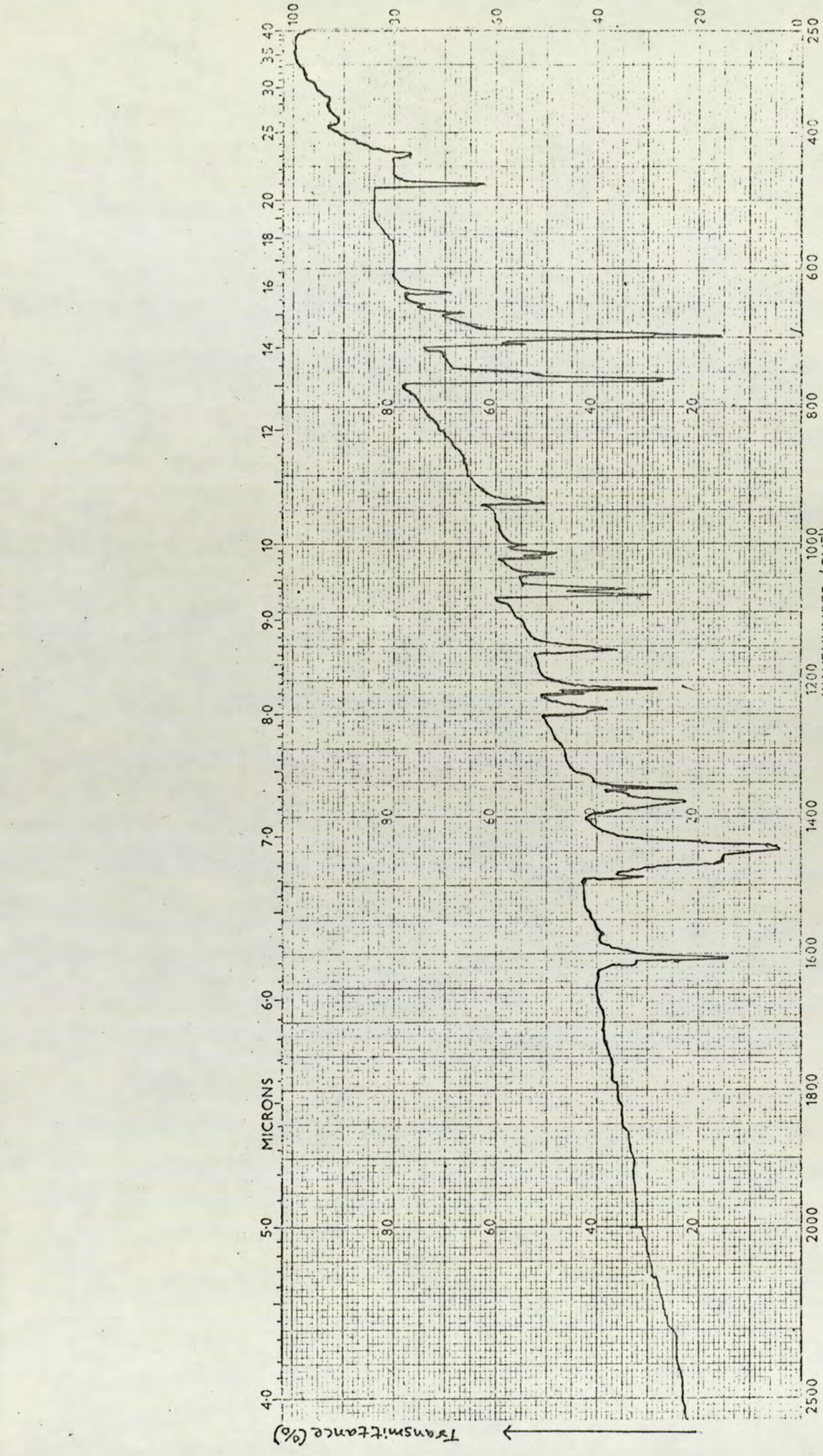

Fig.23(b). Infrared spectrum of Di-triiodotetrakis (pyridine) nickel (II) the spectrum of $Ni(py)_4(I_3)$, which is absent in both free pyridine and in the compound $Ni(py)_4I_2$. A study of the infrared spectra of β-picoline complexes with nickel(II)iodide and nickel(II)triiodide (Table 12.) suggested that a shift of 15 cm^{-1} or more only occurs in bands at 630 cm^{-1} (inplane bending of ring)*; 457 cm^{-1} (out-of-plane bending of ring)* and at 1228 cm^{-1} (band due to the substituent in the ring)* of free β-picoline. In the compound, $Ni(\beta\text{-picoline})_4I_2$, these bands of free β-picoline are found to be shifted to 648, 480 and 1242 cm^{-1} respectively. In the triiodide compound, $Ni(\beta\text{-pic})_4(I_3)_2$ the bands at 630 and 457 cm^{-1} of free β-picoline are shifted to 652 and 482 cm^{-1} respectively. In addition the vibrational band of free β-picoline at ~ 535 cm^{-1} (a band due to the substituent in the ring)* is shifted to 570 cm^{-1} in the compound, $Ni(\beta\text{-pic})_4(I_3)_2$. The overall appearance of the spectrum due to γ-picoline in its complexes of nickel(II) iodide and the triiodide, I_3^-, differs appreciably from that of free base (γ-picoline). The coordination sensitive bands of γ-picoline are[109]: 1608 cm^{-1}(c-c stretching vibration)*, 1224 cm^{-1} (C-H in-plane bending)*; 997 cm^{-1}(ring vibration)*; 800 cm^{-1}, (C-H deformation)* and 515 cm^{-1} (a band due to the substituent in the ring)*. These vibrational bands of the γ-picoline are shifted to higher frequencies on coordination with metal ions. (* The assignment of frequencies of β-picoline and γ-picoline were taken from the work of Green et al.[110] 1×10^4 cm^{-1} = 1000 nm, $1 \times 10^2 cm^{-1}$ = 1×10^5nm.) In the infrared spectrum of $Ni(\gamma\text{-pic})_4I_2$, the coordination sensitive bands of γ-picoline are shifted to 1617, 1232, 1020, 812 and 540 cm^{-1*}. However in the triiodide compound, $Ni(\gamma\text{-pic})_4(I_3)_2$, it is found that, apart from the bands at 812 and 1617 cm^{-1*} which are also found at the same position in NiL_4I_2, the coordination sensitive bands of free γ-picoline at 1223, 997 and 515 cm^{-1*} are found to be shifted to a higher frequencies than found in $Ni(\gamma\text{-pic})_4I_2$. In the infrared spectrum of $Ni(\gamma\text{-pic})_4(I_3)_2$, they are shifted to 1254, 1050 and 577 cm^{-1} respectively. Another vibrational band of γ-picoline at 485 cm^{-1} (out-of-plane ring bending) is shifted to 499 cm^{-1} in the infrared spectrum of $Ni(\gamma\text{-pic})_4I_2$ and to 510 cm^{-1} in $Ni(\gamma\text{-pic})_4(I_3)_2$. Thus the above infrared data suggests that the interaction between the metal ion {nickel(II)} and pyridine bases increased on the formation of the triiodide-complexes,$NiL_4(I_3)_2$. (where L = py, β-pic. or γ-pic.).

As previously stated (page 152) the electronic spectra of the triiodide complexes of nickel(II), $NiL_4(I_3)_2$ (where L = py, β-pic.or γ-pic.) do not give any information regarding the electronic structure of the compounds. In the visible region of the spectrum, the d ↔ d transition bands of the compounds, $NiL_4(I_3)_2$ were completely obscured by the presence of the triiodide,I_3^- ion. It had been hoped that tetrahedral bands might be seen through the I_3^- spectrum.

The measurements of the magnetic susceptibilities of these triiodide complexes, $NiL_4(I_3)_2$ at room temperature gave information concerning the stereochemistry of the nickel(II) ion in the triiodide compounds. The compounds, ditriiodo-tetrakis(pyridine) and -(γ-picoline) nickel(II) are found to be diamagnetic at room temperature. (The parent compounds, $Ni(py)_4I_2$ and $Ni(\gamma\text{-pic})_4I_2$ are paramagnetic at room temperture). Therefore it is believed that in the triiodide complexes, $Ni(py)_4(I_3)_2$ and $Ni(\gamma\text{-pic})_4(I_3)_2$, a large tetragonal distortion occurs which leads to the square planarity of these complexes and hence their diamagnetism. The β-picoline compound of nickel(II)-triiodide, $Ni(\beta\text{-pic})_4(I_3)_2$,is found to be paramagnetic at room temperature (μ_{eff} = 2.83 B.M. at 19°C). This magnetic moment, 2.83 B.M. is consistent with a six-coordinated environment of the nickel(II) ion.

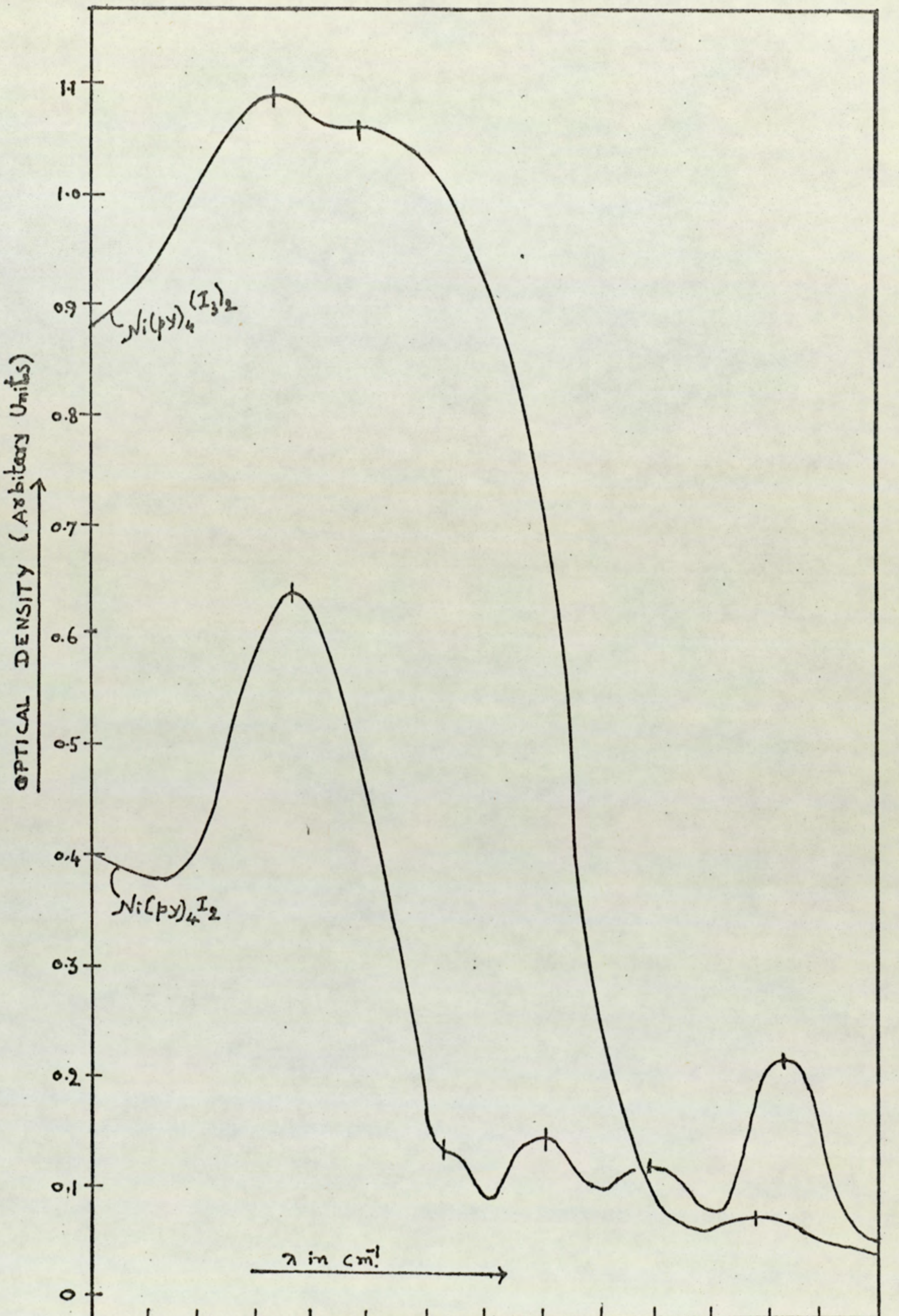

Fig.24. Diffuse Reflectance Spectra of $Ni(py)_4I_2$ and $Ni(py)_4(I_3)_2$.

The possible reason for Ni(β-pic)$_4$(I$_3$)$_2$ being paramagnetic, is that in a pyridine the 1,3 and 5 positions are those of greatest electron density. Therefore any back coordinating charge from metal to the ligand (M →L) is inhibited in β-picoline which already carries an excess charge. Hence in the β-picoline complex, the charge transfer from halogen to ligand and back-donation of electrons from nickel(II) to the ligand (Ni → L) is less in comparison of γ-picoline-triiodide complex, Ni(γ-pic)$_4$(I$_3$)$_2$. This would have the effect of decreasing the in-plane field and thereby increasing the ligand-field symmetry. In otherwords the tetragonal distortion in β-picoline-nickel(II) triiodide complex, Ni(β-pic)$_4$(I$_3$)$_2$, is not large enough to bring about square planarity.

Conductivity data of these complexes, NiL$_4$(I$_3$)$_2$ (where L = py, β-pic, or γ-pic) in nitromethane indicates dissociation of the compounds in that solvent, although the solution spectra were unable, owing to the presence of I_3^- ions,to give any help concerning the structure of the moiety containing the metal ion. However, it was shown beyond reasonable doubt that the compounds were not dissolved as non-electrolytes in nitromethane solution but rather as 1:2 electrolytes.

B. Iodine addition compounds of dithiocyanato-tetrakis(pyridine base) nickel(II), where pyridine base = pyridine, β-picoline or γ- picoline

Reaction of iodine and dithiocyanato-tetrakis(pyridine base)nickel(II) affords a dark-brown crystalline product of the stoichiometry, NiL$_4$(NCS.I$_2$)$_2$ (where L = pyridine, β-picoline or γ-picoline. The same abbreviation,(L), is used for pyridine, β-picoline or γ-picoline in the rest of the discussion).

The parent compounds, NiL$_4$(NCS)$_2$, were extensively studied by Nelson and Shepherd[9,18]. The magnetic and spectroscopic data of the complexes, $NiL_4(NCS)_2$, in Table 13, are consistent with the previous work[9,18]. Thus in the complexes $NiL_4(NCS)_2$, the nickel(II) ion is found to have a six-coordinated environment.

The infrared study of the complexes, $NiL_4(NCS)_2$ and $NiL_4(NCS.I_2)_2$ provides good evidence concerning the manner of bonding of the thiocyanate group to the nickel(II) ion in the complexes, $NiL_4(NCS)_2$ and also the manner of bonding of iodine molecules to the $NiL_4(NCS)_2$ entities. The thiocyanate group may coordinate to a metal ion through the nitrogen (M-NCS) or the sulphur (M-SCN) or both (M-NCS-M') In the first transition series metal complexes[111], the thiocyanate group coordinates to a metal ion through nitrogen. The free thiocyanate ion absorbs at about 750 and 2055 cm^{-1} in the infrared spectrum[112]. (750 and 2055 cm^{-1} are the C-S and C-N stretching vibration respectively). The frequencies of these bands are shifted to 780-860 cm^{-1} and 2065-2095 cm^{-1} respectively in the SCN-Metal complexes, and 690-720 and 2080 - 2195 cm^{-1} respectively in the NCS-Metal complexes[112]. For bridging thiocyanate the ν(C-N) shifts to higher wavenumber than for M-NCS complexes while ν(C-S) usually shifts to an intermediate frequency[113,115]. The C-N and C-S stretching frequencies in the complexes, $NiL_4(NCS)_2$ (Table 13), suggested that the thiocyanate group (SCN) is found to be N-bonded to the nickel(II) ion. This view is supported by the X-ray structural studies which showed that in thiocyanate complexes of cobalt(II)& nickel(II) with pyridine, $M(py)_4(NCS)_2$, the thiocyanate groups were found to be coordinated through nitrogen[114].

However, in the infrared spectra of the compounds $NiL_4(NCS.I_2)_2$, there are pronounced changes in the C-N and C-S stretching frequencies (Table 13) which strongly support the idea that the iodine molecules are bonded to the thiocyanate groups. The infrared data (Table 13) suggest that the stretching frequencies, ν(C-N) and ν(C-S) are changed

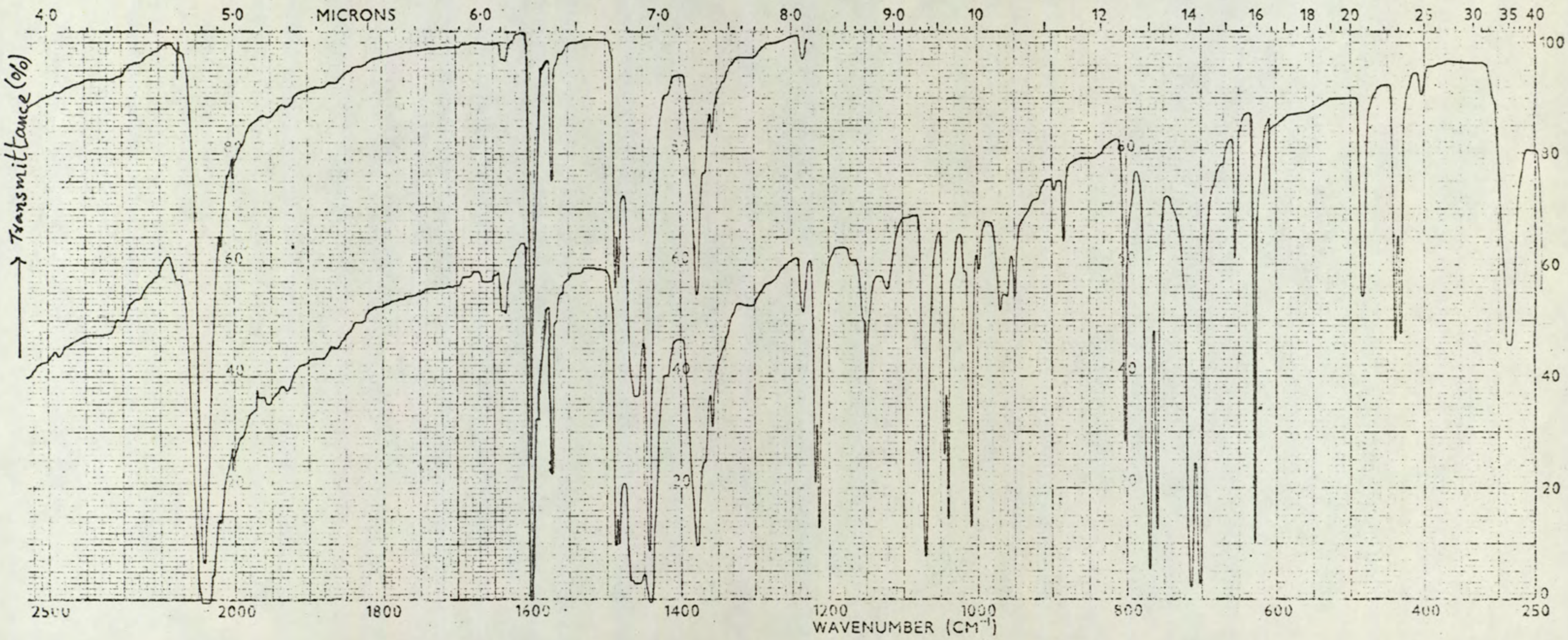

Fig.25(a). Infrared spectrum of Dithiocyanatotetrakis (pyridine) nickel (II)

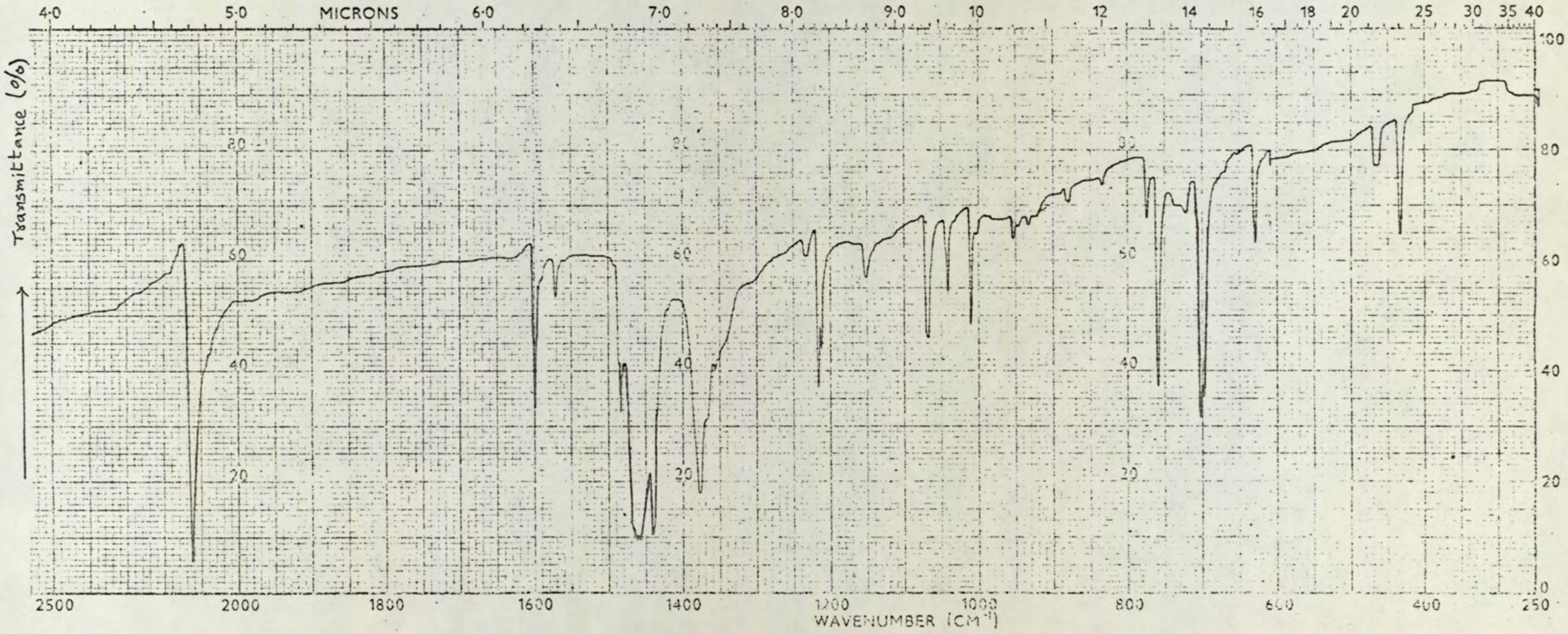

Fig.25(b). Infrared spectrum of iodine adduct of dithiocyanato-*tetrakis* (pyridine) nickel (II) from those characteristics of N-bonded thiocyanate (as stated above for $NiL_4(NCS)_2$) to those expected for bridging NCS groups[115]. Thus in the complexes, $NiL_4(NCS.I_2)_2$, there could be two possibilities in which iodine may coordinate to the thiocyanate groups, M-N-C-S-I-I or N-S-C-N-I-I. A change from M-N to M-S bonding could occur during the formation of the compounds, $NiL_4(NCS.I_2)_2$.

Foster and Goodgame[107], who worked on the compounds, $M(py)_4(NCS.I_2)_2$ (where M = Co or Ni) and $Ni(\gamma\text{-pic})_4(NCS.I_2)_2$, made a distinction of the two possibilities, M-N-C-S-I-I or M-S-C-N-I-I, by studying an electronic spectra of pairs of compounds $ML_4(NCS)_2$ and $ML_4(NCS.I_2)_2$. Jørgensen[116] demonstrated that the ligand field strength, Δ , of NCS is less when coordinated to a metal ion through sulphur than when bonded through nitrogen. Foster and Goodgame[107] studied the electronic spectra of the compounds $M(py)_4(NCS.I_2)_2$ (where M = Co or Ni) and found that in each compound, the energy of the first transition $\{4\ T_{1g}(F) \rightarrow 4\ T_{2g}$ for Co(II) and $3A_{2g} \rightarrow 3T_{2g}$ for Ni(II)$\}$was found to be slightly greater for $ML_4(NCS.I_2)_2$ than for the corresponding compounds $ML_4(NCS)_2$. This result, according to the view of Jørgensen[116], strongly supported that in the compound $ML_4(NCS.I_2)_2$, the NCS groups were still bonded through nitrogen to the metal ion. From the data of the visible spectrum (Table -11) of the compounds $NiL_4(NCS.I_2)_2$ and $NiL_4(NCS)_2$ which were studied here, it is seen that there is a slight increase in the energy of the first spin-allowed transition of nickel(II) ($3\ A_{2g} \rightarrow 3\ T_{2g}$) in the $NiL_4(NCS.I_2)_2$ relative to the corresponding compound $NiL_4(NCS)_2$. (where L = pyridine and γ-picoline only). This result is consistent with the data obtained by Foster and Goodgame[107], which again supported the idea that in the compounds, $NiL_4(NCS.I_2)$, the NCS groups are still bonded to the nickel by nitrogen. Thus it is concluded that these compounds $NiL_4(NCS)_2(I_2)_2$ should be formulated as $ML_4(NCS\text{-}I_2)_2$ con-

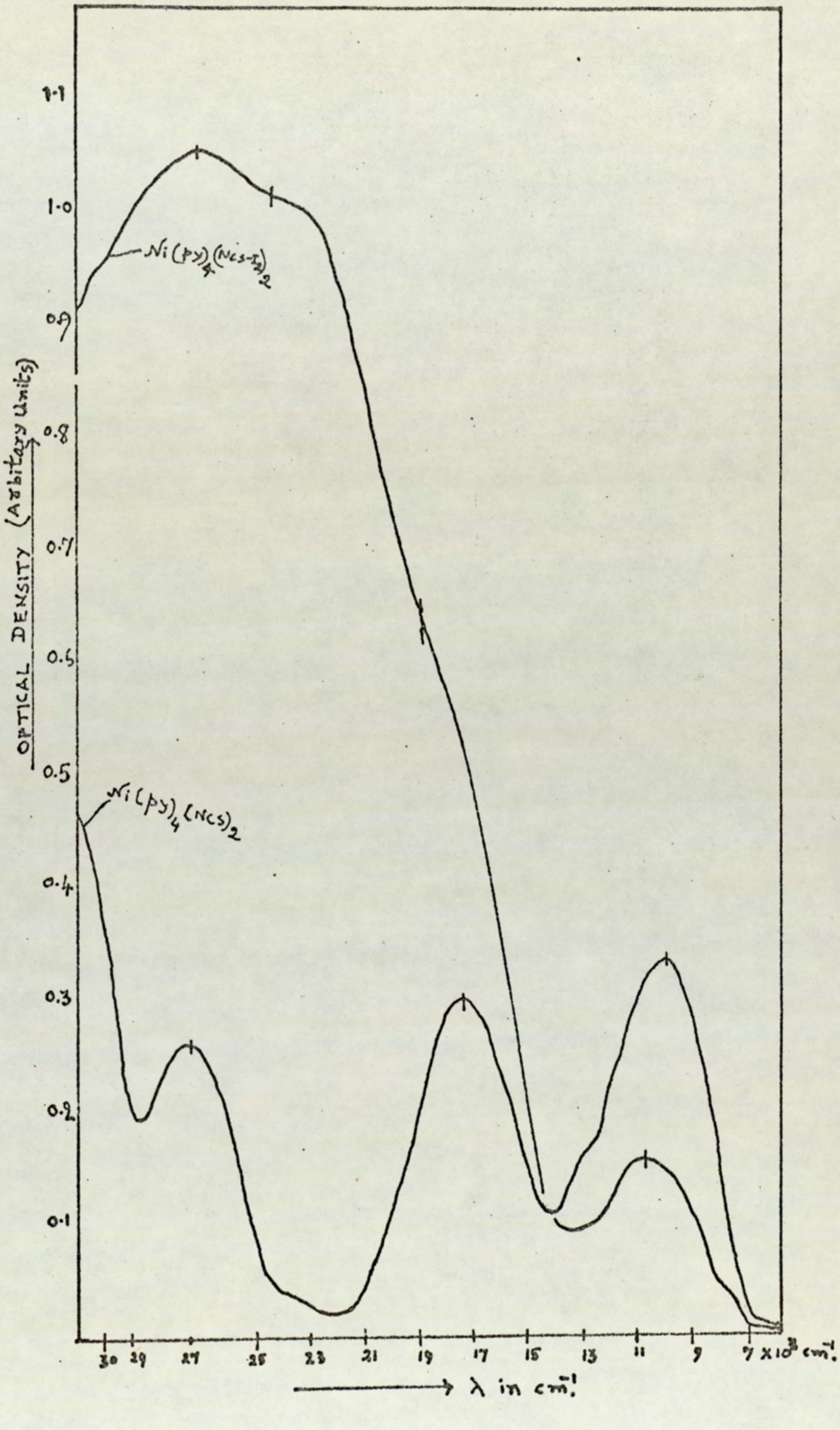

Fig.26. Diffuse Reflectance Spectra of $Ni(py)_4(NCS)_2$ and $Ni(py)_4(NCS-I_2)_2$.

taining coordinated diiodothiocyanate ions, $(NCS\text{-}I_2)^-$.

The magnetic data for the compounds, $Ni(L_4)(NCS.I_2)_2$ at room temperature (Table 11) are consistent with the six coordinated environment of nickel(II) ion. The compounds $NiL_4(NCS.I_2)_2$ are insoluble in nitromethane and therefore the conductivity measurement was taken in dimethylsulphoxide which indicates dissociation of these compounds in that solvent. The conductivity data shows the presence of 1:2 electrolytes in dimethylsuphoxide. Again the solution spectra of these compounds, $NiL_4(NCS.I_2)_2$, are unable, owing to the presence of an iodine containing anion $(NCS\text{-}I_2)^-$, to give any help concerning the structure of the moiety containing the nickel(II) ion.

Spin-state isomerism in the case of nickel(II) has been a subject of interest for a number of years.[94-100] Maki[117] and Ballhausen and Liehr[118], using the weak-field and the strong-field approach respectively, have calculated the effect on the electronic energy levels of applying axial ligand-field perturbations to planar nickel(II) complexes. The relative energies of the lowest singlet state and the lowest triplet state, and therefore the magnetic behaviour, are effected both by a change in the in-plane ligand field and by an axial perturbation of it. An increase in the axial component of the ligand field of a diamagnetic complex reduces the energy of the lowest triplet state relative to the singlet ground state, and eventually leads to the formation of a triplet ground state, with consequent paramagnetism. Such axial perturbations may be due to; (i) solvation, either in coordinating solvents or in solid disolvates (ii) polymerisation of four coordinate complexes in solid or in non-coordinating solvents and (iii) purturbation by the anions X in a complex of the type NiL_4X_2, where L represents the planar field produced by four neutral ligands. In present work the complexes NiL_4X_2

where L = pyridine bases and X = I_3^- or $(NCS-I_2)^-$ were considered to be the example of class (iii) axial perturbation.

The magnetic susceptibilities of some nickel (II) complexes of the type NiL_4X_2, where L = pyridine bases and X = I_3^- or $(NCS-I_2)^-$, have been studied over the temperature range 293 to 93 K. It was previously stated (page 158) that the compounds, $Ni(py)_4(I_3)_2$ and $Ni(\gamma\text{-pic})_4(I_3)_2$ were found to be diamagnetic at room-temperature and therefore have a square-planar environment about nickel(II) ion. However the study of the magnetic susceptibility of the compound, $Ni(\beta\text{-pic})_4(I_3)_2$ as a function of temperature (range 293 to 93K) suggested that the magnetic cross-over had been found in this complex. The compound was found diamegnatic below 200 K. The same compound had a magnetic moment of 2.85 B.M. at room-temperature. This result suggested that in the compound, $Ni(\beta\text{-pic})_4(I_3)_2$, the Spin-singlet-triplet isomerism occurred. This compound appeared to have a spin-singlet ground state (^1E) at low-temperature.

The magnetic susceptibilities of the complexes $Ni(L)_4(NCS-I_2)_2$, (where L = pyridine bases), were also studied over the temperature range 293 to 93 K. These complexes have a room temperature magnetic moment of 3.0± 0.1 B .M. and were found to obey the Curie-Weiss law over the range 293-93 K. The magnetic data are shown in the Table-20. The plots of $1/\chi_M$ against temperature afforded straight lines in all cases. (figure 27).

Goodgame and Venanzi[95], who studied the diamine complexes of nickel(II), found that the complexes with anions of negligible or low coordinating ability were diamagnetic while those with anions of medium to good coordinating power have room-temperature magnetic moments of 3.2 ± 0.1 B.M. From the above conclusion and from the magnetic data obtained for the present work (Table -20) it may be predicted that in

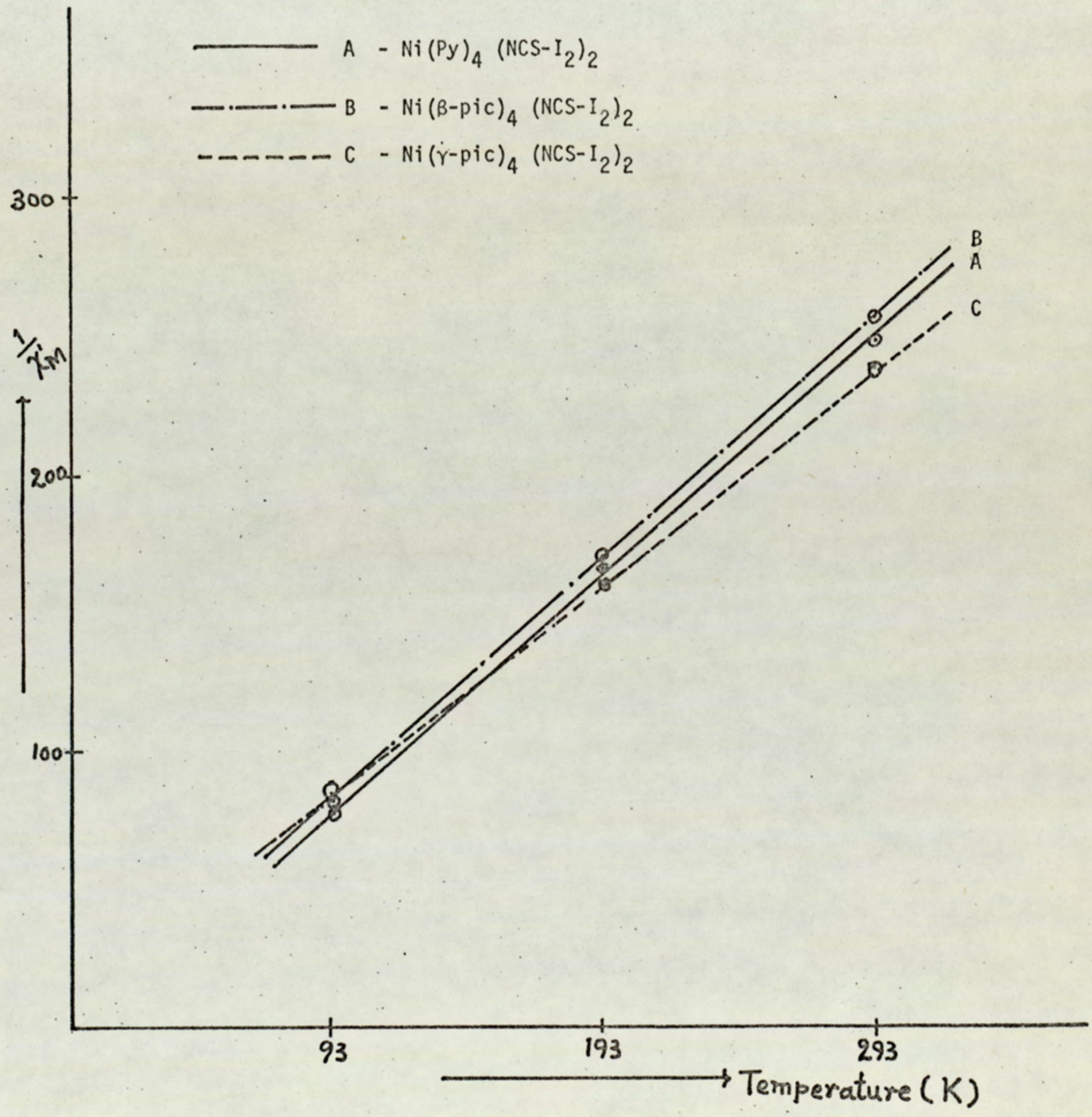

Fig.27. Plot of reciprocal of molar magnetic susceptibility ($1/\chi'_M$) against temperature (K).

the complexes, $NiL_4(I_3)_2$ and $NiL_4(NCS\text{-}I_2)_2$,(where L = pyridine bases), the anion, I_3^- might have lower coordinating ability than the anion, $(NCS\text{-}I_2)^-$.

2. Some Triiodide (I_3^-) Compounds of Manganese(II), Iron(II) and Cobalt(II) with Pyridine Bases:

The triiodide (I_3^-) compounds of Mn(II) with pyridine and β-picoline could not be crystallised from any organic solvent. However, the triiodide compound of manganese(II) with γ-picoline was crystallised from acetonitrile with the composition, $Mn(\gamma\text{-pic})_4(I_3)_2.2s$ (where s = acetonitrile molecule). The iron (II)-triiodide compounds of pyridine and γ-picoline were isolated with the stoichiometry $FeL_4(I_3)_2$ (where L = pyridine and γ-picoline only). The compound $Fe(\gamma\text{-pic})_4(I_3)_2$ was also crystallised from acetonitrile with the composition $Fe(\gamma\text{-pic})_4(I_3)_2.2s$. (s = acetonitrile). The reaction of iodine and diiodotetrakis(pyridine)Co(II) affords the dark brown compound $Co(py)_4(I_3)_2$ while the triiodide-cobalt(II) compound of β-picoline and γ-picoline were crystallised from acetonitrile with the composition $CoL_4(I_3)_2.2CH_3CN$;(where L = β-picoline or γ-picoline).

A study of the infrared spectra of these compounds gave only limited information which nevertheless turned out to be of considerable interest. A number of triiodide-compounds prepared, which were initially anhydrous, had a strong affinity for water and were indeed decomposed by it, giving viscous black oils. Other compounds, such as triiodide compounds of iron(II), manganese(II) and cobalt(II) with γ-picoline (and with β-picoline in Co(II) case) which had proved very difficult to crystallise, and indeed which only crystallised from acetonitrile were found to have retained acetonitrile. The acetonitrile could not be removed without decomposing the compounds to an oil although, as previously stated, the infrared evidence pointed strongly to the acetonitrile being held as a lattice component uncoordinated to the metal ion. The analytical data of these complexes also support the presence of two molecules of acetonitrile in them.

The magnetic moments of the above manganese(II), iron(II) and cobalt(II) compounds at room temperature are consistent with the formation as an octahedral spin-free compounds. The electronic spectra, owing to the presence of triiodide, I_3^-, are so broad and intense that in general the d $\leftrightarrow$ d bands of these compounds are completely obscured and so no information regarding the electronic structure of the compound is available. The conductivity data of the compounds, $Fe(py)_4(I_3)_2$, $M^{(II)}(\gamma\text{-pic})_4(I_3)_2\ 2CH_3CN$ (where M = Fe(II), Mn(II)) in dimethylsulphoxide indicates the dissociation of the compounds in that solvent and it was shown that they behave rather as 1:2 electrolytes in dimethylsulphoxide. However, the nitromethane solutions of the compounds $Co(py)_4(I_3)_2$ and $Co(L)_4(I_3)_2\ 2CH_3CN$ (where L = β-picoline or γ-picoline) are intensely coloured (dark-green). The conductivity data of these compounds also indicates dissociation in that solvent and they appeared to be 1:2 electrolytes. The visible absorption spectra of $Co(L)_4(I_3)_2.2CH_3CN$; (where L = β- picoline or γ-picoline) in nitromethane solution(10^{-3}M) clearly indicates the presence of a tetrahedral cobalt(II) species (λ_{max} ~ 14490 cm^{-1} (ε,320) and ~ 15290 cm^{-1},(ε,350) may be assigned to the $4\ A_2 \rightarrow 4\ T_1(P)$ transition). The compound, $Co(py)_4(I_3)_2$, gives a similar spectra in nitromethane solution. Addition of 10% of the respective pyridine base to nitromethane solution (10^{-3}M) of β-picoline and γ-picoline - Co(II) compounds causes the intense band centered at ~ 15000 cm^{-1} (which associated with the tetrahedral species) to decrease in intensity and the spectra becomes more characteristic of octahedral cobalt(II) species.

3. The triiodide, I_3^-, complexes of cadmium(II) with pyridine bases and some reactions involved in γ-picoline-Cd-triiodide compound:

Reaction of iodine and diio~~di~~dotetrakis(pyridine)Cd(II) in dichloromethane affords a dark-brown crystalline product of the stoichiometry , $Cd(py)_4(I_3)_2$. The conductivity data in dimethylsulphoxide indicated the dissociation of this compound in that solvent and also suggested that the compound, $Cd(py)_4(I_3)_2$, was not dissolved as a non-electrolyte in dimethylsulphoxide solution but rather as a 1:2 electrolyte. The triiodide-Cd(II) compound of β-picoline could not be isolated in crystalline form. The reaction between iodine and diiodotetrakis (γ-picoline)Cd(II) in dichloromethane gave a reddish-brown crystalline product of the stoichiometry, $Cd(\gamma\text{-pic})_4(I_3)_2$. This compound was also crystallised from acetonitrile and found to have retained acetonitrile. The analytical data and infrared evidence supported the presence of acetonitrile which was being held as lattice component uncoordinated to the Cd(II) ion. Although the compounds $Cd(\gamma\text{-pic})_4(I_3)_2$ and $Cd(\gamma\text{-pic})_4(I_3)_2\ 2CH_3CN$ were obtained in a crystalline form, they were decomposed into a dark-brown oily-mass within half an hour. This dark oily-mass was found to be insoluble in common organic solvents and also found unreactive to sodium-thiosulphate in glacial acetic acid. It was noticed that both compounds $Cd(\gamma\text{-pic})_4(I_3)_2$ and $Cd(\gamma\text{-pic})_4(I_3)_2\ 2CH_3CN$ remained unchanged at freezing temperature in a sealed ampoule for long period. The freshly prepared compounds $Cd(\gamma\text{-pic})(I_3)_2$ and $Cd(\gamma\text{-pic})_4(I_3)_2\ 2CH_3CN$, were found to be soluble in all common organic solvents and also found reactive to sodium thiosulphate in glacial acetic acid.

The reaction between cadmium iodide, γ-picoline and iodine at 60-80°C (without using solvent) gave a dark-brown viscous oil. Again this dark-brown oil was found to be insoluble in common organic solvents and also found unreactive to sodium thiosulphate in glacial acetic acid. The action of slow, direct heat to this dark-oil in sublimation apparatus gave a brown solid compound which deposited on the cold finger of the apparatus. This brown compound was recrystallised from petroleum ether. Pale-straw coloured plates were obtained on recrystallisation. Attempts made to separate the organic ligand from this compound by treatment with aqueous sodium hydroxide followed by ether-extraction gave a yellow liquid. The infrared spectra and the melting point of the picrate derivative of this yellow liquid suggested that the liquid obtained during ether-ectraction was nothing but γ-picoline only. The molecular weight of the yellow liquid was found to be 93.0 using mass spectra, (Picolines have a molecular weight of 93.12) which again supported the idea that it was γ-picoline only.

On treatment of the dark-brown viscous oil with concentrated hydrochloric acid the oily compound dissolved slowly in hot acid and crystallised out as a fine powder (orange-yellow) from this solution on cooling. Attempts were made to liberate the ligand from the orange-yellow compound by pyrolysis of the compound in closed vessel(see Fig. 22, page 126) gave a yellow liquid which was again found to be γ-picoline. The infrared evidence and melting point of the picrate derivative of the yellow liquid supported the above conclusion.

Thus owing to the complicated infrared spectra and analytical data obtained for both, the orange-yellow compound (separated by HCl treatment) and a pale-straw coloured compound (obtained by the action of direct heat to the dark-brown oil) and also inability to separate the free organic ligand from them it was not possible at this stage to reach any conclusion regarding the CdI_2-γ-picoline-Iodine reactions.

4. General observation on triiodide(I_3^-) complexes:

Absorption spectra of triiodide(I_3^-) ions were determined in acetonitrile and in 1,2-dichloroethane (Table -19). In both solvents two bands (λ_{max}) were found for I_3^- species. They were at $\lambda_{1(max)}$, ~365 nm and $\lambda_{2(max)}$, ~ 290 nm. More detailed studies on triiodide ions in solutions suggested that the I_3^- ions dissociates in acetonitrile[119]. In the triiodide-complexes, studied here, it was found that the triiodide species, I_3^-, were dissociated in acetonitrile. In a very dilute solution of acetonitrile, the maxima of triiodide ions $\lambda_{1(max)}$ at ~ 365 nm was found to be missing in many triiodide complexes. However, in 1,2-dichloroethane solution, the triiodide (I_3^-) ions are remained present as ion pairs, and the absorption spectra of triiodide ions, in this solvent, are not affected by ion-pair formation[119]. The absorption spectra for all triiodide complexes studied here in 1,2-dichloroethane suggested that in a dilute solution of 2×10^{-5}M, the triiodide species remained uneffected. The maxima (λ_{max}) at ~ 365 nm and ~ 290 nm are found present in all triiodide complexes.

Obviously data obtained by quantitative analysis of the compounds gave empirical compositions. These in general were those which one would expect, namely $M^{II}L_4(X_3)_2$, however it was found that there were two rather surprising exceptions in the cases of cadmium and zinc-triiodide complexes with pyridine base, when it was desired to obtain a set of X-ray diffraction diagrams of all the compounds. It was found that in the case of zinc that it was not possible to isolate a zinc-pyridine base-triiodide and in the case of cadmium, it was found on attempting to carry out quantitative analysis that the substance obtained was complex and it failed to react normally with sodium thiosulphate. As previously stated, more detailed work indicated that instead of the simple coordination compound expected a product had been obtained in which the pyridine ring system had been attacked giving, it was suspected, a product in which the basicity of the pyridine system had been greatly reduced as shown by the fact that the compound dissolved slowly in hot concentrated hydrochloric acid and crystallised out as fine powder from this solution on cooling. The obvious consequence of these two results was that two compounds whose X-ray powder diagrams would have served as useful reference frames were found to be unobtainable, and so a means of obtaining the nature of the geometry of donor groups about some of the metal ions by seeing which complex halides were isomorphous with the products of cadmium and zinc was lost. The underlying assumption made in this work was that one could reasonably expect the ligands to be arranged tetrahedrally about zinc, octahedrally about cadmium and most probably also octahedrally about manganese(II), iron(II) and cobalt(II).

The quantitative analysis of the complex iodides in particular proved to be a most vexatious topic. Whilst it was found to be a straightforward operation to determine the metal content and both iodine and iodide, it was found very difficult to obtain values for carbon, hydrogen and nitrogen that were consistent with the values for metal and halogen. It was observed that combustion of these compounds which contained in the region of 80% of iodine did not appear to follow a regular path as it was found that even with highly crystalline, dry, apparently homogeneous samples different operators could obtain different values for the carbon, hydrogen and nitrogen content. This resulted in rather more weight having to be placed on the metal and halogen analysis results than one would have wished. It was found however that when analysis for carbon, hydrogen and nitrogen had been obtained from several analytical establishments fairly well defined trends in the results became clear and that ultimately satisfactory results were obtained.

As previously mentioned X-ray powder diffraction photographs were taken of all the compounds prepared in the complex halide or pseudohalide series. Even though some photographs were taken several times changing the length of exposure and using fresh samples of compound, it was found in a few instances impossible to produce satisfactory photographs. The X-ray powder photographs for some compounds, e.g. $Ni(\beta\text{-pic})_4(NCS\text{-}I_2)_2$, $Ni(\gamma\text{-pic})_4(NCS\text{-}I_2)_2$, $Co(\beta\text{-pic})_4(I_3)_2.2CH_3CN$ and the iron(II) compounds of the general formula $Fe(L)_4(I_3)_2$ where L = pyridine or γ -picoline, were not obtained because of the fact that they were probably decomposed while being filled into x-ray tubes. The lack of lines and the very dark background suggested strongly that not only were the compounds in each case almost non-crystalline but they were also strongly fluorescent under X-ray irradiation. It had been intended to sort the photographs into isomorphous sets and then hopefully select a number of the group which could reasonably be expected to have a particular geometric arrangement of ligands about the central atom and then to go on to conclude that the same geometric arrangement of ligands was to be found in the case of the other members of a given isomorphous set. This intention was very largely frustrated by the unexpected inability to prepare the required derivatives of cadmium and zinc respectively. However, it was found possible to make positive suggestions in the cases of $Cd(py)_4(I_3)_2$, $Co(py)_4(I_3)_2$ and $Ni(py)_4(NCS\text{-}I_2)_2$ which were found to be isomorphous. In a limited number of cases the diffraction pattern was found to contain so many clear lines as to make comparisons with it very difficult and somewhat unreliable. This was found to be the case in the following instances, $Co(\gamma\text{-pic})_4(I_3)_2$ $2CH_3CN$ and $Mn(\gamma\text{-pic})_4$ $(I_3)_2$ $2CH_3CN$.

CONCLUSIONS

The polyhalide compounds investigated have all been of the types, M^{2+}(pyridine base)$_4(I_3^-)_2$ or $(M')^{2+}$(pyridine base)$_4$(NCS-$I_2)_2$; where M = a divalent first row transition metal, M' = Nickel (II) only and pyridine base = pyridine, β-picoline or γ-picoline.

Owing to the instability of these complexes toward moisture and heat, an inert atmosphere in the preparation of the polyhalide complexes is an essential requirement. The polyhalide complexes, are highly reactive chemically and therefore the solvents which are more inert to halogenation or hydrolysis have to be used as a reaction medium. The quantitative analysis of the complex iodides proved to be a more vexatious topic. It has been found that even with highly crystalline, dry, apparently homogeneous samples, different operators could obtain different values for the carbon, hydrogen and nitrogen content. This results in more weight having to be placed on the metal and halogen analysis results than one would have wished.

The considerable limitation of the electronic spectra, the solution spectra and the X-ray powder photography as structure tools for the study of the metal-polyiodide complexes are well illustrated by this investigation. However, the study of the magnetic susceptibilities provides useful information concerning the structure of the metal-triiodide complexes. The conclusion drawn from this investigation is that at least in the case of nickel (II), it has been found possible to prepare compounds which are either 'planar' or 'tetragonally distorted octahedral' compounds.

The study of the reaction of the CdI_2-γ-picoline-iodine has not been fully investigated. However, some detailed work indicated that instead of the simple coordination compound expected, a product obtained (orange-brown compound) in which the pyridine ring system has been attacked giving a product in which the basicity of the pyridine system has been greatly reduced as shown by the fact that the compound dissolved slowly in hot concentrated hydrochloric acid. Detailed information about the CdI_2 - γ-picoline-iodine could only be obtained if one could separate the complex organic ligand from the orange-brown cadmium compound, and this proved impracticable, dry distillation with sodium hydroxide only yielding the simple pyridine base, γ-picoline.

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