STUDIES OF SOME CO-ORDINATION COMPOUNDS OF IRON AND COBALT

A thesis submitted for
the degree of

DOCTOR OF PHILOSOPHY

by

MARY ELIZABETH FERNANDOPULLE

University of Aston in Birmingham
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ABSTRACT

Part 1 of this thesis is the study of the behaviour of tris 2-2' bipyridyl iron II cation in strongly acidic media. It is shown that the tris 2-2' bipyridyl iron II perchlorate is completely dissociated in concentrated hydrochloric acid to monoprotonated bipyridyl and chloro-ferrate. The pale blue solutions given by the tris bipyridyl iron II perchlorate in concentrated nitric, sulphuric and perchloric acids are attributed to the formation of iron III species including possibly a bis 2-2' bipyridyl complex. A solid of composition $\left[\mathrm{Fe\ (bipy)_2(NO_3)_2}\right]\mathrm{ClO_4}$ has been isolated from the nitric acid solution. Magnetic and Mossbauer data have shown that this complex contains low spin iron III. This species generates the familiar red coloured tris bipyridyl iron II rapidly when dissolved in water in the presence of light, but is very stable in solutions of concentrated acids.

Part II is a study of some aspects of the iron and cobalt complexes of dipyridylamine and tripyridylamine. The low temperature infra red spectra of the bis complexes of cobalt II with 4-methyl and 5-methyl substituted tripyridylamines have been studied and compared with that of the isomorphous nickel II and iron II species. The similarity of the spectra of the iron II complexes with those of the cobalt II species was further confirmed. The ease with which the substituted tripyridylamines form the yellow spin paired bis Co III species has been demonstrated. A green solid containing both Co II and Co III has been isolated from an acetone medium.

The tris dipyridylamine Co II perchlorate is shown to react with hydrogen peroxide forming a spin-paired bis dipyridylamine diperoxy bridged Co III species. This complex on treatment with concentrated hydrochloric and hydrobromic acids formed the corresponding bis dipy am dichloro and dibromo cobalt III complexes which are believed to contain trans halogeno ligands.

All attempts towards the direct synthesis and the oxidation of spin free tris dipyridylamine and spin paired bis tripyridylamine iron II complexes to produce the corresponding iron III species were unsuccessful. Thereby, an effort to place bidentate dipyridylamine and bi- or terdentate tripyridyl amine with respect to iron III in the spectrochemical series proved futile.

However, iron III as its chloride or bromide has been shown to form an oxybridged complex with dipyridylamine which Mossbauer data has confirmed to be unsymmetrically bridged species. Room temperature magnetic measurements gave a spin paired value of 2.2 B.M, however, Mossbauer data showed that the isomershifts corresponded to spin free iron III, thereby indicating that the low moment is due to antiferromagnetic interaction across the Fe - O - Fe bond. A yellow complex possibly a precursor of this oxybridged species has been isolated. Iron III as the thiocyanate formed a spin-free violet black complex of stoichiometry $FeL_{1.5}(SCN)_3$. Ion exchange studies excluded the presence of $[Fe(SCN)_6]^{3-}$ species and Mossbauer data showed the presence of two definite iron sites. Tripyridylamine reacted with iron III as its chloride to form a bright yellow 1:1 complex of stoichiometry $FeLCl_3$. The thiocyanate formed a spin free compound with bidentate tripyridylamine. Stoichiometry $Fe\ L_{1.5}(SCN)_3$. Once again ion exchange studies excluded the presence of hexathiocyanato ferrate III species. Mossbauer data show that iron III was in an unsymmetrical environment. Iron II as the thiocyanate formed a brick-red complex of stoichiometry $FeL\ (SCN)_2$ with terdentate tripyridylamine. Room temperature magnetic measurements gave a moment of 3.74 B.M per iron atom. Mossbauer data showed a singlet with isomer shift corresponding spin paired iron II. Low temperature measurements will reveal the presence of a spin free species too. The reactions of 4 methyl and 5 methyl substituted tripyridylamines with iron III and iron II were found to be similar to those of tripyridylamine itself.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. W.R.McWhinnie for his interest, guidance and encouragement throughout this work and to Dr. G.B. Briscoe for setting up the Mossbauer spectrometer.

My thanks are also due to Dr. G. Cox of the Polytechnic, Wolverhampton for the facility to use the variable temperature Gouy equipment and to the University of Aston in Birmingham for the postgraduate studentship without which this work would not have been possible.

Finally, I wish to thank my husband and children for their encouragement and sacrifices.

Fernandopulle

M.E. Fernandopulle.

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CHAPTER 1.

GENERAL INTRODUCTION.

Current trends in the development of coordination chemistry indicates without any doubt, that the effective study of complex compounds requires a working knowledge of a variety of physical methods. The work covered in this thesis is an attempt to use some of the well known physical techniques and correlate the results obtained from them in the difficult task of structural diagnosis.

Electronic Absorption Spectroscopy:

The visible and ultraviolet spectra of inorganic complexes provide the experimental basis of the application of the crystal field theory. This has proved a very powerful tool in the solution of structural problems.

An electronic spectrum consists of absorption bands at definite wavelengths. Detailed information is obtainable from such a spectrum if the observed absorptions are assigned to specific transitions within the molecule and these transition energies calculated in terms of the crystal field splitting energy Δ (10Dq)[1] and the Racah interelectronic repulsion parameter B[2]. The assignments of these transitions necessarily leads to some knowledge of the stereochemistry of the complex. The variation of Dq and B with the metal or ligand gives rise to the spectrochemical[3] and nephelauxetic series[4].

The spectrochemical series is the arrangement of ligands in order of magnitude of their crystal field splitting parameter Δ. The more common nitrogen donor ligands are placed in the following order.

$Py \backsim NH_3 < en < dipyam < bipy < phen < tripyam < NO_2^- \lll CN^-$

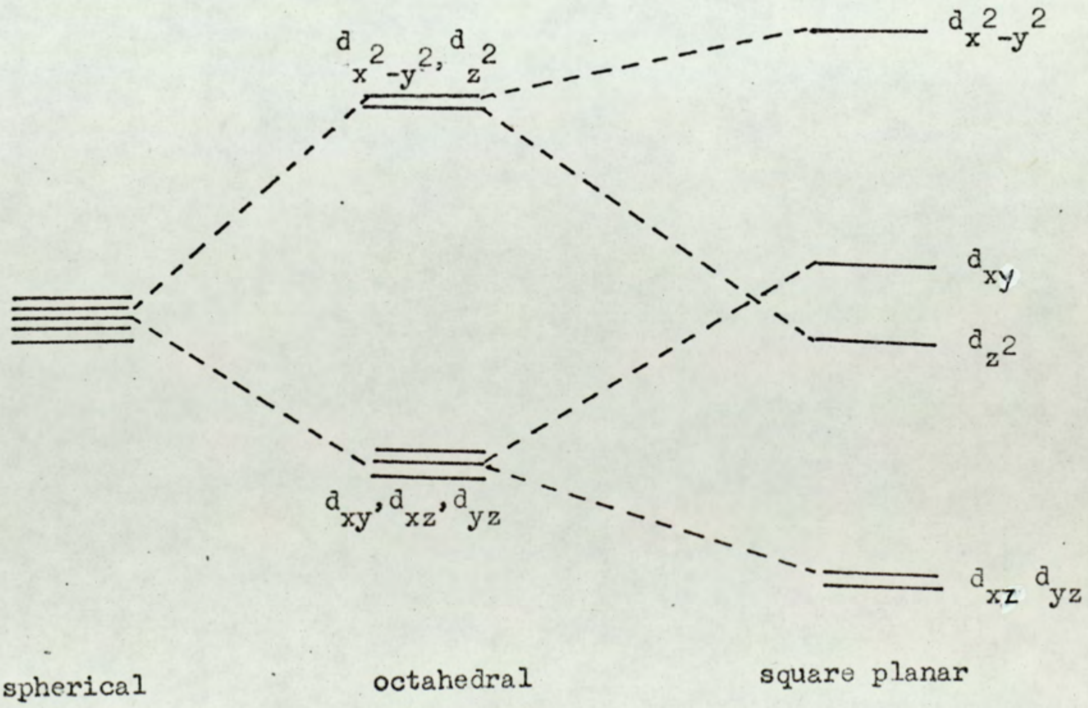
(py-pyridine, en-thylene diamine, dipyam-di- 2 - pyridylamine, bipy - 2.2 bipyridyl, phen - 1 10 phenanthroline, tripyam-tri-2 pyridylamine).

The ligands above dipyridylamine are of the strong field type and cause spin pairing in the iron II complexes.

The magnitude of Dq is determined by a number of factors: interactions from an electrostatic perturbation, the metal-ligand 6 bond, the metal-ligand π bond, the ligand-metal π bond and metal electron - ligand electron repulsions. A measure of Dq can thus provide information about the chemical bonding within the molecule.

The nephelauxetic series[4] (cloud expanding series) is the arrangement of ligands according to the covalent tendencies with respect to bond formation. The ratio of the Racahvalues for the complex B' and the free ion B, $\beta = B'/B$ is used as the index of covalent power.

$F^- > H_2O > urea > NH_3 > en > NCS^- > Cl^- \backsim CN^- > Br^-$



Since octahedral, square planar and tetrahedral fields cause different splitting of the five d-orbitals, geometry has a pronounced effect upon the d-d transitions in complex compounds. Spectral data for these transitions thus provide information about their structure.[5]

Infra red Spectroscopy.

Molecular vibrations are detected and measured either in an infra red or Raman spectrum. The fact that functional groups can be identified by their characteristic vibrational frequencies has made infra red spectroscopy the simplest and most rapid means of assigning a compound to its class. In the field of co-ordination chemistry infra red spectroscopy has aided in the problems of structure determination, cis-trans isomerism, metal ligand site attachment and in determining bond types in these complexes.

Structural isomerism arising in the complex nitropentammine cobalt III $[Co(NH_3)_5(ONO)]^{2+}$ and nitrito pentammine cobalt III $[Co(NH_3)_5(ONO)]^{2+}$ has been resolved by the use of infra red spectral data. The peaks due to the nitrito group (ONO) at 1460 and 1065cm^{-1} decreased in intensity with the growth of peaks at 1430, 1315 and 825cm^{-1} due to the nitro group[6]. After isomerisation only the peaks due to the nitro group are present.

This technique has very elegantly resolved the site of attachment of bifunctional groups. The thiocyanate ligand can be attached to the metal in three ways, i.e. through the sulphur atom M-SCN (thiocyanato), through the nitrogen atom M-NCS (isothiocyanato)[7], or it can act as a bridging group M-SCN-M[8]. Nyholm[7] studied the C-S vibrations of a large number of compounds and has indicated that when the bonding is through the sulphur atom the C-S frequency is in the range 690 - 720 cm^{-1} and if the bonding is via the nitrogen atom the C-S frequency is in the range 780-860cm^{-1}. Chatt and Duncanson[8] studied the infra red spectra of several thiocyanates of platinum II and palladium II and found that the absorption of the $C \equiv N$ frequency of the bridging thiocyanates are in the range 2150 - 2182cm^{-1}. The existence of three linkage isomers of the copper II tri-2-pyridylamine thiocyanate complex has been proved using infra red spectral evidence supported by electronic absorption data[9] viz.

[Cu (tripyam)NCS)$_2$], [Cu (tripyam) (SCN)(NCS)]

and

[Cu (tripyam) (SCN)$_2$]

Cis and trans isomerism in co-ordination compounds has been distinguished using infra red spectroscopy. This has been achieved on the basis that as the trans complex has a centre of symmetry which is not present in the cis complex, the infra red spectrum of the trans is expected to be much simpler than that of the cis. The cis and trans isomers of a number of cobalt III thiocyanates[10] and cobalt III bis ethylene diamine[11] complexes have been distinguished by their spectra.

Infra red spectroscopy has proved very useful in differentiating an ionic bond and a covalent bond in a complex, particularly in the case of nitrates[12], carbonates[13], sulphates[14], perchlorates[15] and iodates[16]. The symmetry of the ions is lowered considerably on co-ordination that the spectrum of the co-ordinated ion is usually more complex than that of the free ions. The free nitrate ion possesses the point group D_{3h} symmetry which on co-ordination through an oxygen atom is lowered to C_{2V}. This lowering of symmetry changes the NO bond orders and consequently the spectrum becomes richer. The free nitrate ions absorbs at 835, 720 and 1390cm^{-1} while the co-ordinated ion absorbs at 1253 - 1290, 1480 - 1530, 970 - 1034 and 780-800, 739 and 713cm^{-1} 17.

The far infra red region of the spectrum 600 - 200cm^{-1} is of great importance in co-ordination chemistry since fundamental modes which involve vibrations of the metal-ligand bond are expected in this frequency region. There has been a lot of controversy in the assignments of the metal-nitrogen bond frequencies of the diamine complexes, however, Nakamoto[18] recently established the assignment of metal-nitrogen vibrations for tris bipyridyl and phenanthroline complexes of Fe II, Ni II and Zn II. Fe-N vibrations in the region 380 - 360cm^{-1}, Ni-N 300 - 240cm^{-1} andZn-N- 240 - 175cm^{-1}. The metal halogen stretching frequencies have been generally established. Very recently, the far infra red spectral data was used to establish the spin crossover of bis (tri - 2 - pyridylamine) cobalt II perchlorate from a spin free environment at room temperature to a spin paired state at liquid nitrogen temperature 19.
The infra red spectrum has been shown to change drastically on cooling with the spectrum at low temperature resembling that of the spin paired bis iron II complex.

Conductivity Measurements.

Conductivity data have been utilized for the interpretation of possible structures in co-ordination compounds since Werner's time[20]. The original use of water as a conductivity solvent has been extended by organic solvents because of problems of hydrolysis and solubility difficulties. An ideal solvent for conductivity determination of the complexes should have a high dielectric constant, low viscosity, low specific conductivity, convenient method of purification and low donor capacity towards metal ions. On this basis acetonitrile, nitromethane and methanol are considered good solvents[21].

However, the co-ordinating power of acetonitrile and its dissociative and solvolyic effects has paved the way for nitromethane to become the most widely used solvent for the determination of molar conductivities of co-ordination compounds. Nitromethane as a solvent gives relatively high conductivity values for a given electrolye, it is easily purified and has a relatively low donor capacity towards metal ions.

Acceptable Λ_M ranges (molar conductivities) for complexes of various electrolytes in nitromethane at concentration of 10^{-3}M are

1:1	75 - 95	ohm^{-1}	cm^{2}	mole^{-1}
1:2	150 - 180	ohm^{-1}	cm^{2}	mole^{-1}
1:3	220 - 260	ohm^{-1}	cm^{2}	mole^{-1}
1:4	290 - 330	ohm^{-1}	cm^{2}	mole^{-1}

Instead of the usual single measurement, the most accurate method is to measure the conductivity over a concentration range. This allows identification of dissociative effects and differences in electrolyte strength[22].

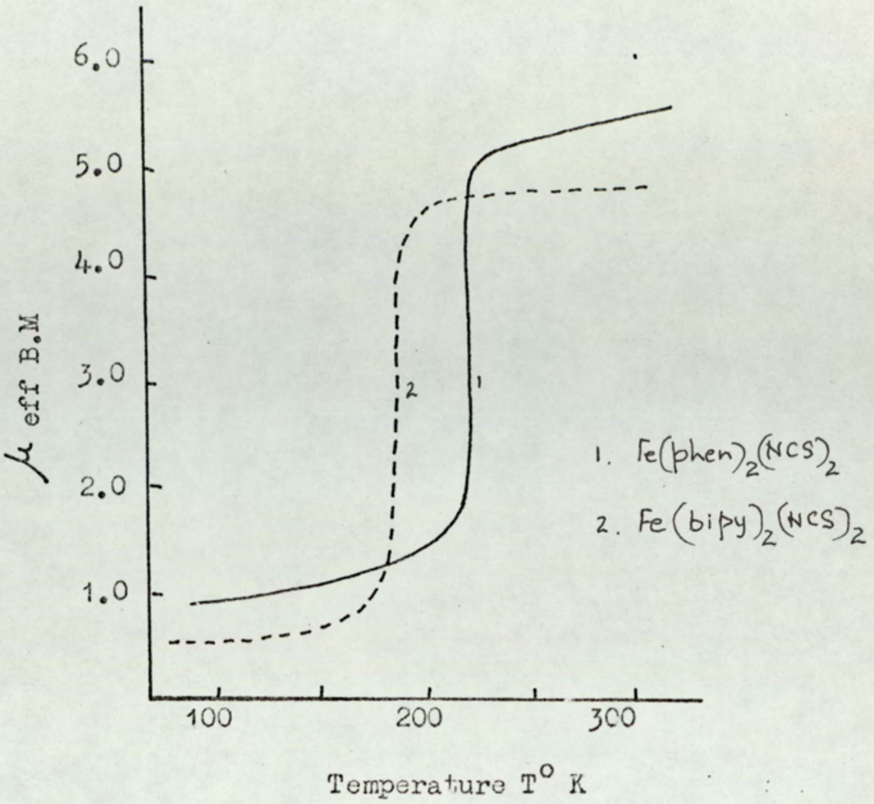
Magnetic Measurements.

The important aspects of magneto chemistry are concerned with the effects arising from incomplete shells of electrons. This condition is fulfilled by the complex compounds of the transitional elements. The spin and orbital angular momentum of unpaired electrons give rise to the phenomenon of paramagnetism and its extensions ferromagnetism and antiferromagnetism. In most coordinations compounds the metal ions which give rise to the paramagnetic effect are kept separated from each other by the ligand molecules which are magnetically inert, so that interactions between electrons of the metal atoms which result in ferromagnetism and antiferromagnetism are greatly reduced. These compounds are said to be magnetically dilute[23].

Magnetic susceptibility measurements of inorganic complexes enables one to correlate valency, bond type and stereochemistry of the metal atom, provided the number of unpaired electrons can be deduced from the magnetic moment.

The valency of the metal atom can usually be inferred from the value of the magnetic moment, e.g. iron III and iron II. These values can then be used to distinguish the type of bonding in the metal complexes. Spin free iron II has 4 unpaired electrons and has a moment 4.9 - 5.5 BM, while spin paired iron II is diamagnetic with no unpaired electrons and it's effective magnetic moment is 0.0. B.M. A few compounds of iron II are known to exist with intermediate spin ($S = 1$) state but these are the exceptions. Iron III compounds usually exhibit a sextet $^6A_1$ or a doublet $^2T_2$ ground state depending on the strength of the crystal field. The $^6A_1$ state with five inpaired electrons usually has a moment of 5.4 - 5.9 B.M. and the doublet $^2T_2$ ground state with one unpaired electron has a moment 2.0 - 2.4 B.M.[23] The sextet and doublet ground states are generally associated with octrahedral or tetrahedral stereochemistry. However the favoured ground state of the five co-ordinate square pyramidal complexes such as chlorobis N.N dialkyl dithio-carbonate iron III and N.N ethylene bis salicylidene iminato nitrosyl iron III is the quartet $^4A_1$ state [24 25]. These compounds have a magnetic moment of 3.9 B.M.

A study of the variation of magnetic moment with temperature has proved very useful in establishing the existence of spin isomerism in a large number of complexes [19.26.30.].



The stereochemistry of an atom could be inferred from a knowledge of the bond type and the co-ordination number as the orbitals used for bond formation generally determine the stereochemistry of the complex ion. The size of the orbital contribution to the magnetic moment also yields information about the sterochemistry of the complex ion, e.g. tetrahedral complexes of cobalt II have a moment closer to the spin only value than that of the octahedral complexes.

$Hg[Co(CNS)_4]$ μ eff = 4.33 BM

$[Co(NH_3)_6](ClO_4)_2$ μ eff = 5.04 BM

Mössbauer Spectroscopy.

The Mossbauer effect is the recoilless emission and resonance absorption of low energy radiation[32]. The application of Mössbauer spectroscopy to chemistry is a consequence of the fact that the position and structure of the resonance lines depend on the state of bonding of the atom.

There are three main types of interaction of the nuclei with the chemical environment which result in changes in the energy required for absorption. They are (1) isomer shift, (2) quadrupole interaction, (3) magnetic interaction.[34]

The nuclear isomer shift is the displacement from zero velocity of the centroid of the Mossbauer resonance spectrum. This is caused by the interaction of the electron density at the nucleus with the positive nuclear charge.

Isomer shift δ

$$\delta = \frac{4\pi}{5} Ze^2 r^2 \quad \frac{\delta r}{r} \left[\psi^2_{abs} (0) - \psi^2_{source} (0) \right]$$

Ze-charge on the nucleus.

$\psi^2 (0)$ electronic density at the nucleus

$$r = r_{ex} - r_{gr}$$

$$= \text{const } \delta r / r. \ \delta \left| \psi_s \ (0) \right|^2$$

Where $\delta \left| \psi_s (0) \right|^2$ is the change in s electron density at the nucleus in going from the source to the absorber. In the case of iron $\frac{\delta r}{r}$ is negative and therefore a decrease in s electron density at the nucleus results in an increase in isomer shift and an increase in s electron density causes a negative isomer shift.

The isomer shift of high spin iron II (d^6) compounds is larger than that of high spin iron III (d^5) compounds, as the 3s electrons of iron II are screened to a greater extent by the additional 3d electron.

However, for low spin iron complexes which have empty orbitals on the ligands, the isomer shift tends to be independent of the oxidation state [35]. The π back bonding deshields the nucleus by withdrawing 3d electrons and thereby increasing the s electron density at the iron nucleus. The stronger the π bonding ability of the ligand the higher the s electron density at the nucleus and the smaller the chemical shift.

$$CN^- < CO < NO^+.$$

The outer orbital expansion of the iron atom by the nephelauxetic effect would also cause a deshielding of the s electrons increasing the s electron density and thereby reducing the isomer shift. A correlation between the isomer shift and the nephelauxetic effect has been proposed by Danon[36].

The quadrupole splitting ΔE of the Mossbauer spectrum arises as a result of the interaction of the electric quadrupole moment of the nucleus with the electric field gradient at the nucleus.

$$\Delta E = \frac{1}{2} e^2 q Q \left(1 + \frac{\eta^2}{3}\right) \frac{1}{2}$$

eq - electric field gradient; η - asymmetry parameter.

The quadrupole splitting yields only the absolute value of the product of the nuclear moment and the field gradient not its sign. The field gradient around the nucleus depends on the electronic configuration of the nucleus and on its environment. Information about the nature of the chemical bond and of the crystal lattice is obtainable from quadrupole splitting data.

The determination of the sign of the electric field gradient is of interest since it can be correlated with the electronic structure of the molecule. Collins[37] showed that the application of a strong magnetic field will perturb the quadrupole split levels and the sign of e^2qQ can then be determined.

Quadrupole splitting is directly related to the point symmetry of the local environment of the metal atom. Thus low spin iron II complexes with $(t_{2g})^6$ configuration in a symmetrical environment will have no electric field gradient.

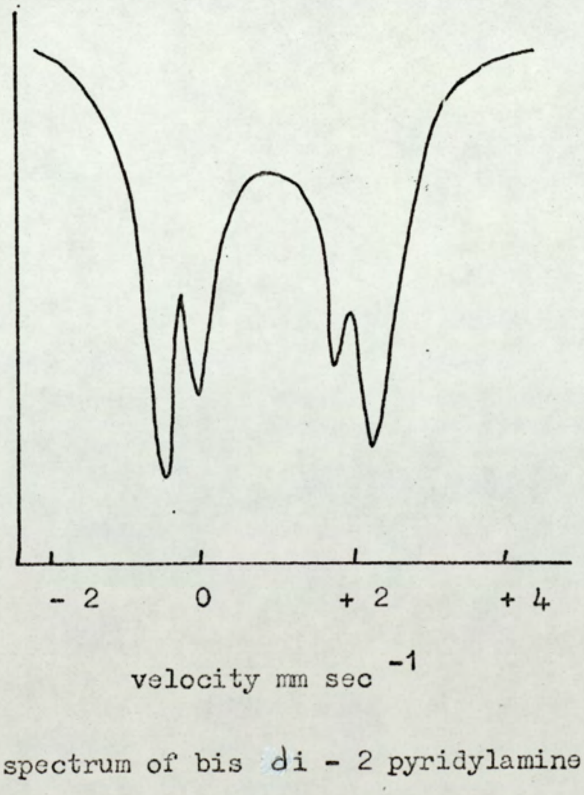
The Mossbauer spectrum of such a compound in a cubic or near cubic environment will be a single absorption without any quadrupole splitting, e.g. Bis (tri-2-pyridylamine) iron II perchlorate[38]. High spin ferrous compounds however, have $(t_{2g})^4$ $(e_g)^2$ configuration which is one electron outside the symmetrically half filled $(t_{2g})^3 (e_g)^2$ d levels. The occupation of the t_{2g} level by the additional electron creates a large electric field gradient which gives rise to a pronounced quadrupole splitting e.g. Tris (di -2- pyridylamine) iron II perchlorate[38]. Quadrupole splitting data could thus be used to distinguish between spin paired and spin free iron II compounds.

In low spin iron II complexes distortions from cubic symmetry results in quadrupole splitting. The Mossbauer spectrum of sodium ferrocyanide has no quadrupole splitting, being spin paired in an octahedral environment $[Fe(CN)_6]^{4-}$. However, when one of the cyanide ligands is replaced by nitrosyl $[Fe(CN)_5NO]^{2-}$ the spectrum is a very well resolved quadrupole doublet. The substitution of cyanide by nitrosyl distorts the octahedral symmetry and gives rise to a large electric field gradient due to π delocalisation of the metal electrons into antibonding orbitals of the nitrosyl group[35].

Spin paired iron III compounds (t_{2g}^5) show a well resolved quadrupole spitting due mainly to the electric field gradient generated by the unpaired 3d electron. Asymmetry of the co-ordination sphere about the iron atom will also contribute to the quadrupole splitting e.g. tris (2.2 bipyridyl) iron III perchlorate[39].

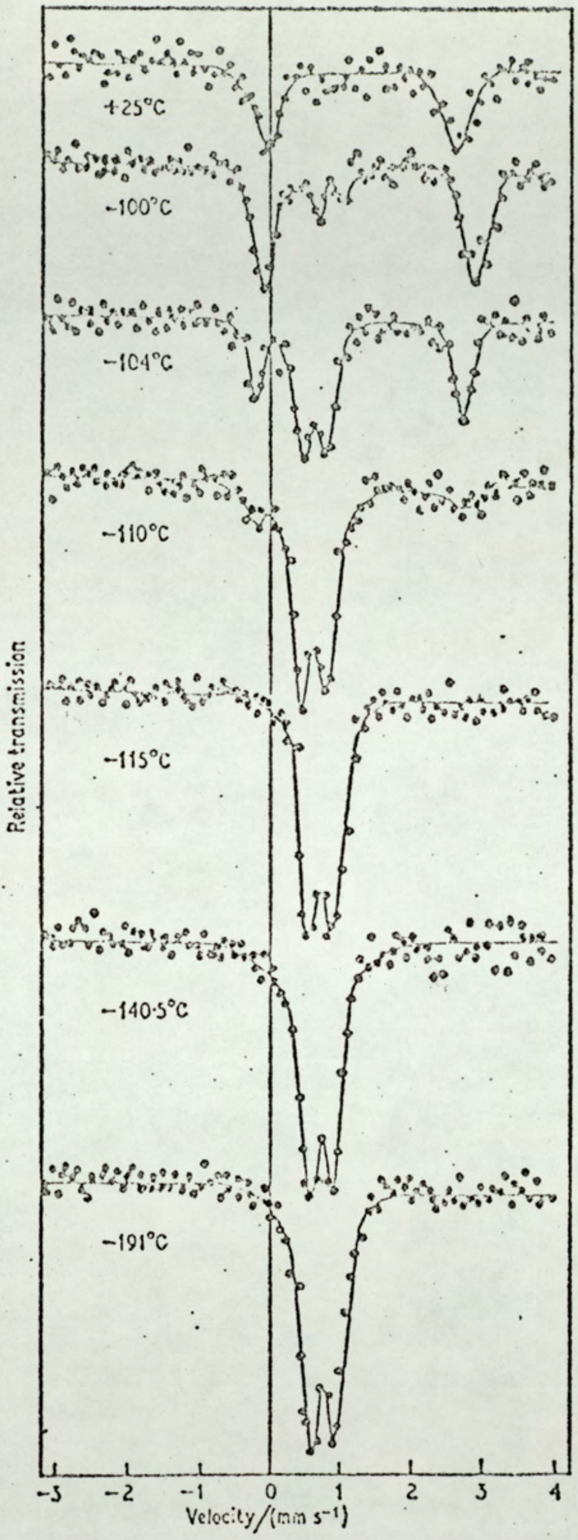
High spin iron III compounds have a symmetrically filled $(t_{2g})^3(e_g)^2$ configuration, thus the valence contribution to the electric field gradient is zero, hence the spectrum of of hexachloroferrate III[39] is a singlet with no quadrupole splitting. However, the binuclear complex monophenanthroline trichloro ferrate III[39] shows an appreciable quadrupole splitting caused by the electric field gradient arising from the co-ordination asymmetry due to differences in electronegativity between the ligand atoms around the iron atom.

The application of quadrupole splitting data to determine the site of the iron atom is well illustrated in the spectrum of bis (di -2- pyridylamine) dithiocyanato iron II[40]. The Mossbauer spectrum consists of two pairs of lines both indicating isomer shifts consistent with spin free iron II. This is in agreement with the presence of two definite iron sites in the compound.



Mossbauer spectrum of bis di - 2 pyridylamine dithiocyanato iron II[40].

McWhinnie[38] found that tri -2- pyridylamine reacted with ferrous chloride giving a complex of stoichiometry [Fe (tripyam) Cl_2]. The magnetic moment of this compound was 3.54 B.M. being



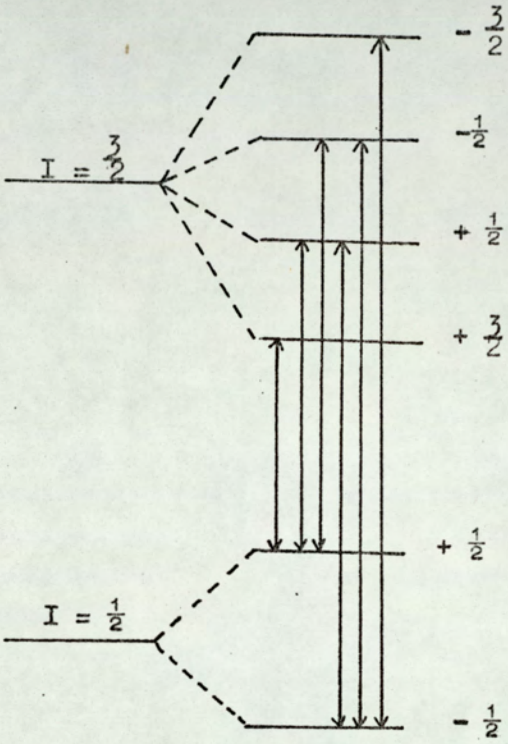
The Mössbauer spectrum of Fe(phen)$_2$(NCS)$_2$ as a function of temperature.

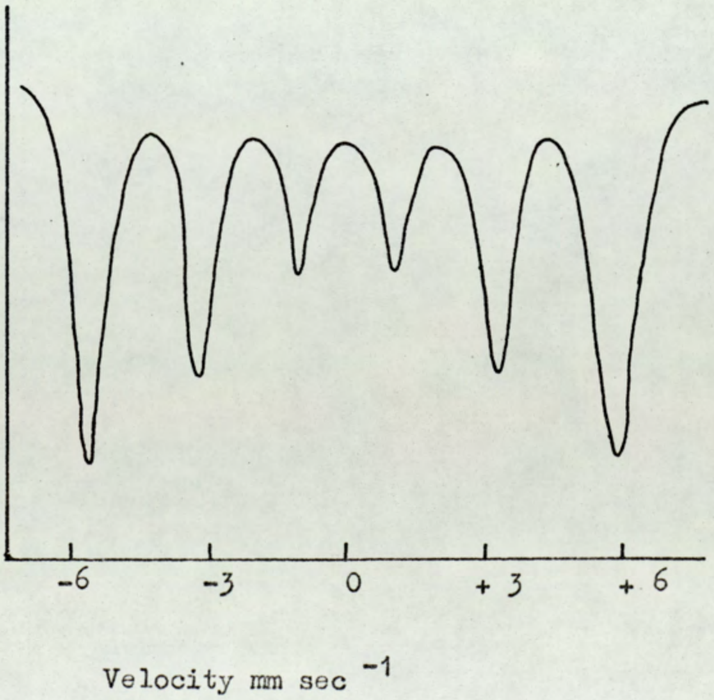
between a spin paired and spin free moment of iron II. The Mossbauer spectrum at room temperature was a sharp singlet without any quadrupole splitting. This is consistent with spin paired iron II in a perfect octahedral symmetry. However, the Mossbauer spectrum at 77° K consisted of a singlet (as seen in the room temperature spectrum) together with a well resolved quadrupole doublet. The isomer shift of the doublet was consistent with the presence of spin free iron II. By correlation of data obtained by other physical techniques this compound was shown to be bis (tri -2- pyridylamine) iron II tetra chloro ferrate II.

Mossbauer spectroscopy has helped to establish the occurence of high spin - low spin equilibria in some iron II [26.28] and iron III [29.30] complexes. The room temperature spectrum of bis 1:10 phenanthroline dithiocyanato iron II complex has an isomer shift and quadrupole splitting typical of high spin iron II complexes[27]. This is in agreement with the room temperature magnetic moment of the compound μeff = 5.2 B.M. However below 174° K both isomer shift and quadrupole splitting change to values consistent with low spin iron II (Fig. 1.1), in agreement with the corresponding magnetic data, indicating a change from $^5T_2 \longrightarrow {}^1A_1$ state. Similar behaviour is reported for the analogous 2.2′ bipyridyl complex[28]. Very recently Fitzsimmons et. al.[30] showed that the Mossbauer data obtained for some iron III complexes were in agreement with the existence of spin isomerism between $^6A_1$ and $^2T_1$ states confirming the deductions from paramagnetic susceptibility measurements. These spectra were more complex due to the presence of a genuine thermal equilibrium and the relative population of the two states as a function of temperature was very evident.

Mossbauer spectroscopy has also been used to establish the presence of cis and trans isomers in co-ordination compounds[41.43.] The relative magnitude of quadrupole splittings has been the basis of distinguishing these isomers.

Magnetic splitting.





The magnetic field produced by the crystal field and the electron shell around the nucleus splits the excited state of ^{57}Fe into four energy levels and the ground state to two levels. The selection rules permit six transitions and this results in six resonance lines in the Mossbauer spectrum [44].

CHAPTER II.

EXPERIMENTAL

Chemicals.

All chemicals were obtained from commercial sources and Analar grades were used where ever possible.

Solvents.

All solvents were obtained from commercial sources and were purified where necessary by literature methods e.g. nitromethane[45] acetonitrile and dimethyl formamide[47].

Analysis.

Microanalytical data for carbon, hydrogen and nitrogen were obtained from :

(a) Analytical Laboratory Department of Chemistry
University of Reading

(b) Analytical Laboratory Department of Chemistry
University of Aston in Birmingham.

Iron was determined by atomic absorption spectroscopy using analar iron metal dissolved in the minimum volume of concentrated nitric acid as stock solution. The calibration graph was obtained by appropriate dilution of this stock solution to the working range 5 - 25 μg Fe/ml [48].

Halides were determined gravimetrically as the silver salt after decomposition of the complex by fusion with sodium carbonate.

Conductivity.

Molar conductivities were measured with a Henelec conductivity bridge using a standard conductivity cell of type E 7591/B and cell constant 1.33. Measurements were made for 10^{-3} M solutions.

Magnetic Susceptibility Measurements.

Paramagnetic susceptibilities were measured by the Gouy method at room temperature. The balance was a semi-micro type of Stantons Instruments Ltd. which was used in conjunction with an electromagnet. A current of 10 amps was used for all measurements. The height to which the tube should be packed was determined by packing the tube to different heights using $Hg\left[Co\, CNS)_4\right]$ and plotting a graph of pull on the sample vs length of the packing. The plateau of the graph was reached at a height of 9 • 5 cms. In all subsequent determinations the tube was packed to a height of 10.5 cms. The tube constants α and β were determined using $Hg\left[Co\,(CNS)_4\right]$ as calibrant taking $\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 20° C.

Magnetic susceptibilities were calculated using the equation

$$10^6 \chi = \frac{\alpha + \beta F'}{W}$$

$\alpha = 0.015$; $\beta = 0.265$; F' = force on the sample

w = weight of the sample

Diamagnetic corrections were made from Pascals Constants as listed by Figgis and Lewis[23].

Infra red spectra

The infra red spectra were recorded using Perkin Elmer 237, 457 and 225 spectro photo meters. Nujol and fluorochemical mulls and KBr discs for solids and liquid films for oils over the range 4000 - 200 cm^{-1}.

Electronic spectra.

Electronic absorption spectra in the ultra violet and visible region were obtained in Unicam Sp 700 and Sp 800 instruments using matched silica cells.

The diffused reflectance spectra were obtained using the SP 735 diffuse reflectance attachment. Magnesium oxide was used as the reference and also as a diluent wherever necessary.

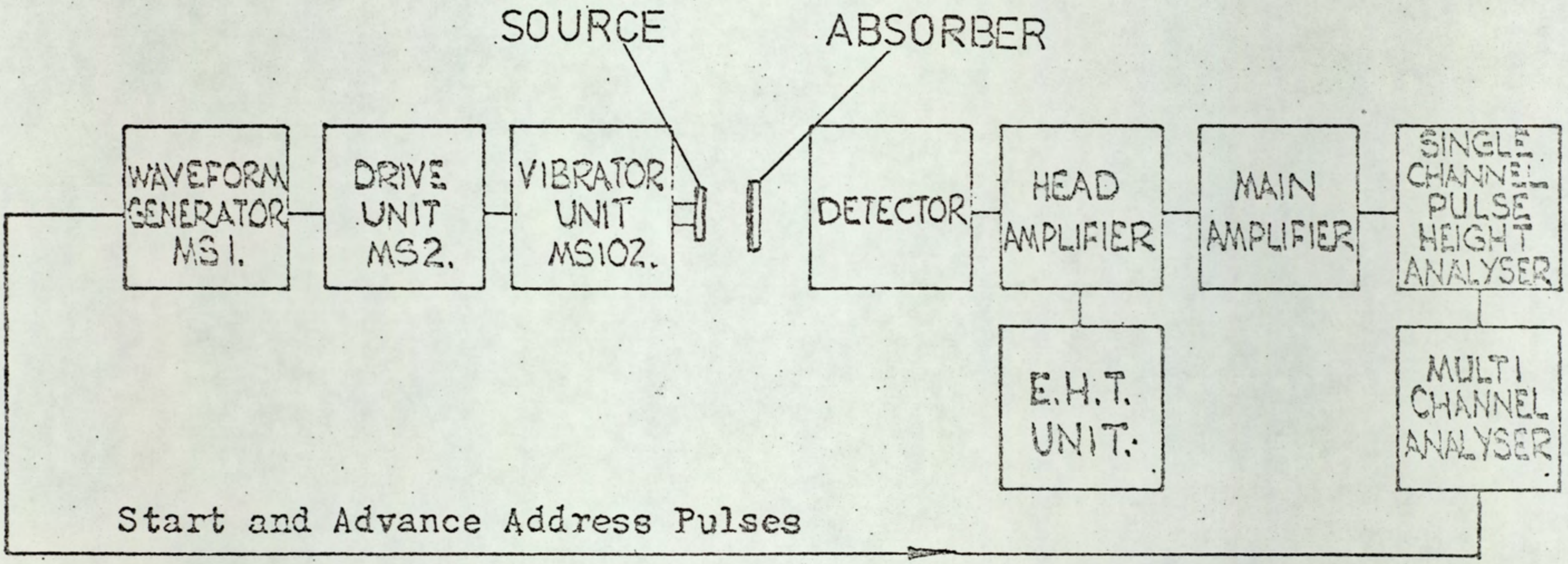
X - ray powder photographs.

X - ray powder photographs were obtained using Cu $k\alpha$ radiation with nickel filters, λ = 1-54 A°. An exposure time 2 - 3 hours was used.

Mossbauer Spectra.

The Mossbauer spectra were obtained with the Centronic Mossbauer Spectrometer. This is a constant acceleration system used in conjunction with Gamma radiation counting electronics and a multi channel analyser. The electronic units (20th Century Electronic) consists of a wave form generator, which generates the drive wave form and also provides the Start and Advance Address pulses for the control of the velocity scan in the range ± 0 - 20 cm sec^{-1}. The scan range is controlled by the velocity control. In our studies a velocity scan of ±6 mm sec^{-1} and ± 4 mm sec^{-1} (i.e. the velocity control positions 0·2 and 0·3) were used. The vibrator unit MS 2 consists of vibration generator and a velocity transducer to which is secured the source. The sample under investigation

Figure 2.1



MOSSBAUER SPECTROMETER

acts as the resonant absorber and is stationary. A Mossbauer proportional counter (Type 805/030) detects the radiation passing through the absorber and is amplified through a Preamplifier (Type NE 5287 Nuclear Enterprises) and fed into the internal amplifier and the single channel analyser of the Laben 400 Spectroscope to select the pulses due to 14.4 Kev line for iron.

The pulses from the velocity wave form generator are fed into the Multichannel Analyser (Laben 400) so that a spectrum is built up of the number of counts against source velocity (number of channels = 400). The spectrum is continuously available in graphical form on a built-in oscilloscope. The data are printed out (Automatic print out) on an electric typewriter (Olivetti 84). This was fed into the computer in the form of punched cards and a Fortran programme was used to plot counts vs channels. A Fortran least squares curve fitting programme to fit the Lorentzians was subsequently used on the University of Aston ICL 1905 E computer.

The source used was Co^{57} (25 M.C.) diffused in a palladium matrix and was obtained from Radio chemical Centre, Amersham. Calibration of the channel widths was done using the known separations of the peaks of natural iron absorber. The reference points was the peak position of stainless steel absorber and the zero point of natural iron.

Measurements were made on powdered samples mounted between perspex holders held together with sello tape.

Satisfactory spectra of natural iron with ca. 12 per cent absorption for the most intense peaks could be recorded in 3 hours (Fig. 2.2). The constancy of the peaks were checked once

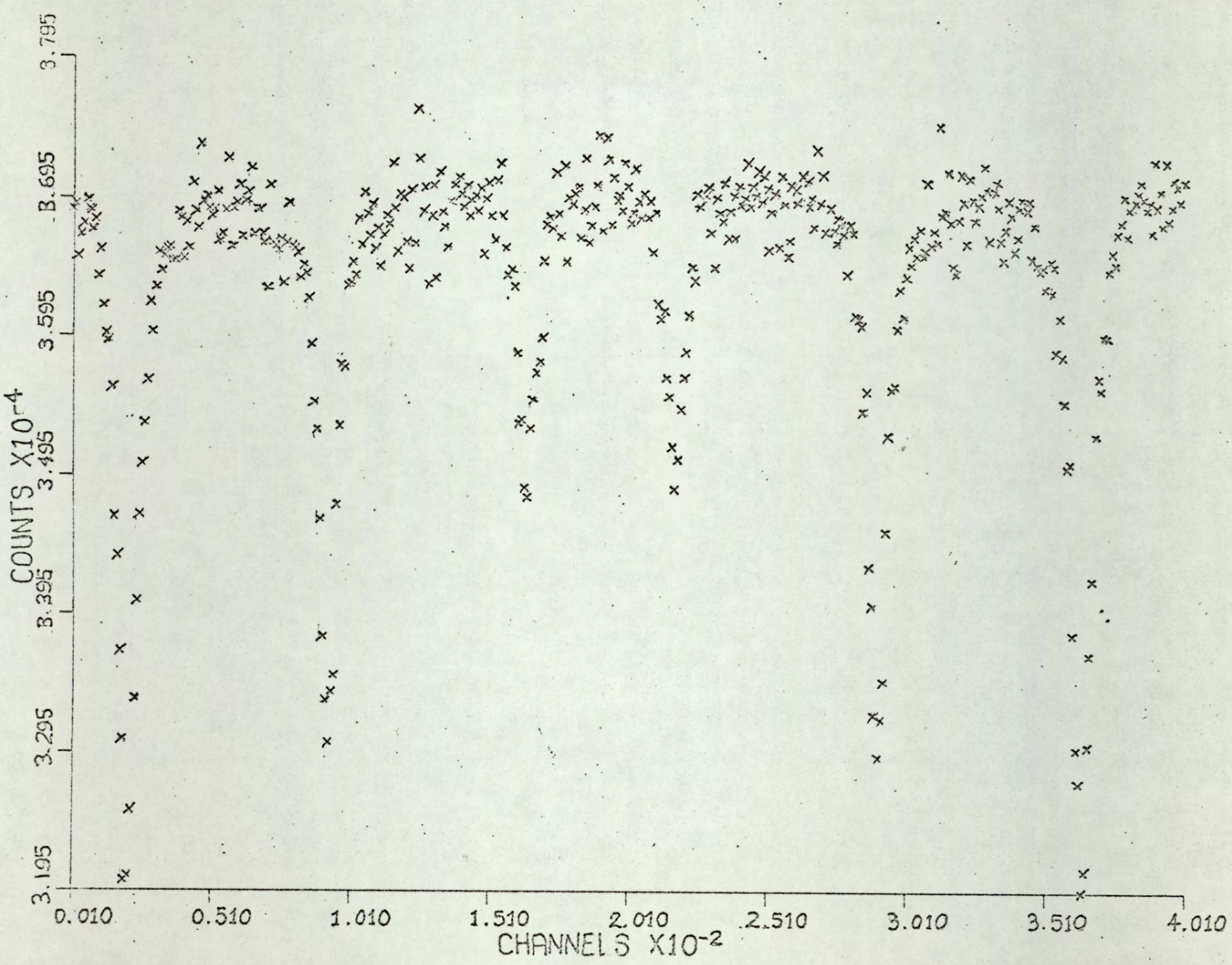


Fig. 2.2 Mossbauer spectrum of natural iron

a week with the natural iron and stainless steel absorbers. The behaviour of the spectrometer was constant over periods of weeks.

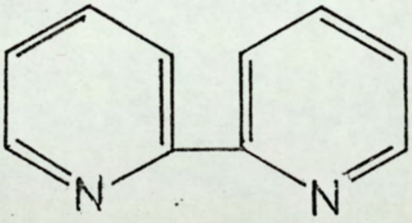
Due to unadvoidable delays it was not possible to commission the low temperature equipment.

CHAPTER III

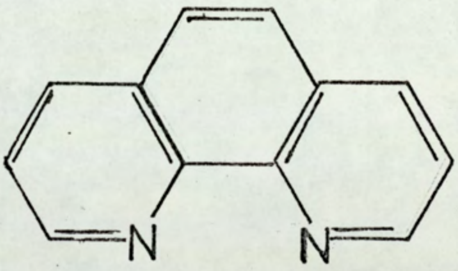
The chemistry of the tris 2 • 2 bipyridyl iron II cation in some strongly acidic media.

Introduction.

Several workers have investigated the co-ordinating ability of numerous ligands containing the $-N=\overset{|}{C}-\overset{|}{C}=N-$ grouping. The strong chelating ability of these bidentate ligands has been attributed to the delocalisation of d electrons of the transition metals into the π orbitals of the ligands. This dπ-pπ bonding is known to impart some aromatic character to the chelate ring[49]. The best known and most frequently used members of this class of ligands are 2 - 2′ bipyridyl and 1 : 10 phenanthroline. They both function as typical bidentate chelate molecules



2 . 2′ BIPYRIDYL



1:10 PHENANTHROLINE

co-ordinating through the nitrogen atoms with the formation of five membered chelate rings.

Bipyridyl and phenanthroline behave as weak bases (pk_a (bipyridyl) = 4.5 and pk_a (phenanthroline) = 4.98)[50] usually forming the monoprotonated species. The ultra violet spectrum of monoprotonated bipyridyl consists of two bands at 33,000 and 41,150 cm^{-1}. The diprotonated bipyridyl has a single band at 34,480 cm^{-1}. The two bands of monoprotonated phenanthroline are at 36,230 and 45,050 cm^{-1}. [51]

The infra red spectrum of the complexed ligand is slightly modified from that of the free ligand. The ring frequencies between 1600 - 1000 cm^{-1} tend to undergo small shifts to higher wave numbers on co-ordination to a metal atom. Also the bands characteristics of the free ligand (bipyridyl) at 995 and 759 cm^{-1} shifts to 1010 cm^{-1} and 749-739 cm^{-1}. [52]. The spectra of the cis - bis bipyridyl complexes are shown to be more complex than the trans - bis 2.2′ bipyridyl complexes in the region 700 - 800 cm^{-1}. [53]. The far infra red region of the spectrum is of great interest because vibrations of the metal to ligand bond are expected in this region. The assignment of bands due to the metal-nitrogen vibrations of the tris chelate complexes of iron, nickel and zinc has been resolved recently [18]. The Fe - N, Ni - N and Zn - N stretching bands have been assigned at 375 - 360, 300 - 240 and 240 - 175 cm^{-1} respectively.

The most widely studied compounds of the ligands are perhaps the red coloured diamagnetic tris chelate iron II cations. The absorption responsible for the characteristic deep colour is now known to be due to a Laporte allowed transition of the $t_{2g} \longrightarrow \pi^*$ type [51].

The presence of more intense charge transfer bands has complicated the study of the d$\longleftrightarrow$d transitions of the complexes of these ligands. The assignment of the $^3A_{2g} \longrightarrow {}^3T_{2g}$ (F) transition for the tris chelated nickel complex has been resolved by Robinson[54]. The lowest frequency bands correspond to the spin forbidden $^3A_{2g} \longrightarrow {}^1E(D)$ transitions. Palmer & Piper[55] confirmed this by work with single crystals of the tris chelated cations. They obtained a 10Dq value of 1280 cm^{-1} with respect to nickel II whilst the ligand field splitting parameter with respect to the iron II complex was estimated to be between 16,500 and 19,000 cm^{-1}. This substantial increase in Dq from a spin free to a spin paired environment has been attributed to a decrease in metal-ligand distance on transfer of electron density from e_g to the t_{2g} orbitals.

Apart from the very stable, bright red, spin-paired, tris chelate complexes of iron II, the mono and bis ligand chelates are also known. For the bis ligand complexes of the type FeL_2X_2 (where L is 2 . 2'bipyridyl or 1 : 10 phenanthroline) the spin state of the complex is known to be a function of X. When X = Cl, Br, I or N_3 the complexes formed are high spin, the magnetic moment being independent of temperature. When X = CN^-, NCO^- or NO_2^-, the stronger field of these ligands, the complexes formed are spin paired at room temperature[56]. However, when X = NCS^- or $NC\ Se^-$ the paramagnetic susceptibilities of these complexes show anomalous temperature dependence[57]. The room temperature moment 5 • 0 B.M and on cooling this decreases sharply at a critical temperature (which is 174° K for $Fe\ (phen)_2\ (NCS)_2$ 232°K for $Fe\ (phen)_2\ (NCSe)_2$, 216° K and 210°K for the two polymorphs of $Fe\ (bipy)_2\ (NCS)_2$) and at 77° K the moment 1 B.M indicative of a change from a spin free to a spin paired environment $^5T_{2g} \longrightarrow {}^1A_{1g}$ state [26-28]. Mossbauer spectral data confirmed this spin change unambiguously. The large quadrupole splitting at room temperature characteristic of the $^5T_{2g}$ ground state, observed for the iso thio cyanato and iso selenocyanato complexes changed on cooling to liquid nitrogen temperature to a small quadrupole split compatible with the $^1A_1$ ground state. Likewise the position of the isomer shift also changed on cooling. The values of ν CN are also known to alter on cooling [58].

The direct reaction of 2 . 2′ bipyridyl and 1 : 10 phenanthroline with solutions of iron III salts do not yield the tris chelated iron III complexes instead brown binuclear species are obtained[59]. These compounds have been the subject of much investigation [60-66]. These have now been formulated with a single oxo bridge with ν Fe - O - Fe $\sim$ 840 cm^{-1} [65]. The effective magnetic moment of these compounds is around the spin only value for one unpaired electron and this anomalous moment has been attributed to the anti ferromagnetic inter-actions between two spin free iron atoms via the oxo bridge[66]. Mossbauer spectral data has proved a very useful tool to comfirm this interpretation. The isomer shift recorded was consistent with spin free iron III and the presence of only one set of lines in the spectrum was indicative of only one iron site in the complex. This was compatible with a symmetrically bridged species[39].

The tris chelated iron III complexes were obtainable only by oxidation of the corresponding iron II complexes[67]. The temperature dependence of the magnetic moments of the tris chelated perchlorates has been attributed to the small degree of delocalization of the t_{2g} electrons onto the ligands[68]. Nyholm[67] reported that the blue tris chelated iron III bipyridyl complex turned red on long exposure to sunlight but no significance was attached to this observation at that time.

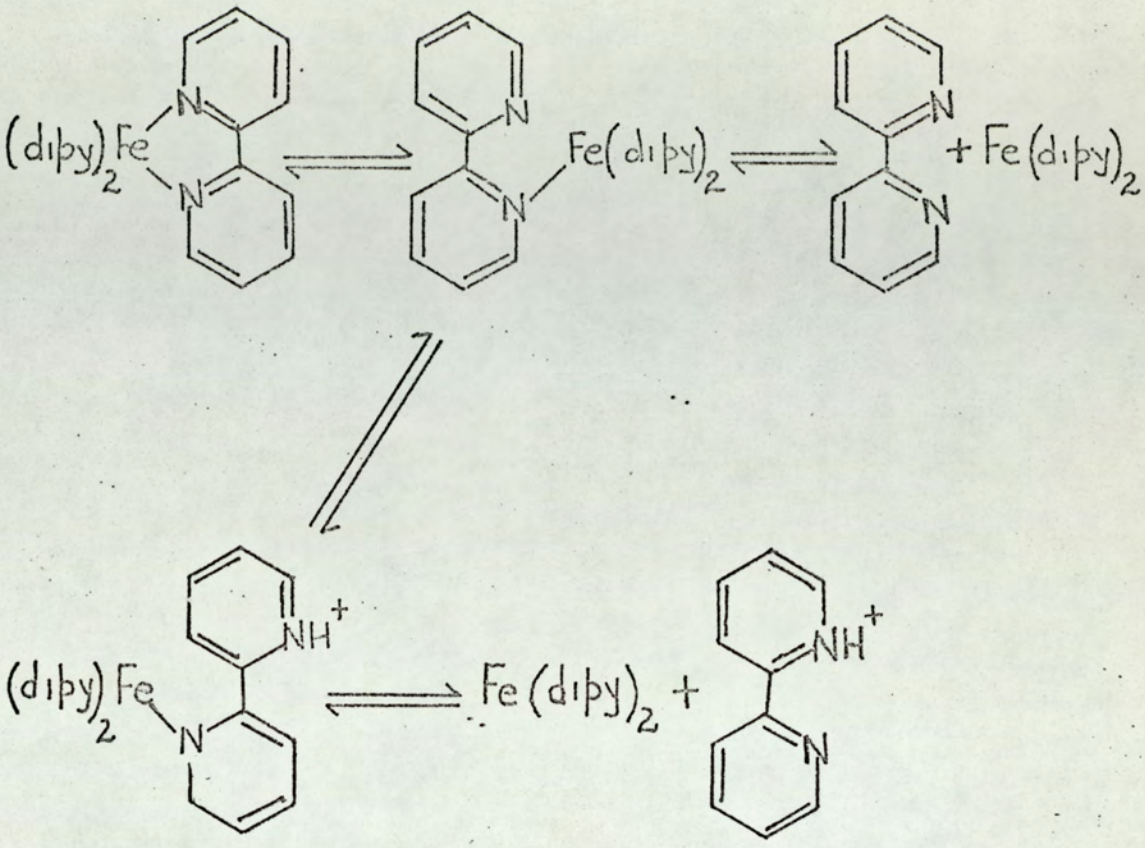
Very recently Wehry & Ward[69] have found that the tris 1 : 10 phenanthroline iron III undergoes photo reduction to the corresponding iron II species in acidic aqueous media. This reduction was found to take place only in the presence of ultra violet light. A study of the effect of acid concentration and added scavengers to trap the products indicated that water is the electron donor in the photo reduction. The quantum yield of the iron II species was found to vary from zero in 98% sulphuric acid to reach a steady maximum value at 8 · 5 M acid.

The behaviour of the tris complexes in strong acid has been investigated by several workers [70-73]. The tris iron III complexes $[Fe(bipy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ are both stable in 98% sulphuric acid where as $[Ni(phen)_3]^{2+}$ is immediately decomposed. The rate of decomposition of the iron complexes is dependent on the concentration of free water and is a bimolecular rate process[74]. The dissociation of the tris chelated phenanthroline iron II species has been shown to be acid independent but the dissociation of the corresponding bipyridyl complex is dependent on the hydrogen ion concentration. It has also been shown to vary with the type of acid used being different in perchloric than in sulphuric or hydrochloric acid. Baxendale and George[70] explained the hydrogen ion dependence on the basis of the formation of a protonated intermediate.

$$[Fe(bipy)_3]^{2+} + H^+ \rightleftharpoons [Fe(bipy)_3H]^{3+}$$

They suggested that $[Fe(bipy)_3]^{2+}$ reacts more slowly than $[Fe(bipy)_3H]^{3+}$ and that a limiting rate is reached at high acid concentrations.

Basolo et. al[72] however, explain this on the basis of the greater flexebility of the ligand allowing one co-ordinated nitrogen to dissociate while leaving the other intact.



Mechanisms based on either postulate will satisfy the H^+ dependence of the dissociation of $[\text{Fe (bipy)}_3]^{2+}$.

Healy and Murmann[73] obtained evidence for the existence of protonated species in acid solution. The formation of these species was found to be accompanied by changes in spectra and magnetic susceptibilities which were reversible on dilution. They demonstrated that the dissolution of the deep red tris chelated iron II species in concentrated perchloric acid resulted in a slow reaction yielding a pale blue solution. The absorption spectrum of this solution indicated that the absorption maximum changed from 522 n.m (red solution) to 620 n.m. (blue solution) and the molar extinction co-efficient reduced from 8,700 to 15. This change in colour was accompanied by a change in magnetic moment, the blue solution was found to be paramagnetic with μeff = 5 · 2 B.M. Dilution of this pale blue solution with dilute acid regenerated the familiar red colour of the tris chelated complex but only partially.

The mono and bis 2 . 2′ bipyridyl complexes as prepared by Basolo and Dwyer[75] were found to be decomposed in strong acid but a transient pink colour together with the infra red spectrum of the solids suggested contamination with the tris complexes. Hence the iron II species derived from the tris bipyridyl iron II complex in strong acid is probably not the mono or bis bipyridine complex.

Healy and Murmann[76] extended these investigations to the 2 - pyridinal alkylimine complexes which are structurally similar to the tris (2 · 2′ bipyridyl) iron II. The tris (2 - pyridinal propylimine) iron II complex parallels the kinetic behaviour of tris (2 · 2′ bipyridyl) iron II. The dissociation shows acid dependence but does not reach a limiting rate. Salt effects and behaviour in strong acids are similar to the 2 · 2′ bipyridine complex. It is not necessary to include a term for the hydrolysis of the Schiff base in the intermediate which would have been expected if the mechanism involved Basolo's half-bonded structure. The following mechanism is proposed for the dissociation of the tris -2- pyridinal -n- propylimine iron II complex involving a protonated form of the cation and some degree of dissociation to Fe $^{2+}$.

$$[\mathrm{Fe\ L_3}]^{2+} \xrightleftharpoons{\text{fast}} [\mathrm{Fe\ L_3\ H}]^{3+} \rightleftharpoons [\mathrm{Fe\ L_3\ H_2}]^{4+}$$

$$\longrightarrow [\mathrm{Fe\ L_2}]^{2+} + \mathrm{L} + 2\mathrm{H}^{+}$$

However, the following assumptions are made (a) the initial equilibrium is attained rapidly (b) the molar absorbancies of $[\mathrm{Fe\ L_3}]^{2+}$ and $[\mathrm{FeL_3H}]^{3+}$ are essentially identical (c) the steady state approximation can be applied to $[\mathrm{FeL_3H_2}]^{4+}$ and (d) the spin free complex formed in strong acid is not kinetically important at low acidities.

The only evidence for protonated bipyridyl $[Fe(bipy)_3H]^{3+}$ at low acidities is derived from solubility studies with $[Fe(bipy)_3](ClO_4)_2 \cdot 2H_2O$. The solubility decreases in the pH range 2 - 3 but this may be explained by several other phenomena. The evidence for protonated tris (2 - pyridinal -n- propylimine) iron II is more convincing. On the basis of increased stability in strong acid and steric considerations it is doubtful that the interaction is localized around the individual nitrogen atoms. Interactions with the aromatic part of the ligand is more probable. The change in magnetic susceptibility and thereby the spectral changes may be explained by involving either the protonated form or the half bonded intermediate.

It was of interest to make a systematic study of the behaviour of the tris (2 . 2' bipyridyl) iron II complex in some strong acid media so that a more plausible explanation could be found for the reversible changes in spectra and magnetic susceptibility as observed by Healy and Murmann[73].

Experimental.

The Mossbauer spectrum of di nitrato bis (2. 2' bipyridyl) iron III perchlorate at 77° K was recorded using a $Pd/^{57}Co$ source by P.C.M.U. Harwell.

Magnetic Measurements of solutions of tris (2. 2' bipyridyl) iron II perchlorate, tris (2. 2' bipyridyl) iron III perchlorate in concentrated nitric acid were made by the Gouy method using nickel chloride solutions as the calibrant[23].

χ for a 6.93% nickel chloride solution was calculated given

$$10^6 \chi = (10{,}030/T)\ (y/100) - 0.72\ (1 - y/100)$$

$$10^6 \chi = 1 \cdot 73$$

where y is the weight per cent of nickel chloride in the solution.

Taking this value of χ and $\alpha = 0.096$, the tube constant β was calculated, given

$$10^6 \chi = \frac{\alpha + \beta F'}{w} \quad ; \beta = 0.228$$

where F' = force on the sample and the w = weight of solution Thereafter, using these constants the magnetic susceptibility of nickel chloride was calculated with 'w' as the weight of nickel chloride in the solution. This was further checked with copper sulphate solutions.

The magnetic susceptibility of dinitrato bis (bipyridyl) iron III perchlorate at 85° K was obtained using the low temperature Gouy equipment of the Department of Physical Sciences, The Polytechnic, Wolverhampton. Quantitative measurements of tris (2.2 bipyridyl) iron II was carried out colorimetrically. The molar extinction co-efficient of 8,650 for the charge transfer band at 522 n.m. was utilised for the calculation.

Estimation of ferrous iron in ferrous/ferric mixtures was with standard solution of ceric ammonium nitrate.

Tris (2.2′ bipyridyl) iron II perchlorate and Tris (2.2′ bipyridyl) iron III perchlorate.

The tris chelate complexes of iron II and iron III as their perchlorates were prepared by the methods of Burstall & Nyholm[67].

Di-nitrato bis (2.2 bipyridyl) iron III perchlorate.

Tris (2.2 bipyridyl) iron II perchlorate (0·5g) was dissolved in concentrated nitric acid (5 ml) and evacuated over sodium hydroxide when blue - green crystals were obtained. Attempts to recrystallize this compound were unsuccessful.

Elemental Analysis.

Found C = 40.3; H = 2 . 8; Fe = 9 · 5; N = 13 . 7

$C_{20}H_{16}ClFeN_6O_{10}$

Requires C = 40 · 3; H = 2 · 8; Fe = 9 · 9; N = 14 . 2

Table 1

Infra red absorption of some 2. 2 bipyridyl complexes of iron.

1	2	3	4	Assignments
	3470 br	3450 br		ν H_2O
3080 v.w.	3108 v.w.	3115 v.w.	3115 v.w	C-H str
3060 w	3080 w	3080 w	3080 w	
		1630 w	1620 sh	C = C
1580 v.s.	1610 v.s.	1608 s	1608 s	and
1560 s	1570 w	1588 w	1588 w	C = N str
		1570 w	1565 w	
1500 w		1530 w	1522 w	C = C
	1470 s	1500 w	1500 sh	
1460 sh	1445 v.s.	1470 v.s.	1470 sh	C = N str
		1445 v.s.	1450 v.s	and
1450 v.s	1428 s	1430 s.sh	1430 v.s	C - H bend
1415 v.s.	1318 s	1318 m	1318 s	

Table 1 Continued

1	2	3	4	Assignments
			1485 v.s.	ν_4 ONO$_2$
			1285 v.s.	ν_1 ONO$_2$
1270 v.w	1275 w	1270 w	1275 sh	
1250 s	1245 m	1245 m	1250 m	C = C str
	1220 v.w			
1212 w	1170 w		1175 w	C - H in
1140 m	1160 w		1160 v.w	plane bend
	1090 v.s.br	1080 v.s. br	1090 v.s.br	ν_3ClO$_4^-$
1090 v.s.				
1085 s				C - H in
1065 m				plane bend
1040 s			1048 w	C - H out of plane bend
			1015 s	ν_2 ONO$_2$
995 s	1025 w.sh	1020 w.sh		
975 sh	1000 w			C - C str

continued ....

Table 1 Continued

1	2	3	4	Assignments
895 m	965 m	940 v.w	970 v.w	
	930 v.s		930 v.w	C - H
755 v.s	965 v.s	765 v.s	838 v.w	
	748 w.sh		778 s	out of
740 sh	733 s	733 s	765 v.s	plane bend
			740 w	
			728 s	
			810 m	ν_6 ONO_2
655 m	650 v.w	650 v.w	690 m	C - C
620 w		638 s.sh	672 m	bend
	622 s	625 s	622 s	ν_4 ClO_4
430 w	475 w	470 v.w	468 w	ring
403 s	420 w	420 w	420 w	torsion
	370-380 w.br	360 v.w	335 v.w	ν Fe - N
		350 v.w	325 w	

continued .....

Table 1. Continued

1 - 2. 2 bipyridyl

2 Tris (2 . 2 bipyridyl) iron II perchlorate

3 Tris (2. 2 bipyridyl) iron III perchlorate

4 Di-nitrato bis (2. 2 bipyridyl) iron III perchlorate

Results and Discussion.

a) Solutions of $[\mathrm{Fe\ (bipy)_3}](\mathrm{ClO_4})_2$ in concentrated hydrochloric acid

The tris (2 . 2′ bipyridyl) iron II complex as the perchlorate was soluble in concentrated hydrochloric acid yielding a pale yellow solution. When this yellow solution was diluted as soon as it was prepared it changed to pink, the visible absorption spectrum of the pink solution indicated the regeneration of the original tris complex. Quantitative measurements showed that nearly 10 per cent of the tris complex originally introduced was regenerated. However, when the hydrochloric acid solution was diluted after half an hour or more, no regeneration of the tris complex occurred. The ultra violet spectrum of the yellow hydrochloric acid solution indicated the presence of protonated bipyridyl. The peak maximum at 298 n.m. suggested mainly monoprotonated bipyridyl to be present since bipy H^+ has a characteristic band at 301 n.m.[77,78]. In addition to bands attributed to protonated bipyridyl the spectrum also showed a band at 370 n.m (Figure 3.1). This band at 370 n.m is also present in the spectrum of a solution of ferrous chloride in concentrated hydrochloric acid and is attributed to an anionic chloro complex of iron[79]. It is clear that virtually complete dissolution of the tris (2 · 2′ bipyridyl) iron II species occurs in this medium.

$$[\ \mathrm{Fe\ (bipy)_3}\ ]^{2+} \rightleftharpoons \mathrm{Fe}^{2+} + 3\ (\mathrm{bipy})$$

$$3\ (\mathrm{bipy}) \xrightleftharpoons{\mathrm{H+}} 3\ [\ \mathrm{bipy\ H}\ ]^{+} \xrightleftharpoons{\mathrm{H+}} 3\ [\ \mathrm{bipy\ H_2}\ ]^{2+}$$

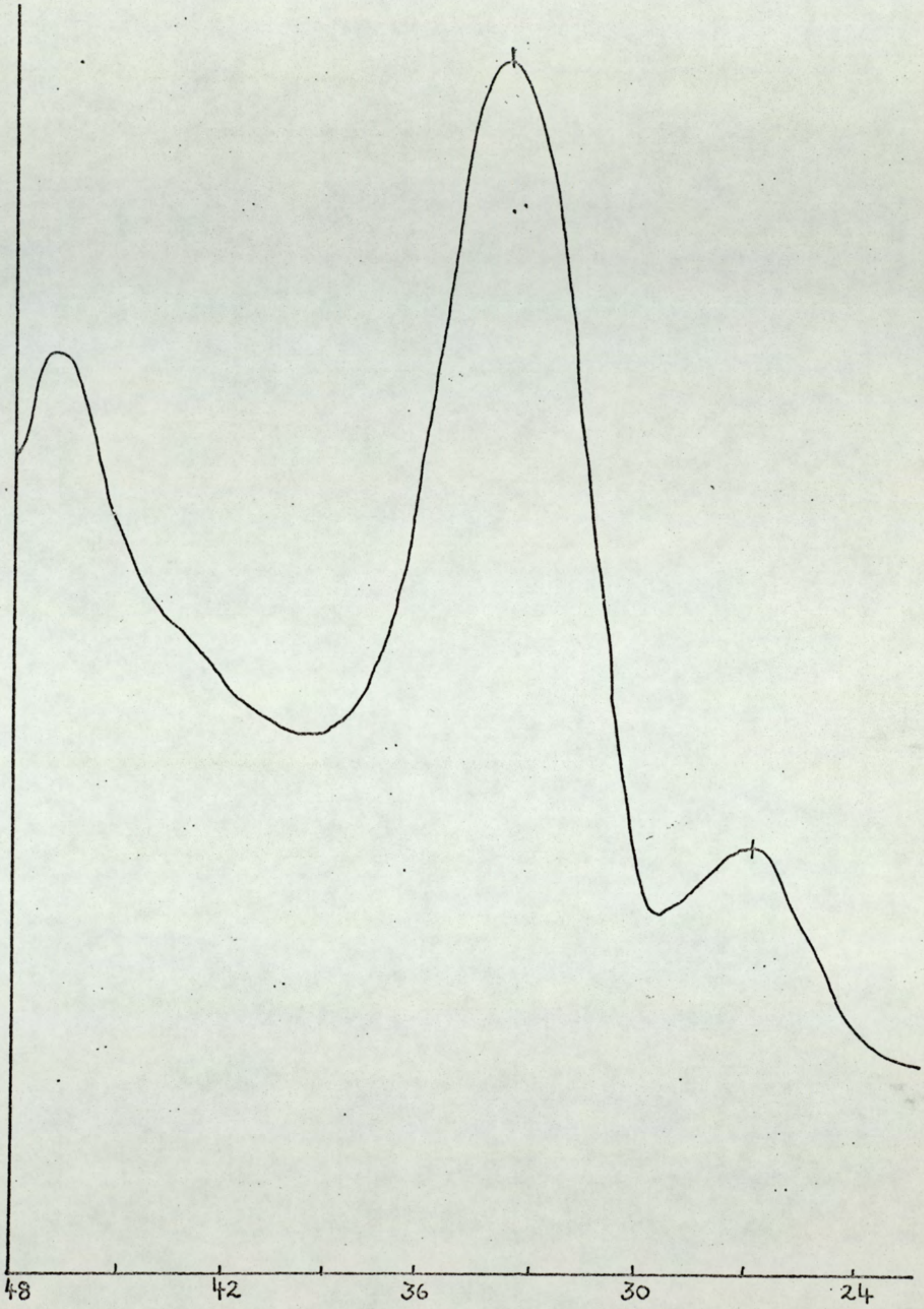


Fig 3.1 Absorption spectrum of tris (2.2 bipyridyl) iron II perchlorate in concentrated hydrochloric acid

$$Fe^{2+} \xrightleftharpoons{Cl^-} [Fe\ Cl_n]^{(n-2)-}$$

$$Fe^{2+} \xrightleftharpoons{(0)} Fe^{3+} \xrightleftharpoons{Cl^-} [Fe\ Cl_n]^{(n-3)-}$$

b) Solutions of $[Fe(bipy)_3](ClO_4)_2$ in concentrated perchloric acid.

In close agreement with Healy and Murmann the deep red tris (2 • 2′ bipyridyl) iron II species slowly dissolved in perchloric acid giving a pale blue coloured solution. The visible spectrum of this solution showed a band at 610 n.m. which had an apparent molar extinction co-efficient of 15 $mol^{-1}\ cm^2$. The ultra violet spectrum indicated the presence of protonated bipyridyl. The broad band with a peak maximum 288 n.m. was probably a composite band due to the presence of both the monoprotonated and diprotonated species. Dilution of the blue solution with water regenerated the familiar red colour of the tris chelate complex. The intensity of the band at 522 n.m. indicated that only ca 10 per cent of the tris complex originally introduced was regenerated.

c) Solutions of tris (2 • 2′ bipyridyl) iron II perchlorate in concentrated sulphuric acid.

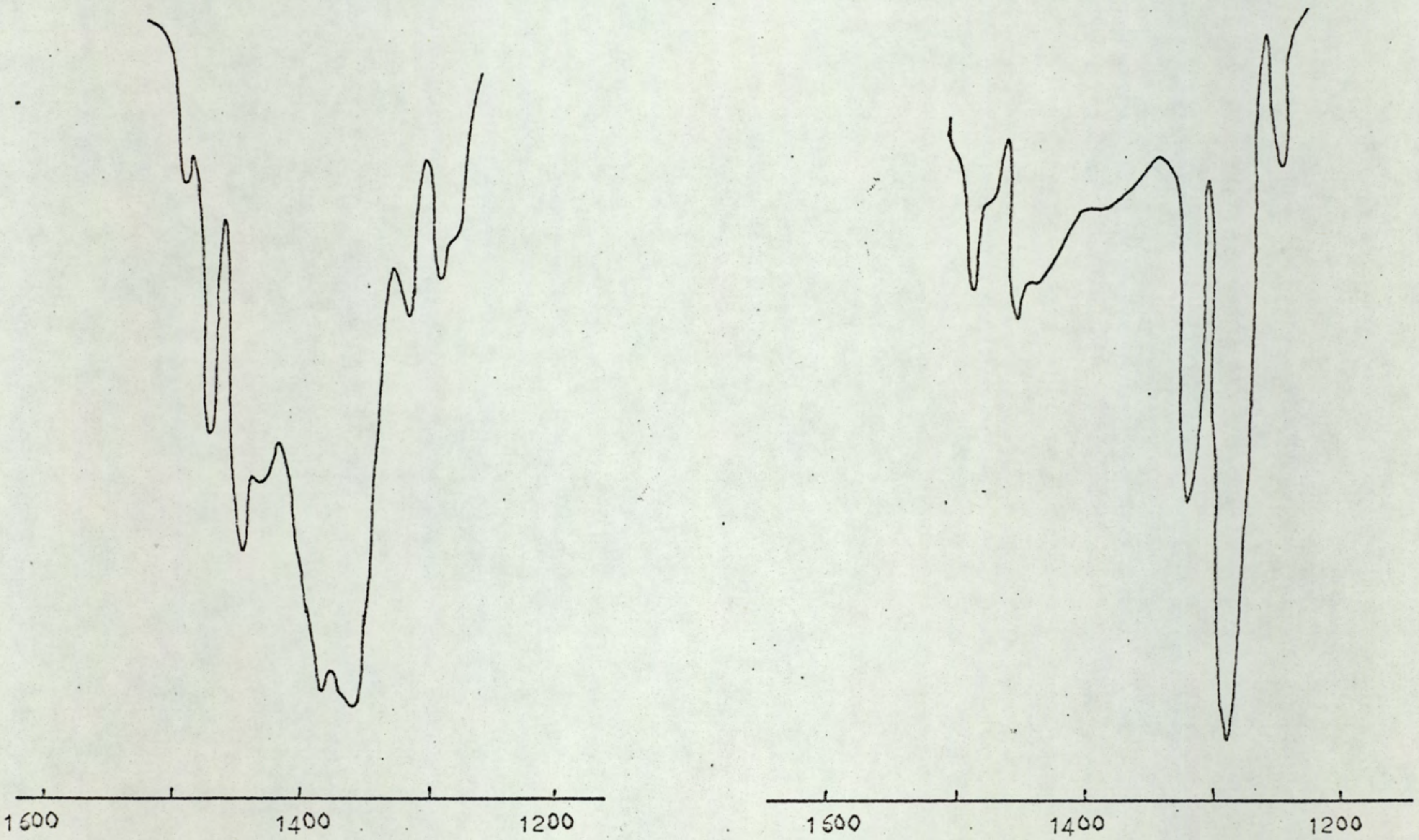
The tris 2 • 2 bipyridyl iron II perchlorate dissolved in concentrated (98%) sulphuric acid also yielding a pale blue solution. The rate of production of the blue colour was faster than in perchloric acid. The visible spectrum was also very similar with a broad band at 610 n.m. but the apparent molar extinction co efficient was much higher being 90 $mol^{-1}\ cm^2$.

Dilution with water gave a colourless solution probably due to the decomposition of the complex by the warm acid. However, careful dilution with small quantities of water did not alter the apparent extinction co-efficient, indeed, addition of large quantities of water resulted in regeneration of 10 per cent of the original tris complex. Since 98% sulphuric acid has a very small concentration of water, the tris complex was treated with different concentrations of sulphuric acid. This did not increase apparent molar extinction co-efficient clearly indicating that the intensity of the blue colour achieved with concentrated sulphuric acid is not related to the concentration of the hydroxonium ion.

d) Solutions of tris 2 · 2′ bipyridyl iron II perchlorate in concentrated nitric acid.

Tris 2 · 2′ bipyridyl iron II perchlorate dissolves very readily in concentrated nitric acid yielding a bright blue solution. The visible absorption spectrum of this solution shows a band at 610 n.m. similar to that obtained in sulphuric and perchloric acids. However, the apparent molar extinction co-efficient value is much higher being 160 mol^{-1} cm^{2}. The blue nitric acid solutions are very stable with absolutely no change in spectra over a few days. The ultra violet spectrum indicated the presence of protonated bipyridyl with a peak maximum at 300 n.m. The behaviour on dilution was similar to that in the other acids bringing about the regeneration of the tris complex. Colorimetric estimation indicated that 25% of the tris (2 · 2′ bipyridyl) iron II cation originally introduced as the perchlorate was regenerated.

Fig.3.2 Infra red spectra(1600-1200cm^{-1}) of dinitrato bis bipyridyl iron111 perchlorate



KBr disc

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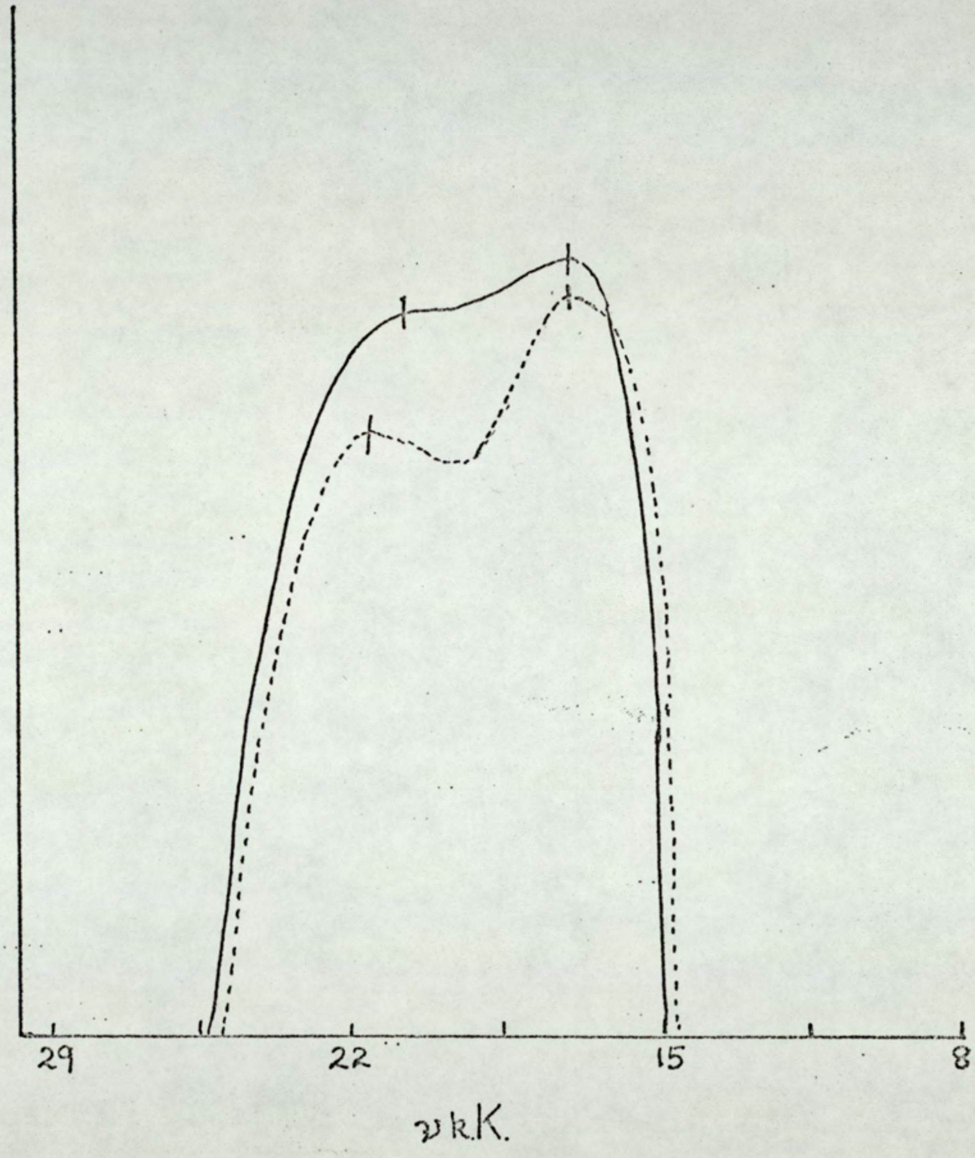


Fig 3.3 Diffuse reflectance spectra

-----Tris (2.2 dipyridyl) iron III perchlorate

——— Dinitrato bis (2.2 bipyridyl) iron·III perchlorate

A bluish green solid was isolated from the solution of tris 2 • 2′ bipyridyl iron II perchlorate in concentrated nitric acid. The infra red spectrum of this complex indicated that the perchlorate was in the ionic state. The mull spectra contained bands characteristic of co-ordinated nitrate groups with absorption bands ν_4 at 1430 cm^{-1}, ν_1-1285 cm^{-1}, ν_2-1015 cm^{-1}

and ν_6 - 810 cm^{-1}.

However, when potassium bromide was used as the sampling matrix only bands due to ionic nitrate were indicated - a strong band ν_3 at 1350 cm^{-1} and ν_2 at 835 cm^{-1} (Fig 3.2). This is a clear example of ion interchange where the presence of a large excess of bromide ions has caused a replacement of the nitrate ions in the complex.

Elemental analysis of this compound indicated a stoichiometry $Fe\ (bipy)_2(NO_3)_2\ (ClO_4)$. The diffuse reflectance spectrum showed the presence of two bands at 20 .3 k.K (sh) and 16 . 4k K (Fig 3.3) similar to that observed for a sample of tris (2 • 2′ bipyridyl) iron III perchlorate synthesised by the method of Brustall and Nyholm[67] (21 • 3 kK. and 16• 3 kK). However, infra red data, elemental analysis and more particularly Mossbauer spectral data suggest that it is not in fact the tris (2 . 2′ bipyridyl) iron III complex. The Mossbauer spectrum at room temperature consisted of a clearly resolved quadrupole doublet with a chemical isomer shift of 0 .32 mm sec^{-1} (relative to sodium mitroprusside) and a quadrupole splitting of 1 • 58 mm sec^{-1} (Fig 3.4) . There was no significant change in the Mossbauer spectrum on cooling to 77° K except that the isomer shift δ was 0 . 40 mm sec^{-1} and ΔE the quadrupole splitting was 1 • 75 mm sec^{-1}. This data is consistent with the presence of spin paired iron III in a single environment.

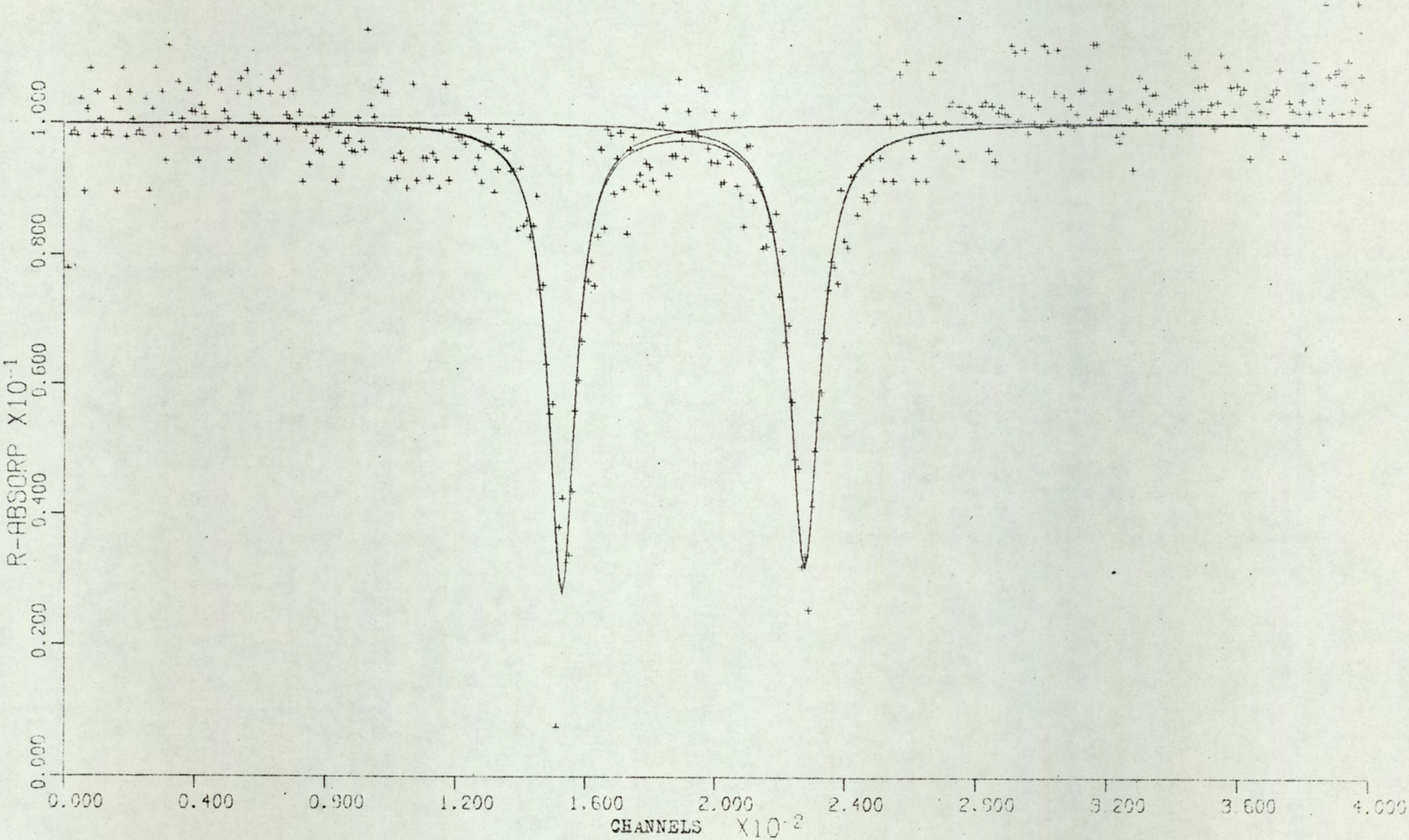


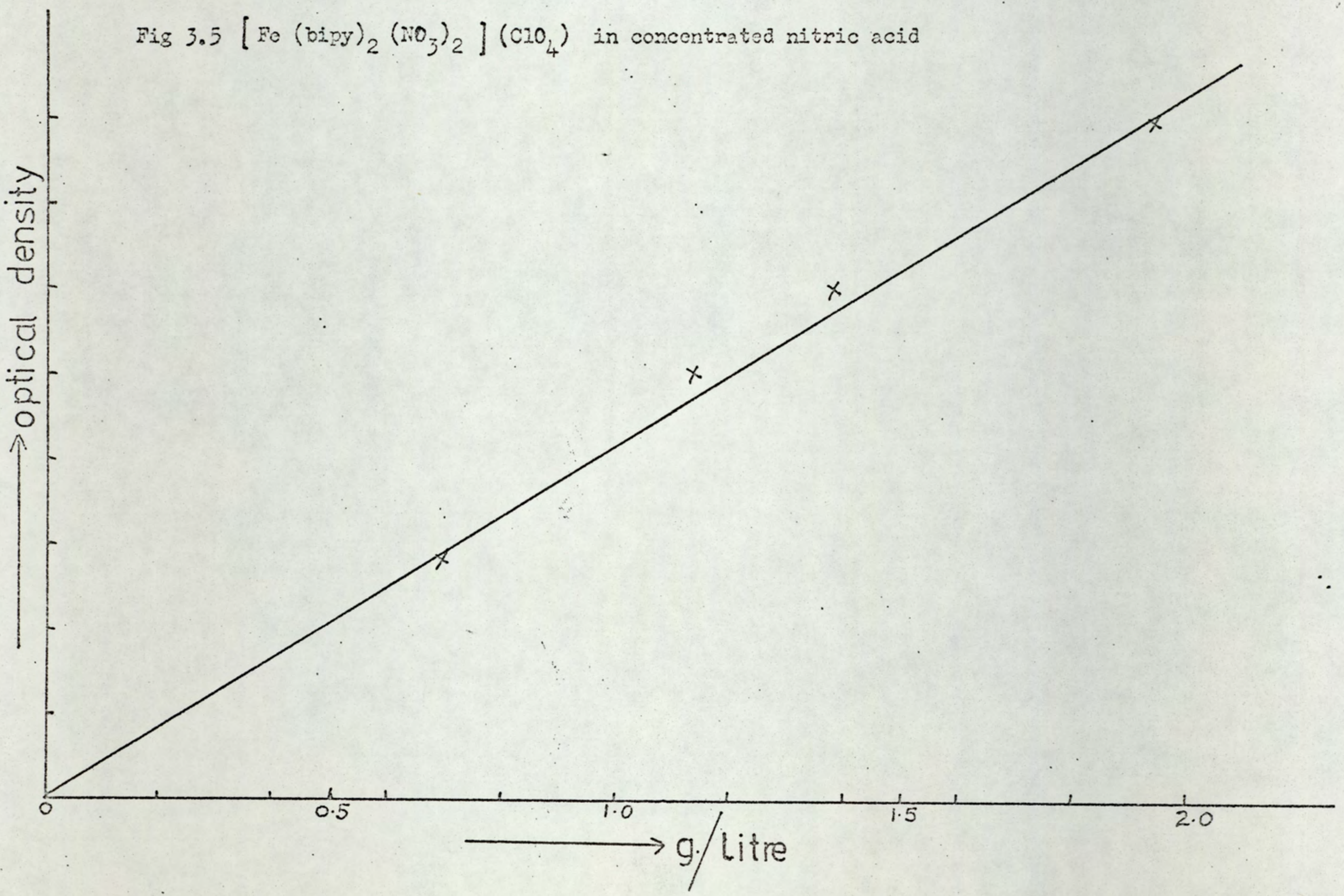
Fig.3.4 Mossbauer spectrum of $[Fe(bipy)_2(NO_3)_2](ClO_4)$

The effective magnetic moment as determined by the Gouy method gave a value of 2.16 B.M. at 298° K and 2 .03 B.M. at 85° K in conformity with the Mossbauer data, confirming the presence of low spin t_{2g}^5 iron III without any anomalous behaviour on temperature variation. The corresponding Mossbauer and magnetic data for the tris 2 . 2 bipyridyl iron III perchlorate[39] are isomer shift $\delta = 0 \cdot 29$ mm sec^{-1} (300° K) and $0 \cdot 32$ mm sec^{-1} (80° K). Quadrupole splitting parameter $\Delta Eq = 1 . 69$ mm sec^{-1} (300°)K and $1 \cdot 80$ mm sec^{-1} (80° K). Effective magnetic moment $= 2 \cdot 24$ B.M.

The dinitrato bis (2· 2′ bipyridyl) iron III perchlorate dissolves in concentrated nitric acid giving a bright blue solution. The visible absorption spectrum was exactly similar to that obtained by the dissolution of tris (2 · 2′ bipyridyl) iron II perchlorate in concentrated nitric acid. The wavelength of maximum absorption was at 610 n.m. and the apparent molar extinction co-efficient was 130 mol^{-1} cm^2. Solutions in concentrated perchloric acid and sulphuric acid were exactly similar with λ_{max} at 610 n.m. but the apparent molar extinction co-efficients were 130 mol^{-1} cm^2 in perchloric acid and 120 mol^{-1} cm^2 in sulphuric acid. The nitric acid solutions obeyed Beers Law (Fig 3.5) indicating that only one type of species is responsible for the colour. From the data available it appears to be established that the species responsible for the blue colour are iron III compounds.

The solid material discussed above may be tentatively identified as dinitrato - bis - 2 · 2′ bipyridyl iron III perchlorate with presumably a cis configuration[80]. However the blue species in solution is less easily identifiable. Tris (2 · 2′ bipyridyl) iron III perchlorate also dissolves in

Fig 3.5 $[Fe(bipy)_2(NO_3)_2](ClO_4)$ in concentrated nitric acid



concentrated nitric acid giving similar blue solution with λ_{max} = 610 n.m. but apparent molar extinction co-efficient = $190\ \text{mol}^{-1}\ \text{cm}^{2}$. This band is probably of change transfer origin and occurs in similar positions for the tris and cis - bis complexes. The fact that the solutions prepared from the tris (2 · 2 bipyridyl) iron III complex show greater values of the apparent molar extinction co-efficient suggests that this may be the major species responsible for the colour. It thus seems necessary to invoke a disproportionation of the dinitrato bis (2 . 2′ bipyridyl) iron II perchlorate in solution.

$$3\left[\text{Fe}\ (\text{bipy})_2(\text{NO}_3)_2\right]\left(\text{ClO}_4\right) \rightleftharpoons 2\left[\text{Fe}\ (\text{bipy})_3\right]^{3+} + \text{Fe}^{3+} + 6\left(\text{NO}_3\right)^- + 3\left(\text{ClO}_4\right)^- \qquad (1)$$

However, determination of the magnetic moments of solutions in concentrated nitric acid does not suggest that reaction (1) is important, since the effective magnetic moment of solutions obtained from $\left[\text{Fe}\ (\text{bipy})_2\ (\text{NO}_3)_2\right]\left(\text{ClO}_4\right)$ $\mu_{eff} = 2 \cdot 4$ B.M. Tris (2 · 2′ bipyridyl) iron III perchlorate = 2.3 B.M. and Tris 2 · 2′ bipyridyl iron II perchlorate = 2 · 4 B.M. These values are consistent with the presence of spin paired iron III, whereas if (1) is important there will be a reasonable concentration of spin free iron III in the solution which will cause an increase in the value of the magnetic moment.

An alternative view is that the following equilibria are set up

$$\left[\text{Fe}\ (\text{bipy})_3\right]^{3+} \rightleftharpoons \left[\text{Fe}\ (\text{bipy})_2\right]^{3+} + \text{bipy} \qquad (2)$$

$$\left[\text{Fe}\ (\text{bipy})_2\right]^{3+} \rightleftharpoons \left[\text{Fe}\ (\text{bipy})\right]^{3+} + \text{bipy} \qquad (3)$$

$$[\text{Fe (bipy)}]^{3+} \rightleftharpoons [\text{Fe}]^{3+} + \text{bipy} \qquad (4)$$

$$\text{bipy} + \text{H}^{+} \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} [\text{bipy H}]^{+} \qquad (5)$$

Thus the extra bipyridyl present in solutions prepared from the tris complex may increase the effective concentration of the low spin species. Addition of excess 2 · 2′ bipyridyl to solutions of the dinitrato bis complex and the tris complex in nitric acid had no immediate effect indicating that reaction (5) is fast. However, on standing the apparent extinction co-efficient for the 610 n.m. band increased for all solutions no matter how they were prepared. The results suggest that the solutions contain both bis and probably some tris (2 · 2′ bipyridyl) iron III species.

Earlier experiments gave different values for the molar extinction co-efficient of the blue species generated from tris (2 · 2′ bipyridyl) iron II perchlorate in the three different acids - nitric, sulphuric and perchloric. This is a direct indication of the differing efficiency with which these acids generate the iron III species, which must be related to their oxidising powers rather than to their strength as acids.

$$[\text{Fe (bipy)}_3]^{2+} \rightleftharpoons [\text{Fe (bipy)}_2]^{2+} + \text{bipy}$$

$$[\text{Fe (bipy)}_3]^{2+} \overset{(0)}{\rightleftharpoons} [\text{Fe (bipy)}_3]^{3+}$$

$$[\text{Fe (bipy)}_2]^{2+} \overset{(0)}{\rightleftharpoons} [\text{Fe (bipy)}_2]^{3+}$$

$$[\text{Fe (bipy)}_3]^{3+} \rightleftharpoons [\text{Fe (bipy)}_2]^{3+} + \text{bipy}$$

$$\text{bipy} + \text{H}^{+} \rightleftharpoons [\text{bipy H}]^{+}$$

When the complex dinitrato bis bipyridyl iron III perchlorate is dissolved in water a bluish violet solution is produced. The absorption spectrum of this solution has a broad band at 610 n.m.

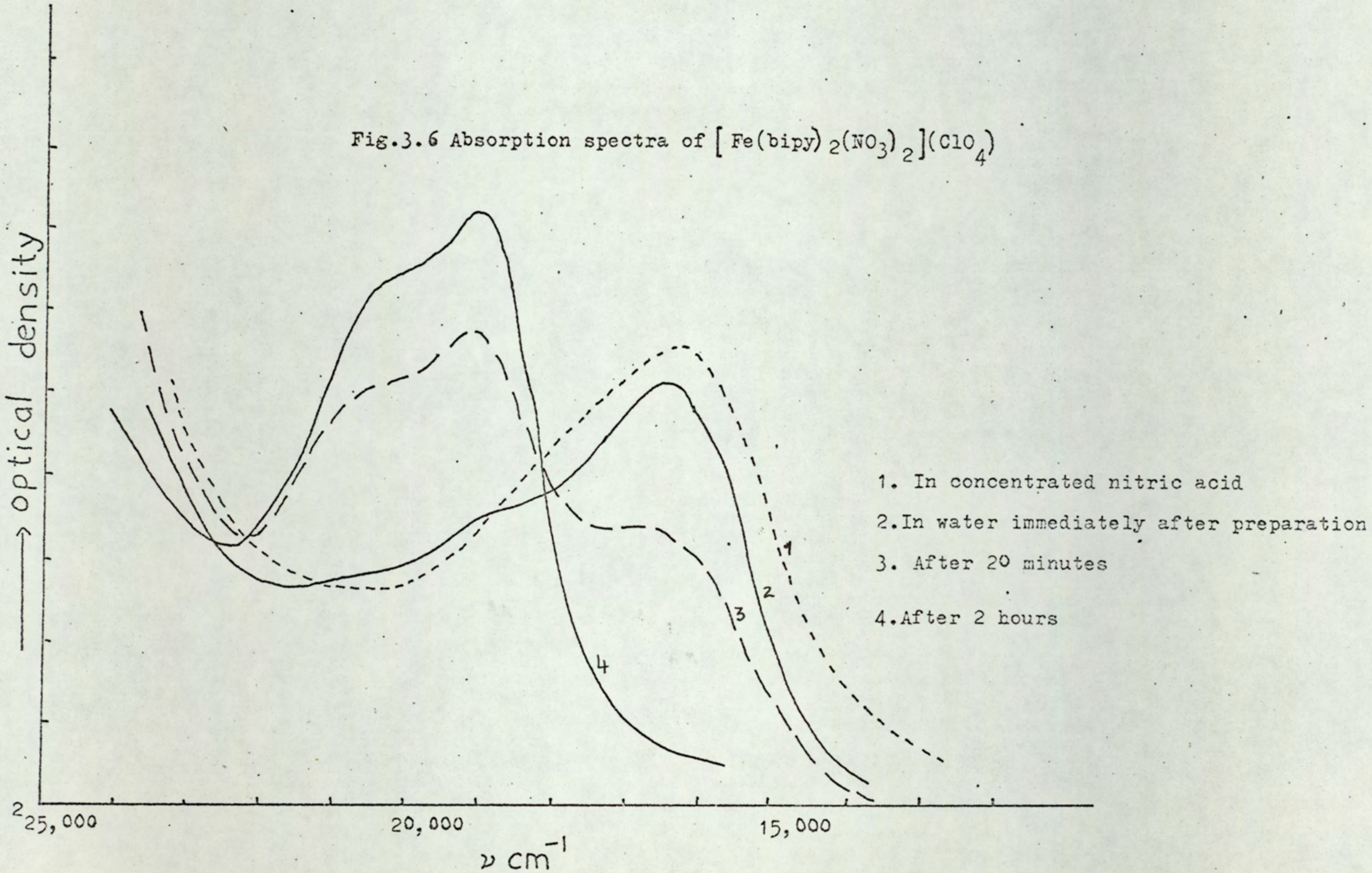


Fig.3.6 Absorption spectra of $[Fe(bipy)_2(NO_3)_2](ClO_4)$

and a hump at 522 n.m. On standing this solution gradually becomes red and has the absorption band characteristic of tris bipyridyl iron II at 522 n.m. This change may be followed spectrophotometrically (Fig. 3.6) and is attributable to a change in exidation state from iron III to iron II as $[\mathrm{Fe\ (bipy)_3}]^{2+}$. In a typical experiment 25% of the iron originally introduced as $[\mathrm{Fe\ (bipy)_2(NO_3)_2}](\mathrm{ClO_4})$ appears as $[\mathrm{Fe\ (bipy)_3}]^{2+}$ determined colorimetrically[81]. Redox titrations of such solutions with ceric ammonium sulphate indicate that when the intensity of the absorption band of $[\mathrm{Fe\ (bipy)_3}]^{2+}$ at 522 n.m. has reached a maximum and constant value, the total ferrous content of the solution corresponded to 33% of the iron originally introduced. It is of interest that the tris (2 . 2′ bipyridyl) iron III perchlorate does not show any evidence of decomposing rapidly to $[\mathrm{Fe(bipy)_3}]^{2+}$ in aqueous solution.

Very recently, Wehry and Ward[69] demonstrated that the related tris (1 : 10 phenanthroline) iron III species undergoes photo reduction to tris (1 : 10 phenanthroline iron II $[\mathrm{Fe\ (phen)_3}]^{2+}$ with the quantum yield varying from zero for 98% sulphuric acid to reach a steady maximum at 8 · 5 M acid. Water was considered to be the electron donor in the photo reduction.

$$[\mathrm{Fe\ (phen)_3}]^{3+} \underset{\longleftarrow}{\xrightarrow{h\nu\ (\mathrm{H_2O})}} [\mathrm{Fe\ (phen)_3}]^{2+} + \mathrm{H}^+ + \mathrm{O\ H}$$

In the phenanthroline case ultra violet light was required to bring about the reduction, however our experiments were carried out in a laboratory entirely lit by fluorescent strip lighting and it has been previously found that the U.V. flux is sufficient to give trouble when handling photo sensitive species.

It is of interest that when the reactions in aqueous solutions were carried out away from direct light there was no rapid formation of tris (2 . 2'bipyridyl) iron II and even after a prolonged time, the amount formed was negligible.

Since the experimental results indicate that less than 50 per cent of the iron appears as iron II, it is possible that there are two competing reactions taking place. The fact that the amount of tris bipyridyl iron II formed in the absence of light is negligible supports the occurence of a photochemical reduction. The competing reaction may be a hydrolytic one.

$$\left.\begin{aligned} &[\mathrm{Fe\ (bipy)_2(NO_3)_2}]^{+} \underset{}{\overset{h\nu}{\rightleftharpoons}} [\mathrm{Fe\ (bipy)_2(NO_3)_2}] \\ 3\,&[\mathrm{Fe\ (bipy)_2(NO_3)_2}] \rightleftharpoons 2\,[\mathrm{Fe\ (bipy)_3}](\mathrm{NO_3})_2 + \mathrm{Fe(NO_3)_2} \end{aligned}\right\} \text{(a)}$$

$$2\,[\mathrm{Fe\ (bipy)_2(NO_3)_2}]^{+} \overset{H_2O}{\rightleftharpoons} [\{\mathrm{Fe\ (bipy)_2(NO_3)}\}_2\,\mathrm{O}] + 2\mathrm{HNO_3} \qquad \text{(b)}$$

If the hydrolytic reaction is more favcured and takes place twice as fast then the formation of only 33% of iron II is explicable. From equations(a) it is apparent that 22% of the iron is generated as tris (2 . 2' bipyridyl) iron II. The hydrolytic reaction necessarily leads to the formation of a binuclear oxygen bridged species with the release of hydrogen ions to the solution. This would account for the acidity of the aqueous solution. There can also be a contribution to the acidity if water is the electron donor in the photo reduction.

These results also tend to suggest that the regeneration of tris 2 . 2' bipyridyl iron II when solutions of the complex in concentrated acids are diluted, may also be light sensitive.

In conclusion, these results are in close agreement with some of the observations made by Healy and Murmann, however, their results must necessarily be reinterpreted. The observed moment of 5 . 2 B.M for the perchloric acid solution of tris (2. 2 bipyridyl) iron II perchlorate probably arises from a mixture of high spin and low spin ferrous and ferric species.

The blue colour of the solutions formed in concentrated acids is due to the presence of an iron III species. The formation of the blue species from a solution of dinitrato bis (bipyridyl) iron III perchlorate clearly indicates that a 1 : 2 ratio of iron : bipyridyl is sufficient to generate the blue species. The nature of the iron species in solution is not easily recognizable, it is probably a combination of both the bis and the tris (2 . 2' bipyridyl) iron III complexes.

CHAPTER IV

A study of the cobalt complexes of some 2 - pyridyl amines

There has been considerable interest in the complexes formed by the potentially chelating ligands di -(2 - pyridyl)amine and tri - (2 - pyridyl)amine and some of their substituted derivatives. The presence of the bridging - NH grouping in di - (2 - pyridyl)amine makes the ligand potentially tribasic but no evidence is available to show that the - NH group possesses basic properties[82].

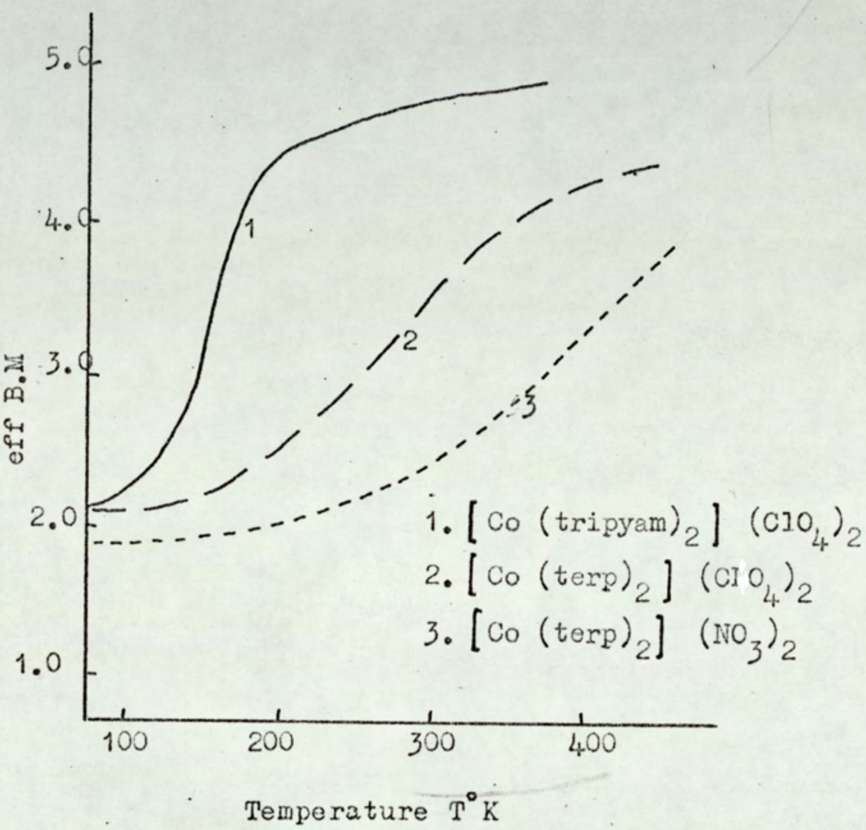
Di - (2 - pyridyl)amine was first used as a ligand by Kirshner to prepare some copper II[83a] and cobalt II[83b] complexes. This ligand has been subsequently investigated rather extensively and complexes containg the ligand in 1 : 1, 2 : 1 and 3 : 1 ratio with the metal ion are known. Values of the ligand field splitting parameter Δ (10 Dq) of 11,000 cm^{-1} with respect to cobalt II and 11,100 cm^{-1} with respect to nickel II have been estimated. Using the rule of average environment[86] for the complex $[Cr(dipyam)_2 Cl_2]Cl$. a Δ value of 19,800 cm^{-1} with respect to chromium III has been estimated. The tris complex of iron II is spin free[40], this is compatible with the suggestion[88] that the $^1A_{1g}$ state of iron II will be stabilized only by ligands with a Δ value greater than 11,700 cm^{-1}. No reports of cobalt III and iron III complexes have been published.

The potentially terdentate ligand tri - (2 - pyridyl)amine is unique in its ability to form a virtually cubic environment with ions such as iron II ($^1A_{1g}$) as demonstrated by Mössbauer spectroscopy[38]. This ligand has the ability to co-ordinate in a bidentate or terdentate manner and this can be detected by the infra red spectra of the complexes[15]. The terdentate ligand is of the strong field type and a ligand field strength of 12,800 cm^{-1} has been estimated with respect to nickel II[89], Δ of the bidentate ligand with respect to nickel II has been found to be 11,000 cm^{-1}. The value of Δ with respect to chromium III has been calculated to be 18,800 cm^{-1} using the rule of average environment for the complex $[Cr\ tripyam\ Cl_3]$ [87]. The spectro-chemical series with respect to chromium III is therefore

$$F < H_2O < NCS^- < py \sim tripyam < dipyam < NH_3 < en < CN$$

The reactions of this ligand with various metal salts have been investigated. A number of isomeric pairs of compounds which differ only in the co-ordination behaviour of the ligand have been isolated e.g. $[Cu\ (tripyam)_2]\ (ClO_4)_2$ and $[Cu\ (tripyam)_2\ (ClO_4)_2]$ [15]. $[Co\ (tripyam)_2]\ (NO_3)_2$ and $[Co\ (tripyam)_2\ (NO_3)_2]$ [90]. The behaviour of the 4 - and 5 - methyl substituted derivative have been found to be essentially similar to tri - 2 - pyridylamine itself[91]. However, the substitution of a nitro group to one ring makes the ligand essentially dibasic[92].

In addition to the isomeric pair of cobalt II nitrate complexes, the perchlorate[15], halide[89] and thiocyanate complexes[90] of cobalt II have been characterised. The bis tri - 2 - pyridylamine cobalt II perchlorate is of special interest since the somewhat anomalous room temperature magnetic moment of 4.85 B.M for this octahedral complex has been shown to be due to the presence of a Boltzmann distribution of thermally accessible levels resulting in a mixing of the $^4T_1$ and ^2E states[19]. The detailed magnetic behaviour of this complex resembles that of the di iso thiocyanato bis 1 : 10 phenanthroline iron II and that of the polymorphs of the corresponding tris 2, 2 bipyridyl iron II complexes[56] more closely than that of the spin cross-over situations reported in other cobalt II complexes[94].



We cannot therefore speak of a geniune thermal equilibrium involving the ^4T and ^2E states. By contrast, the high spin hexafluoro phosphate salt was found to obey the Curie - Weiss law. This parallels the observations made by Stoufer[95,96] and Baker[97] on the anion dependence of the magnetic properties of the cobalt II cross-over systems.

The recently synthesised 4 - and 5 - methyl substituted derivatives of tri (2 - pyridyl)amine[98] have been found to have a greater ligand field strength (Δ 4-methyl = 12,950 cm^{-1} and 5 methyl = 13,050 cm^{-1})[92] than tri - (2 - pyridyl)amine (Δ = 12,800 cm^{-1})[89].

It was therefore hoped that the greater ligand field strength of these ligands coupled with the low symmetry component of the ligand field arising from the presence of the methyl groups might combine to stabilise the ^2E state of the cobalt II complexes. However, it was found that though the magnetic moment was lower (4 - methyl complex = 4.45 B.M 5 - methyl complex = 4.12 B.M) than that reported for the tri - (2 - pyridyl)amine complex (4.85 B.M) these complexes obeyed the Curie - Weiss Law[91].

This type of anomalous magnetic moment of cobalt II complexes could arise as a consequence of the presence of an admixture of cobalt III complex with the cobalt II complex where the paramagnetic componant independently obeys the Curie - Weiss law or due to a mixture of the ^4T and ^2E states where both energy states obeyed the Curie - Weiss Law.

Barnard et.al.[19] also showed that the change in spin state on cooling bis tri - (2 - pyridyl)amine cobalt II perchlorate was accompanied with significant changes in the far infra-red spectrum whilst the spin free hexafluoro phosphate salt showed no change.

It was of interest to study the far infra-red spectra of the cobalt II complexes of 4 - methyl and 5 - methyl substituted tri - (2 - pyridyl)amines both at room and liquid nitrogen temperatures and compare them with the spectra of the corresponding spin free nickel II and spin paired iron II complexes. As a consequence of this study the possibility of synthesising some cobalt III complexes of these terdentate ligands was exploited and few substitution reactions were examined.

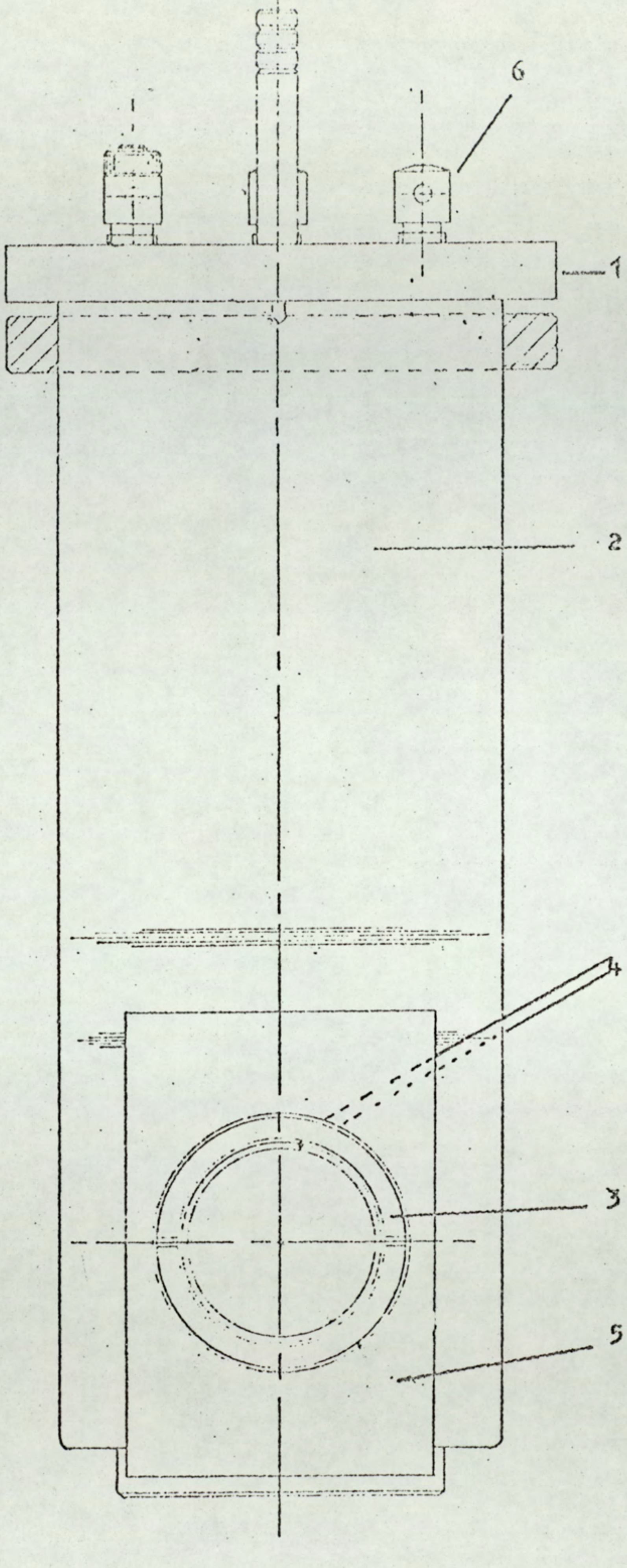


Fig.4.1 R.I.I.K.Variable temperature I.R.Unit

Experimental.

The infra red spectra at - 185° C were measured using Perkin Elmer 225 spectro meter with the R.I.I.K variable temperature I.R. unit V.L.T.2.

The unit consists of an outer jacket, cell holder and refrigerant vessel sample cell with thermocouple and temperature control as shown in Fig. 4.1.

The unit was placed in the sample compartment of the spectro-photometer and evacuated for about ten minutes with the window heaters on so as to eliminate the condensation of vapours. Heating of the windows was by use of a temperature control P.S.I. The Dewar was then filled with liquid nitrogen to produce a temperature near - 185° C. This temperature was attained within 20 - 25 minutes and was detected by the potentiometer. The spectrum was run about 5 minutes after equilibrium was attained. The vacuum was then cut off and the unit was allowed to reach room temperature before another sample was examined.

1 - metal cap 2 - stainless steel jacket
3 - locking ring for rectangular back plate (5)
4 - retaining rings for the window mounts.
6 - plug for connection to thermocouple

Preparations

Tri - (2 - pyridyl)amine

Tri - (2 - pyridyl)amine was prepared by the method of Wibaut and La Bastide[112].

Analysis: C = 72.3 H = 4.8 N = 22.7

$C_{15}H_{12}N_4$ requires C = 72.5 H = 4.9 N = 22.6

2. 4 - and 5 - methyl 2 - pyridyl di - (2 pyridyl)amine

The 4 - and 5 - methyl substituted di -(2- pyridyl)amines was prepared as reported by Lancaster and McWhinnie[98].

Analysis: 4 - methyl product C = 73.1 : H = 5.2 : N = 21.5.

5 - methyl product C = 73.4 : H = 5.3 : N = 21.1

$C_{16}H_{14}N_4$ Requires: - C = 73.3 H = 5.4 N = 21.4 %

3. Tris di - (2 - pyridyl)amine cobalt (II) perchlorate

Tris (di - (2 - pyridyl)amine cobalt II perchlorate was prepared according to the method reported by Goodgame[84].

Analysis: C = 46.5 H = 3.5 N = 16.7

$C_{30}H_{27}Cl_2CoN_9O_8$ requires: C = 46.7, H = 3.5, N = 16.4

4. Bis tri - (2 - pyridyl)amine cobalt (II) perchlorate

Bis tri - (2 - pyridyl)amine cobalt II perchlorate was prepared as reported by Kulasingam[15].

Analysis: C = 47.6 : H = 3.3 : N = 14.6

$C_{30}H_{24}Cl_2CoN_8O_8$ requires: C = 47.7 : H = 3.3 : N = 14.9

5. Bis 4 - methyl - 2 pyridyl di - (2 pyridyl)amine and bis 5 - methyl - 2 pyridyl di - (2 pyridyl)amine nickel II perchlorates

The above complexes were prepared as reported earlier[92].

Analysis: - 4 - methyl product C = 49.0 H = 3.6 N = 14.2

5 - methyl product C = 49.0 H = 3.5 N = 14.0

$C_{32}H_{28}N_8NiCl_2O_8$ requires: C = 49.1 H = 3.6 N 14.3 %

6. Bis 4 - methyl - 2 pyridyl di - (2 pyridyl)amine and bis 5 methyl - 2 - pyridyl di - (2 pyridyl)amine iron II perchlorates

These complexes were prepared as reported earlier[92].

Analysis: - 4 - methyl complex - C = 49.1 H = 3.6 N = 14.3

5 - methyl complex - C = 49.1 H = 3.8 N = 14.2

$C_{32}H_{28}N_8Fe.Cl_2O_8$ requires: C = 39.3 H = 3.6 N = 14.4

7. Bis 4 - methyl 2 - pyridyl di - (2 - pyridyl)amine cobalt II perchlorate

Cobalt II perchlorate hexahydrate (0.35g) in triethyl ortho formate (10 ml) was added to 4 - methyl - 2 - pyridyl di - 2 - pyridylamine (0.7g) in triethyl ortho formate (10 ml) and warmed gently for 2 - 3 minutes. A buff coloured product deposited instantly. This was filtered off and washed thoroughly with ethanol.

8. Bis 5 - methyl - 2 pyridyl di - (2 - pyridyl)amine cobalt II perchlorate

Cobalt II perchlorate hexahydrate (0.35g) in triethyl ortho formate (10 ml) was added to 5 - methyl - 2 pyridyl di - (2 pyridyl)amine (0.7g) in triethyl ortho formate (10 ml). A buff coloured product deposited immediately. This was filtered and washed thoroughly with ethanol. Attempts to recrystallise compounds 7 and 8 in acetone / ethanol resulted in the formation of a mixture of yellow and buff products.

9. Bis 4 - methyl - 2 pyridyl di - (2 - pyridyl)amine cobalt III perchlorate.

Cobalt II perchlorate hexahydrate (0.35g) in ethanol (10 ml) was added to 4 - methyl 2 - pyridyl di - (2 pyridyl)amine (0.7g) in ethanol (10 ml). The solution was refluxed for 10 minutes and allowed to stand overnight. A yellow product was deposited. This was recrystalised from acetone / ethanol.

The yield improved considerably when the ethanolic solutions of cobalt II and ligand were treated with a few drops of hydrogen peroxide (30%) and sodium perchlorate (0.2g) and heated under reflux for 15 minutes. On setting aside a yellow product deposited. The crude material was recrystallised from acetone / ethanol to afford bright yellow crystals.

10. Bis 5 - methyl 2 - pyridyl di - (2 - pyridyl)amine cobalt III perchlorate

Cobalt II perchlorate hexahydrate (0.35g) in ethanol (10 ml) was added to 5 - methyl - 2 - pyridyl di - (2 - pyridyl)amine (0.7g) in ethanol (10 ml). Sodium perchlorate (0.2g) was added to the reaction mixture and the solution was heated under reflux for 30 minutes. The solvent was then evaporated off and the pasty mass taken up in acetone (10 ml). A bright yellow product was deposited. This was recrystallised from ethanol / acetone .

Attempts to prepare the cobalt III complexes of tri - (2 - pyridyl)amine by this and other methods were unsuccessful, presumably due to the immediate precipitation of the cobalt II complex which failed to react further.

11. Attempts to isolate oxidation intermediates.

Several attempts were made by varying reaction conditions to isolate possible intermediates in the oxidation of cobalt II to cobalt III in the above syntheses. One experiment reproducibly afforded a compound containing cobalt in both oxidation states:-

Cobalt II perchlorate hexahydrate (0.35g) in acetone (10 ml) was added to 4 - methyl - 2 - pyridyl di - (2 pyridyl)amine (0.7g) in acetone (10 ml). The solution was heated under reflux for 15 minutes and then set aside overnight. A green product was deposited which was recrystallised from ethanol for which available data suggest the formula

$$[\mathrm{Co}\ (4\ \mathrm{mpdpa})]\ [\mathrm{Co}\ (\mathrm{OH})_4]\ (\mathrm{ClO}_4)\ 7\ \mathrm{H_2O}$$

Reactions of the cobalt III complexes

12. Trinitro 4 - methyl 2 - pyridyl di - (2 pyridyl)amine cobalt III dihydrate

Bis 4 - methyl 2 - pyridyl di - (2 pyridyl)amine cobalt III perchlorate (0.5g) in ethanol (10 ml) was refluxed for 10 minutes with a saturated ethanolic solution of sodium nitrite (10 ml). The yellow solid dissolved and the colour of the solution became orange. On setting aside for 30 minutes an orange product was deposited. This was recrystallised from ethanol.

13. Trinitro 5 methyl 2 - pyridyl di - (2 pyridyl)amine cobalt III hydrate.

Bis 5 methyl 2 - pyridyl di - (2 - pyridyl)amine cobalt III perchlorate (0.3g) in ethanol (10 ml) was added to a saturated solution of sodium nitrite in ethanol (10 ml). The reaction mixture was refluxed for 10 minutes when the solution became orange coloured. On allowing this solution to cool an orange coloured product was deposited. This was recrystallised from ethanol.

14. Reaction with ammonium thiocyanate

Bis 5 methyl 2 - pyridyl di - (2 pyridyl)amine cobalt III perchlorate (0.5g) in ethanol (10 ml) was added to a saturated ethanolic solution of ammonium thiocyanate (10 ml). The mixture was stored at room temperature for 10 minutes when the solution became orange, followed by the separation of an orange- brown solid. This was filtered and washed thoroughly with ethanol. Attempts to recrystallise this compound from ethanol were unsuccessful as the compound changed from orange-brown to greenish brown. This change of colour also occurred on standing for a few days.

When the above reaction mixture was heated under reflux for 10 minutes the solution turned yellow and then green and a bright green product was deposited. This was washed thoroughly with ethanol. Attempts to recrystallise this product were unsuccessful.

Bis 4-methyl 2 - pyridyl di - (2 pyridyl)amine cobalt III perchlorate reacted with ammonium thiocyanate yielding the orange brown Co III complex and the paramagnetic green complex.

Bis 4 - methyl and 5 - methyl 2 - pyridyl di - (2 - pyridyl) amine cobalt III perchlorates did not react with a saturated ethanolic solutions of sodium chloride and saturated solutions of potassium cyanide caused complete replacement of the pyridyl ligands.

Bis tri 4 - methyl tri - (2 - pyridyl)amine cobalt III perchlorate

The analytically impure sample of the suspected bis (tri - 4 - methyl tri - (2 - pyridyl)amine cobalt II perchlorate[91] was recrystallised from acetone when a bright yellow product was obtained.

Cobalt III complexes of di - (2 pyridyl)amine

Di -μ- peroxo tetrakis di - (2 pyridyl)amine dicobalt perchlorate

Tris di - (2 pyridyl) amine cobalt II perchlorate (0.5g) (prepared following the method of Goodgame[84]) in ethanol (10 ml) was heated under reflux with hydrogen peroxide (1 ml, 30%) for 10 minutes. The solution first became dark brown, then greenish and on setting aside a red brown product deposited. This was recrystallised from ethanol.

Attempted synthesis of dihalogeno bis di - (2 - pyridyl)amine cobalt III complexes.

Di -μ- peroxo tetrakis di - (2 pyridyl)amine dicobalt perchlorate (0.3g) was treated with concentrated hydrochloric acid (2 ml). The colour changed from red-brown to greenish-brown. Water 10 ml) was then added and the mixture heated under reflux for 5 minutes when a brownish solution was obtained. On setting aside this solution a pale green product was deposited. The product was washed with water but no recrystallisation solvent was found. The compound dissolved in hot water yielding a brownish solution but no well defined material could be isolated. Analysis suggested the stoichiometry $[Co\ (dipyam)_2\ Cl_2\ ]\ (ClO_4)$ dipyam. 2 HCl . H_2O. Replacement of hydrochloric acid by hydrobromic acid in the above preparation gave a brownish compound of composition

$[Co\ (dipyam)_2\ Br_2\ ]$ Br, H_2O

Table 4.1

Analytical data for Cobalt II and Cobalt III complexes of 2 - pyridylamines

Complex	Colour	Found %			Required %			No
		C	H	N	C	H	N	
[Co (II) (4 mpdpa)$_2$] $(ClO_4)_2.H_2O$	Buff	48.5	3.8	14.3	48.0	3.7	14.0	1
[Co II (5 mpdpa)$_2$]$(ClO_4)_2.H_2O$	Buff	47.5	3.4	14.2	48.0	3.7	14.0	2
[Co II (6 mpdpa)$_2$]$(ClO_4)_2$	Beige	48.7	3.6	14.4	49.1	3.6	14.3	3
[Co III (4 mpdpa)$_2$]$(ClO_4)_3$	Yellow	44.0	3.4	13.3	43.6	3.2	12.8	4
[Co III (5 mpdpa)$_2$]$(ClO_4)_3.H_2O$	Yellow	42.4	3.4	12.9	42.7	3.3	12.5	5
[Co III (tri 4m-tripyam)$_2$]$(ClO_4)_3$. 3 H_2O	Yellow	43.8	4.0	11.1	43.9	4.2	11.3	6
[Co III (4 mpdpa)$_2$][Co II $(OH)_4$] ClO_4. 7 H_2O	Green	39.8	3.6	11.4	40.7	5.1	11.9	7

continued....

Table 4.1. Continued

Complex	Colour	Found %			Required %			No.
		C	H	N	C	H	N	
[Co III (4mpdpa) (NO$_2$)$_3$].2 H$_2$O	Orange	38.6	3.3	20.2	38.8	3.6	19.8	8
[Co III (5mpdpa) (NO$_2$)$_3$].4 H$_2$O	Orange	35.5	3.9	18.4	36.1	4.1	18.3	9
[Co III (5mpdpa)(NSC)$_3$(5mpdpa) Co III](ClO$_4$)$_3$.H$_2$O	Orange-brown	38.7	3.0	13.1	37.4	2.6	13.7	10
[{Co III (5mpdpa)}$_2$(NSC)$_3$][Co(NSC)$_4$](ClO$_4$).H$_2$O	Green	38.8	2.4	16.8	38.3	2.4	17.2	11
[(dipyam)$_2$ Co(O$_2$)$_2$ Co (dipyam)$_2$](ClO$_4$)$_2$	Red-Brown	45.0	3.8	15.8	45.1	3.5	15.8	12
[Co III (dipyam)$_2$ Cl$_2$] ClO$_4$.dipyam.2H Cl.H$_2$O	Pale green	43.2	3.7	15.5	43.3	3.5	15.2	13
[Co III (dipyam)$_2$ Br$_2$] Br . H$_2$O	Brown-green	35.7	3.0	12.4	36.4	3.0	12.7	14

Table 4.2

Infra red spectra (600 - 200cm^{-1}) of iron II, nickel II and cobalt II complexes

$[Ni(4mpdpa)_3]$ $(ClO_4)_2$	$[Co(4mpdpa)_2]$ $(ClO_4)_2$	$[Fe(4mpdpa)_2]$ $(ClO_4)_2$	$[Ni(5mpdpa)_2]$ $(ClO_4)_2$	$[Co(5mpdpa)_2]$ $(ClO_4)_2$	$[Fe(4mpdpa)_2]$ $(ClO_4)_2$
560m	560m	563m	581s	580s	580s
555m	556m	556m		544sh	
530w	544s			524s	530s
515s	515s	157s	526s		510m
		504s		498w	
498s	497s		499w	488sh	482s
462v.s	484w	486v.s	490		
	476m			482m	485w
439v.s	458v.s		449s	458w	
	432s				
420w	405w	405w	441s	440sh	
		392m		433s	
397m	384w	380m	397m	397m	397w
			384m	394sh	384w
			375m	384w	
375m	375w	365m	369w	375m	375w
369w		358sh		370w	370w
357sh	358w		357m	357m	357sh

continued

Table 4.2. Continued

$[\mathrm{Ni(4mpdpa)_2}](\mathrm{ClO_4})_2$	$[\mathrm{Co(4mpdpa)_2}](\mathrm{ClO_4})_2$	$[\mathrm{Fe(4mpdpa)_2}](\mathrm{ClO_4})_2$	$[\mathrm{Ni(5mpdpa)_2}](\mathrm{ClO_4})_2$	$[\mathrm{Co(5mpdpa)_2}](\mathrm{ClO_4})_2$	$[\mathrm{Fe(5mpdpa)_2}](\mathrm{ClO_4})_2$
354m	354 w		354 m	354 m	350 m
351 m	350 w		351 m	351 sh	
			344 w		
334 w	334 w	336 w	340 w	340 m	335 w
		327 w	335 m	335 m	327 m
327 s	326 m	323 w	327 s	327 s	
323 s	323 m	314 w	323 s	323 s	323 m
315 w	315 w		320 sh		
302 m	302 m	303 s	316 sh	315 s	302 m
298 w			302 w	302 m	289 m
288 m	288 m	289 w	284 m	289 m	281 m
278 s	280 s	278 m	278 m	278 m	277 m
266 w	260 s	265 w	268 m	266 m	265 w
253 s	253 sh	253 w	257 sh	253 m	253 m
246 s	246 w	246 m	246 s	246 s	246 m
227 s				227 s	226 s
222 sh	227 w	227 m		222 sh	222 sh
	222 v.w	222 w		222 sh	222 sh
213 w	213 v.w	213 w		213 m	213 sh
208 w		207 w			208 w

Table 4.3.

Magnetic, conductivity and electronic spectral data for Cobalt II Complexes of methyl substituted tri - 2 - pyridylamines

Complex	Electronic Spectrum (kK)			Λ_M^a	μ_{eff}^b B.M.
	${}^4T_{1g} \longrightarrow {}^4T_{2g}$	${}^4T_{1g}(F) \longrightarrow {}^2T_{1g}(G)$	${}^4T_{1g} \longrightarrow {}^4T_{1g}(P)$		
$[\mathrm{Co\ II}\ (4\mathrm{mpdpa})_2](\mathrm{ClO_4})_2\ \mathrm{H_2O}$	11.6	19.0 sh	22.5	135	4.25-4.45
$[\mathrm{Co\ II}\ (5\mathrm{mpdpa})_2](\mathrm{ClO_4})_2\ \mathrm{H_2O}$	11.7	18.8 sh	22.1 sh	150	4.12-4.54
$[\mathrm{Co\ II}\ (6\mathrm{mpdpa})_2](\mathrm{ClO_4})$	10.8	18.9 sh	22.9	157	4.85

a - Molar conductivity ($\Omega^{-1} . \mathrm{cm}^2 . \mathrm{mol}^{-1}$) In nitromethane

b - Room Temperature moment.

Table 4.4

Magnetic, conductivity and spectral data of cobalt III complexes of substituted tri - 2 - pyridylamines

Complex No (c.f.Table 4.1.)	(nitromethane) Λm	μ eff B.M	Electronic spectra (k.K)	Some infra red absorptions ν C $\equiv$ N, NO_2, ClO_4, H_2O
4	225	0.15	22.0	1090 s.br 623 s
5	220	0.0	16.4 w.sh 22.1	3500 br 1095 s.br 623 s
7	214	4.3	7.6, 15.7, 16.8, 22.1	3600 sp 3525 sp 1090 s.br 623 s
8	25	0.0	14.9 w.sh 22.0 sh	1420 s, 1300 s, 830 . 820
9	15	0.2	14.3 w.sh 22.0 sh	1420 s 1305 s, 830.818
10	230	0.8	23.0 8.5 sh	2103 s.sp 2070 sh 2060 s 1090 s br 623
11	180	4.5	23.0, 16.0, 7.5	2103 s.sp 2060 v.s 1100 s.br. 625 m 310 s.br CO-NCS

Table 4.5.

Conductivity and Spectral data of cobalt III complexes of di - 2 - pyridylamine

Complex	Electronic Spectra (k.K)	Some infra red absorptions (ν cm^{-1})	Λ_M
$[Co(dipyam)_2(O_2)]_2(ClO_4)_2$	15.3 sh 19.2	1100, 1060 ν_3 ClO_4 623 ν_4 ClO_4 885 s.sp $\nu(O - O)$	150 ^{d}
$[Co(dipyam)_2Cl_2]ClO_4$ dipyam • 2 H Cl	17.5 26	3390 N-H 1103, 630 ClO_4 405, 386, 376, 370 Co - N ? 328, 300, 265, 249 357 ν_{as} Co-Cl ?	70^c
$[Co(dipyam)_2Br_2]$ Br	9.6 w. 16.2 sh 25. v.br.sh	394, 382, 276, 367 342, 318, 285 228, 211 ν_{as} Co-Br	170^c

d - D.M.F. c - nitromethane as solvent.

Results and Discussion

a) Cobalt II Complexes: Initial preparations of the bis 4 - methyl and 5-methyl tri - (2 pryidyl)amine cobalt II complexes had a low effective magnetic moment for spin free octahedral complexes, but plots of χ_M vs $^1/T$ were linear with no change of spin state[91]. It was subsequently found that other specimens of these complexes could be prepared which had higher effective magnetic moments but were identical to the above both analytically and spectroscopically. Barnard[19] has demonstrated that quite drastic changes occur in the low frequency infra red spectrum when bis tri - (2 - pyridyl)amine cobalt II perchlorate undergoes change of spin state on cooling. In particular, the spectrum initially similar to that of $[\mathrm{Ni\ (tripyam)_2}]\ (\mathrm{ClO_4})_2$ ($^3A_2$ ground state) becomes similar to that of $[\mathrm{Fe\ (tripyam)_2}]\ (\mathrm{ClO_4})_2$ ($^1A_1$ ground state) on cooling. Thus the infra red spectra (600 - 200 cm $^{-1}$) of the two series $[\mathrm{M\ (5mpdpa)_2}](\mathrm{ClO_4})_2$ and $[\mathrm{M\ (4mpdpa)_2}]\ (\mathrm{ClO_4})_2$ (M = Fe II, Co II, Ni II) at both 293°K and 88°K were examined. In both series the major differences between the spectra at the two temperatures was the superior resolution obtained on cooling. However, although the data indicated that no change of spin state occurs on cooling $[\mathrm{Co\ (5\ mpdpa)_2}]\ (\mathrm{ClO_4})_2$ and $[\mathrm{Co\ (4\ mpdpa)_2}]\ (\mathrm{ClO_4})_2$ confirming the conclusions obtained from magnetic measurements, we did observe that the two cobalt II complexes showed some weak bands corresponding in position to major bands in the spectra of the iron II complexes (Table 4.2). It was apparent, that some low spin species was present in a small enough quantity to just lower the effective magnetic moment without interfering with the stoichiometry obtained from analytical data. It is now known (see below) that the corresponding cobalt III complexes are readily prepared and that their far infra-red spectra are indeed very similar to those of the iron II complexes of these ligands. It is therefore certain that the low spin contaminant in some preparations of $[Co\ (4\ mpdpa)_2\ ]\ (C10_4)_2$ and $[Co\ (\ 5\ mpdpa)_2\ ]\ (C10_4)_2$ is the corresponding cobalt III complex. The fact that higher values of μeff are obtained when the cobalt II complexes are prepared in the absence of air is in accord with this. This is further confirmed by the isolation of bis tri - 4 methyl - tri - (2 - pyridyl)amine cobalt III perchlorate by careful recrystallisation of the suspected cobalt II complex which failed to give satisfactory analytical data and also had a very low effective magnetic moment[91].

The electronic spectra of the cobalt II complexes are entirely consistent with an octahedral stereochemistry. Though three spin allowed transitions from the ground state may be expected

ν_1 - ${}^4T_1 \longrightarrow {}^4T_{2g}$

ν_2 - ${}^4T_1 \longrightarrow {}^4A_{2g}$

ν_3 - ${}^4T_{1g} \longrightarrow {}^4T_{1g}$ (P)

only two are observed since the ${}^4T_{1g} \longrightarrow {}^4A_{2g}$ being a two election transition is usually obscured. The lowest energy band between 10.5 - 12 kK may be assigned as ${}^4T_{1g} \longrightarrow {}^4T_{2g}$ (ν_1) and the band between 22 and 23 kk as ${}^4T_{1g} \longrightarrow {}^4T_{1g}$ (P) (ν_3). Using Lever's graphical method[79] the value of Dq/B was read off directly knowing the value of the ratio of the transition energies ν_3/ν_1. Using this value of Dq/B the value of ν_3/B was then read off, the values of the ligand field splitting parameter Δ was thus evaluated to be 12.95 kK for 4 - methyl and 5 - methyl 2 - pyridyl

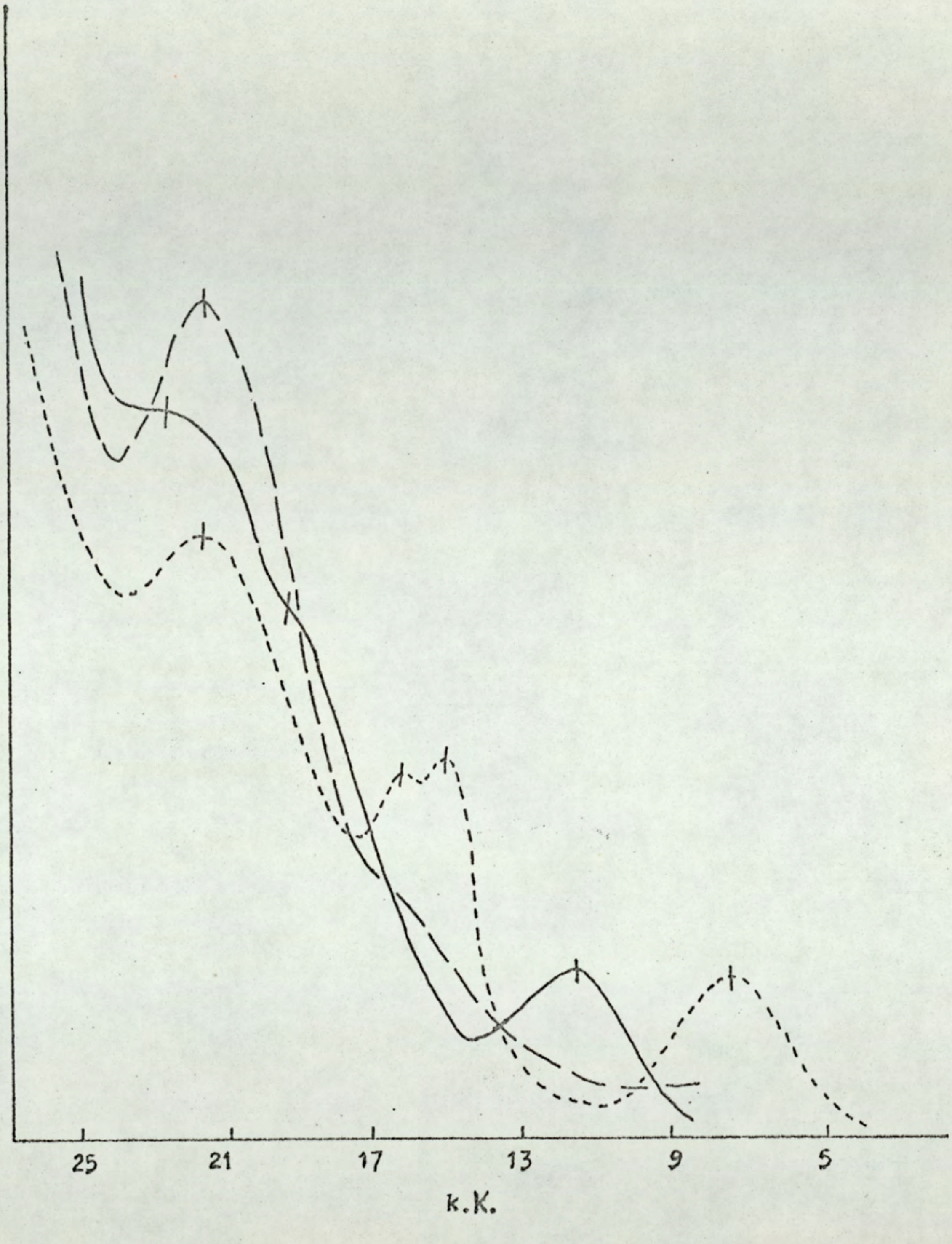


Fig4.2. Diffuse reflectance spectra of

———— $[Co(4mpdpa)_2](ClO_4)_2$

- - - - - $[Co(4mpdpa)_2][Co(OH)_4](ClO_4).7H_2O$

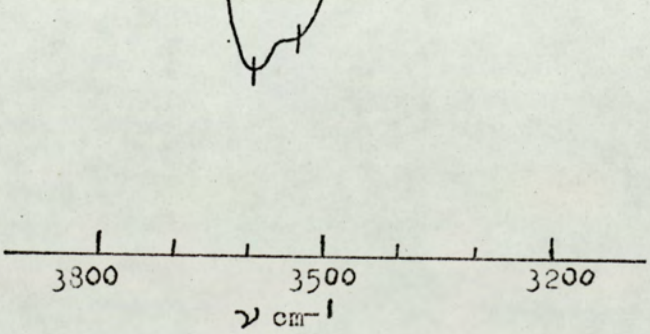
— — — $[Co(4mpdpa)_2](ClO_4)_3$

di - (2 pyridyl)amines and 12.1 kK for 6 - methyl 2 pyridyl di - (2 pyridyl)amine. The reduced racah parameter B$'$ of approximately 800 cm^{-1} for 4- and 5-mpdpa and 900 cm^{-1} for the 6-methyl ligand were obtained. Apart from the fact that $[Co\ (6\ mpdpa)_2]\ (ClO_4)_2$ seems less covalent than the corresponding nickel II complex, these data agree well with values estimated with respect to nickel II[92]. The above values of Δ and B lead us to expect the weak two electron transition $^4T_{1g} \longrightarrow {}^4A_{2g}$ (ν_2) close to 23 kK hence the shoulder observed close to 19 kK is probably a spin forbidden transition $^4T_{1g}(F) \longrightarrow {}^2T_{1g}(G)$ similar to that observed for tris di - (2 - pyridyl)amine cobalt II perchlorate[84].

b) <u>Cobalt III complexes:</u> In contrast to the experience with tri (2 - pyridyl)amine, complexes of 4 - methyl and 5 - methyl 2 - pyridyl di - (2 - pyridyl)amine with cobalt III were readily prepared. They are bright yellow diamagnetic materials which dissociate as 1 : 3 electrolytes in nitromethane when prepared as the perchlorate salts (Table 4.4). The electronic spectrum shows one spin allowed band at approximately 22 kK for both $[Co\ (4\ mpdpa)_2]\ (ClO_4)_3$ and $[Co\ (5\ mpdpa)_2]\ (ClO_4)_3$ which may be assigned in the terminology of O_h symmetry as $^1A_{1g} \longrightarrow {}^1T_{1g}$. Under our experimetal conditions no splitting of this band was observed. Higher frequency d — d bands are masked by ligand absorptions. The position of the $^1A_{1g} \longrightarrow {}^1T_{1g}$ band may be compared with that for $[Co\ (2 - 2'\ bipyridyl)_3]^{3+}$ at 22.3 k.K. [100].

The preparative conditions for the cobalt III complex of 4 - methyl - 2 - pyridyl di - (2 - pyridyl)amine was varied in the hopes of isolating an intermediate in the oxidation of the

Cobalt II system. Using acetone as solvent a green paramagnetic material was reproducibly obtained which on recrystallisation from ethanol afforded a compound analysing for $[\text{Co III}\ (4\text{mpdpa})_2]\ [\text{Co II}\ (\text{OH})_4]\ \text{ClO}_4.7\text{H}_2\text{O}$ that the ion $[\text{Co III}\ (4\text{mpdpa})_2]^{3+}$ is present is proved by infra red and electronic spectroscopy. The diffuse reflectance spectrum (Table 4.4 Compound 7) contains additional bands characteristic of a tetrahedral cobalt II species and the positions of the observed bands at 15.7 kK and 16.8 kK agree well with those reported for the cobalt II ion in a tetrahedral Co O_4 environment ($[\text{Co(OH)}_4]^{2-}$ ---- 16.1 and 17.2 kK)[101]. Direct titration of the complex with E.D.T.A. suggests 50% of the cobalt to be Co II and the effective magnetic moment of 4.3 B.M is compatible with cobalt II in a tetrahedral environment. The infra red spectrum in addition to containing evidence for the presence of water shows two sharp bands at 3,525 cm^{-1} and 3,600 cm^{-1} which are compatible with bonded OH groups. Thus there is reasonable



support for a surprising formulation, however the compound does not help in the elucidation of the mechanism of formation of the $[\text{Co}\ (4\text{mpdpa})_2]^{3+}$ ion.

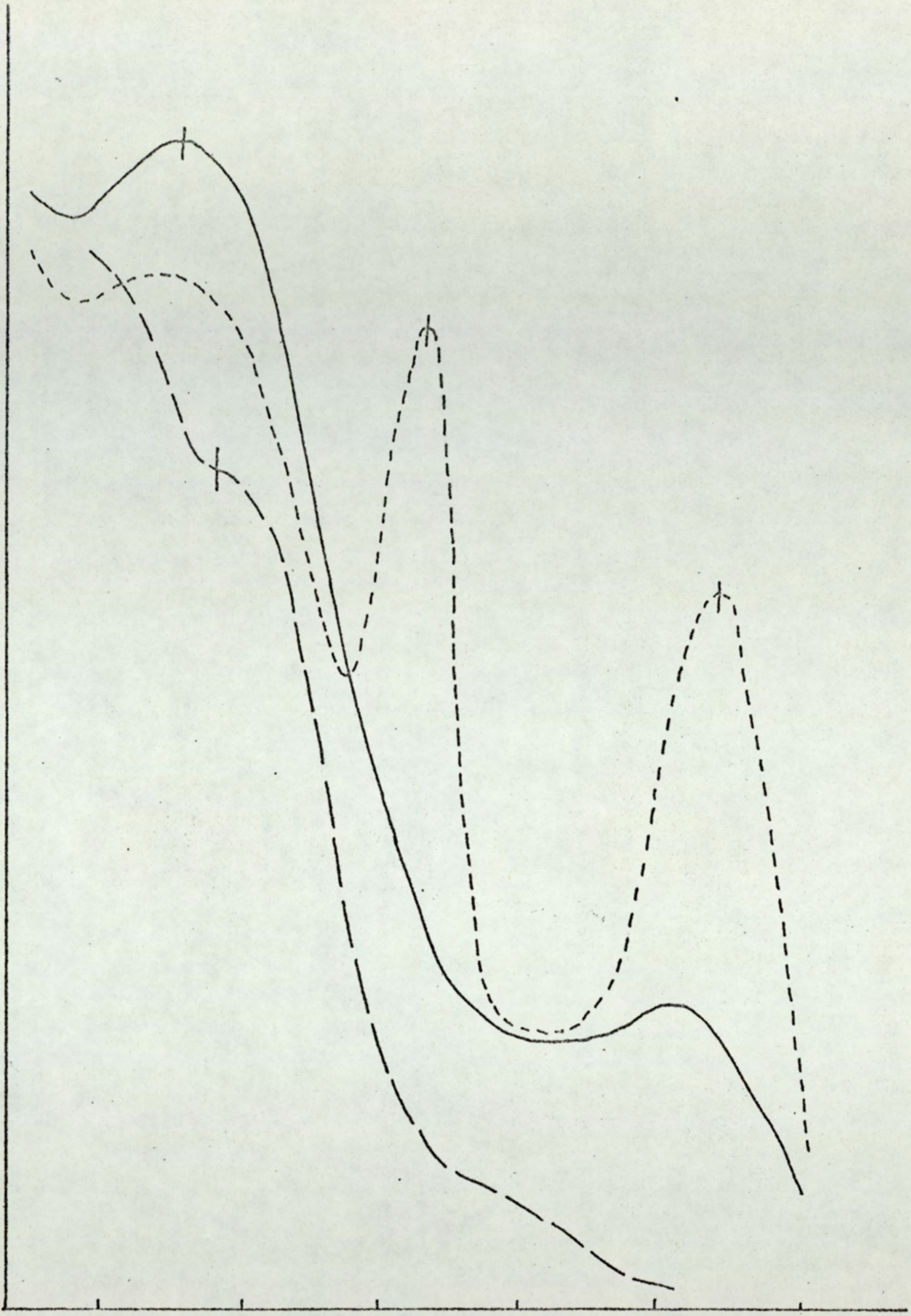


Fig.4.3 Diffuse reflectance spectra of

— — —$[Co(4mpdpa)(NO_2)_3]$

———$[Co_2(4mpdpa)_2(NCS)_3](ClO_4)_3$

- - - - -$[Co_2(4mpdpa)_2(NCS)_3][Co(NCS)_4](ClO_4)$

The reactivity of the new cobalt III complexes of substituted tri - (2 - pyridyl) amines with nucleophiles such as nitrite and thiocyanate ions was investigated. The nitrite ions reacted smoothly replacing one of the pyridylamine ligands resulting in the formation of orange coloured uncharged complexes (Compounds 8 and 9 Table 4.1) Analytical data support the formulations $[\text{Co (4 or 5 mpdpa) } (NO_2)_3]$ and infra red spectroscopy clearly indicates the presence of terdentate 4 - methyl and 5 - methyl - 2 - pyridyl di - (2 - pyridyl)amine and also that nitro ($\nu\ NO_2$ 1420, 1300, 830 and 820 cm^{-1}) rather than nitrito groups are present.[6] The electronic spectra are also consistent with a $Co\ N_6$ chromophore.

The reaction with thiocyanate was much more complex. Thiocyanate is able to co-ordinate to a metal ion as a unidentate ligand in two ways, either through the nitrogen atom ---- isothiocyanato, or the sulphur atom - thiocyanato. The group may also function as a bridging ligand. The type of bonding is usually distinguished by infra red spectroscopy. The infra red spectrum of the orange-brown complex formed at room temperature (compound 10 Table 4.4) shows the $C \equiv N$ stretching vibration to be split into two sharp bands at 2103 and 2060 cm^{-1} with a shoulder at 2070 cm^{-1} which might suggest that the thiocyanate groups are weakly bridging. There is also indication of the presence of terdentate 5 - methyl - 2 pyridyl di - (2 pyridyl)amine and ionic perchlorate. Conductance data supports dissociation to a 1 : 3 electrolyte and together with analytical data the following formulation is proposed $[\text{(5 mpdpa) Co III } (NSC)_3 \text{ Co III (5 mpdpa)}] (ClO_4)_3\ H_2O$. This compound is weakly paragmagnetic (μ eff = 0.8 B.M) either due to a temperature independent paramagnetism (T.I.P) or due to contamination with cobalt II species. The latter cannot be ruled out as on standing the compound becomes greenish-brown for which both magnetic and electronic spectral data suggest the formation of a cobalt II species. The bright green compound isolated on heating the above reaction mixture is distinctly paramagnetic ($\chi_g = 8.20 \times 10^{-6}$ c.g.s units) The infra red spectrum shows that $\nu C \equiv N$ is split into a sharp band at 2103 cm^{-1} and a broad band 2060 cm^{-1}. Perchlorate is distinctly ionic and comparatively weaker than Compound 10 and the pyridylamine ligand is terdentate. The electronic spectrum clearly indicates that the presence of a tetrahedral cobalt II species and the bands at 7.5 kK and 16.0 kK support the presence of tetra isothiocyanato cobaltate II ion (c.f 7.8 kK and 16.3 kK obtained for $Hg[Co(NCS)_4]$ and $[(CH_3)_4N]_2[Co(NCS)_4]$ [103]. The spectral and analytical data support the formulation $[(5\ \text{mpdpa})\ Co\ III\ (NSC)_3\ Co\ III\ (5\ \text{mpdpa})][Co\ II\ (NSC)_4]\ ClO_4$. The ease of reduction of cobalt III to cobalt II under these conditions is of interest.

The failure to isolate any complex that might reasonably be regarded as an intermediate in the oxidation of cobalt II to cobalt III using substituted tri - (2 - pyridyl)amines prompted the investigation of the oxidation of tris di - (2 - pyridyl) amine cobalt II perchlorate. The action of hydrogen peroxide on this complex resulted in the formation of a red-brown material (Compound 12 Table 4.1) which was diamagnetic supporting the formation of a cobalt III species. The analytical data leads to the stoichiometry $Co\ (\text{dipyam})_2\ (O_2)\ ClO_4$. The presence of a peroxo group is indicated by a strong infra red band at 885 cm^{-1} which is not characteristic of the organic ligand and may

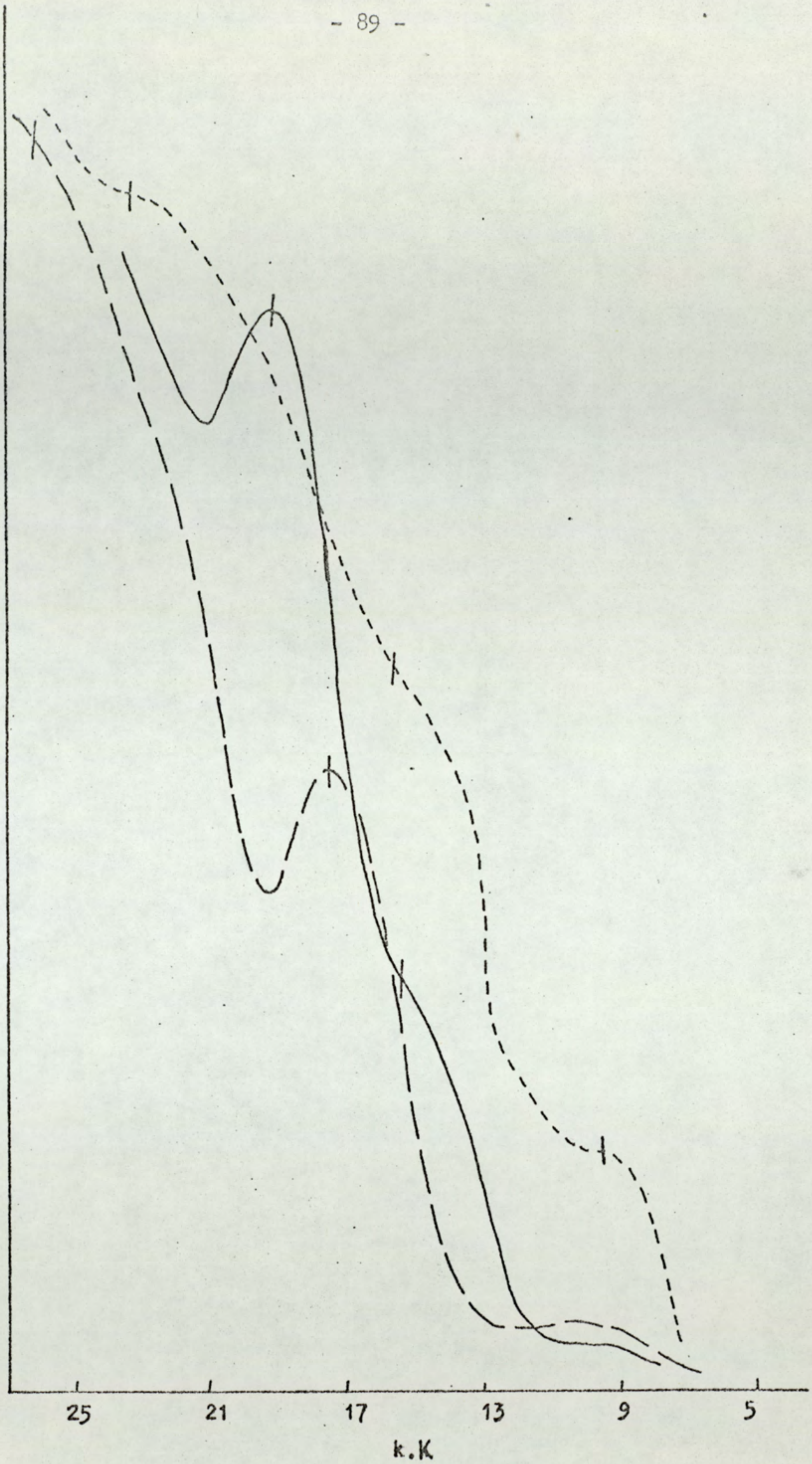


Fig.4.4 Diffuse reflectance spectra of

——— $[Co(dipyam)_2O]_2(ClO_4)_2$

- - - - - - $[Co(dipyam)_2Cl_2](ClO_4$

— — — $[Co(dipyam)_2Br_2]Br$

therefore be assigned as ν (0 - 0)[104]. The choice between a monomeric structure (Λ_M = 75.D.M.F.) or a dimeric structure (Λ_M = 150 D.M.F) is not easily made on the basis of conductivity measurements since the above figures are, or could be, interpreted either as 1 : 1 or 1 : 2 electrolytes. A dimeric formulation is used in Table 4.1 since the precedents in cobalt III chemistry are for bridging rather than chelating peroxo groups[105]. However, di -μ- peroxo compounds are rare, even ethylene diamine affords a μ- peroxo -μ- ethylene diamine intermediate[106].

The reaction of peroxo complexes of cobalt III and ethylene diamine[106] or other polyammines[107] with strong hydrochloric acid usually affords the thermodynamically less stable trans isomer of the dichloro complex. In the case of di - (2 pyridyl)amine there is doubt about the feasibility of a trans configuration as a recent crystal structure determination has shown that the copper II ion in bis di - (2 - pyridyl)amine copper II perchlorate to be in a distorted tetrahedral environment[108]. However, rather more general surveys of the chemistry of terdentate pyridylamine ligands suggests that the flexibility of the rings may be sufficient to permit a trans stereochemistry in some cases[82, 109]. It was therefore of interest to study the reaction of the above peroxo complex with concentrated hydrochloric and hydrobromic acids. The reaction reproducibly afforded the pale green chloro complex and the green-brown bromo complex (Compounds 13 and 14, Table 4.1). The presence of protonated di - (2 - pyridyl)amine is suggested by the infra red spectra, in particular an N-H band at 3390 cm^{-1} is characteristic of this species. The chloro complex comes down as the perchlorate but apparently in the bromo complex the bromide ion is sufficiently large to effect precipitation. The electronic spectrum especially that of the chloro complex closely resembles that reported for trans $[Co\ (en)\ Cl_2]\ Cl$ (en - ethylene diamine) and other trans Co III chloro complexes[110]. The diamagnetism of these complexes excludes the possible presence of a cobalt II species as the acid decomposition of μ- peroxo pentamino cobalt III is known to give cobalt II species.

It has been shown that a study of the infra red spectra of complexes in the metal ligand vibration region can be a useful criterion in the assignment of stereochemistry [II,III]. The complexity of the far infra red spectra of the two compounds did not permit the confident assignment of cobalt - halogen vibrations,, however, the absorptions at 228 and 211 cm^{-1} in the bromo complex may be tentatively assigned as ν_{as} Co - Br. Since $\nu_{Br}/\nu_{Cl} = 0.7$, the ν_{as} Co - Cl is probably the band at 357 cm^{-1}. The other absorptions though complex are most likely due to metal - nitrogen vibrations. Though only one band due to the asymmetric metal - halogen stretch is expected in a trans complex, the appearance of more than one band does not necessarily exclude this. However, if the complexes are trans dihalogeno complexes then isomerisation to the cis isomer should be possible, but repeated dissolution in water and evaporation to dryness led to the recovery of the unchanged complexes.

In conclusion, it must be mentioned that the work done by Barnard[19] on the bis tripyridylamine cobalt II complexes established the existence of a spin 'crossover' situation in the perchlorate complex. This anomalous magnetic behaviour was also shown to be anion dependent which however, is a common phenomenon in d^7 'crossover' systems.[95-97] Barnard also showed that the change of spin state was accompanied by drastic changes in the far infra red spectrum. It was therefore hoped that the infra red spectra of the cobalt II complexes of the corresponding 4 - methyl and 5 - methyl substituted ligands will indicate that the low magnetic moments of these complexes[91] could be attributable to the existence of a mixture of spin states viz. ^4T and ^2E. The results obtained however, indicated that the low magnetic moments were due to the presence of a low spin contaminant which has been found to be the corresponding cobalt III complex.

Though it was initially hoped, that the slightly greater ligand field splitting parameter Δ for the substituted ligands, together with the low symmetry component of the ligand field arising from the presence of the methyl groups might favour the ^2E state of the cobalt II ions the results obtained however, suggest that the anomalous magnetic behaviour is unique for the parent compound. Not only does the change of anion from ClO_4^- to PF_6^- remove the anomalous magnetic behaviour of $[Co(tripyam)_2](ClO_4)_2$, but also the introduction of substituents does likewise. The phenomenon is therefore a function of the lattice $[Co(tripyam)_2](ClO_4)_2$ rather than a function only of the cation.

The crystal field splitting energies Δ and the Racah interelectronic repulsion parameters B have been calculated for the 4 - methyl, 5 - methyl and 6 - methyl substituted tri - (2 - pyridyl)amines with respect to cobalt II. The cobalt III complexes of 4 methyl and 5 methyl 2 - pyridyl di - (2 - pyridyl)amine have been prepared. A green coloured complex containing both cobalt III and cobalt II has been isolated. Substitution reactions of these complexes with nitrite and thiocyanate ions have been studied.

The reaction of hydrogen peroxide on the tris di - (2 - pyridyl)amine cobalt II perchlorate resulted in the formation of a peroxybridged cobalt III species. The action of concentrated hydrochloric and hydrobromic acid on this complex formed dihalogeno cobalt III complexes which are suspected to have trans halogeno ligands.

CHAPTER V

Some aspects of iron complexes with - 2 pyridylamine ligands

Most co-ordination compounds are considered to be magnetically dilute as the interactions between metal atoms is negligible. Those in which the interaction is considerable are the ferromagnetic and antiferromagnetic compounds. Polynuclear compounds which are formed by the bridging of two or more mononuclear complex ions form the intermediate class.

The magnetic behaviour of simple mononuclear iron III complexes is generally uncomplicated. The low spin compounds exist in a doublet ground state - $^{2}T_{2}$, with one unpaired electron and the high spin compounds exhibit the $^{6}A_{1}$ or sextet ground state with five unpaired electrons. The symmetry adapted by such compounds is either octahedral or tetrahedral. Deviations from the normal low spin or high spin behaviour can arise for complexes of iron III when the ligand field strength Δ is of the same order as the mean pairing energy whereby the $^{2}T_{2}$ and $^{6}A_{1}$ states can exist in thermal equilibrium. This situation is known to exist in the dialkyl thiocarbamato complexes of iron III[25]. Very recently, Fitzsimmons[30] used Mossbauer spectroscopy to demonstate unambiguously the existence of a thermal equilibrium between sextet and doublet electronic states in some tris (mono thio - β - diketonato) iron III complexes.

The quartet ground state for iron III-^{4}T, which is forbidden in an octahedral stereochemistry is known to be stabilised in a square pyramidal geometry. The five co-ordinate halogeno bis (N.N dialkyl dithio carbonato) iron III complexes[24] have been shown to stabilise iron III in the unusual ground state ^4T of intermediate spin $S = 3/2$ (μeff = 3.9 BM). The Mossbauer spectra of these complexes[113] have been found to have a pronounced quadrupole splitting (2.58 mm sec$^-$) which is consistent with the very large electric field gradient generated by the asymmetry of the complex and the d - electron distribution.

On the other hand, binuclear complexes of iron III can give rise to paramagnetic moments which are not characteristic of any of these ground states - $^6A_1$, $^4T_1$ or $^2T_2$. These anomalous moments could arise due to antiferromagnetic interactions between iron atoms of similar or different spin states i.e. ($^6A_1$ + $^6A_1$) or ($^6A_1$ + $^4T_1$) etc.

The direct reaction of iron III salts with chelates like 2 . 2′bipyridyl and 1 : 10 phenanthroline are known not to yield the tris chelated iron III species, instead brown binuclear products are obtained. These compounds especially $[\text{phen}_2\,\text{Fe(OH)}]_2\text{Cl}_4$ have been the subject of much investigation[60-65]. The low moment of these complexes was initially attributed to interaction between the iron atoms (with spin state $S = \frac{1}{2}$) via the oxygen bridge where a π bonding mechanism can operate between the metal-ligand - metal system. The presence of an Fe - O - Fe system can be identified from the infra red spectra by a band in the region 800 - 900 cm^{-1} which is associated with metal - oxygen - metal vibration. The magnetic behaviour of a number of oxygen bridged shiff base complexes of iron III was explained by Lewis[114] in terms of interaction between two iron atoms with $S = 3/2$ or $S = 5/2$ ground states. The anomalous moment of the analogous 2 . 2′bipyridyl and 1 : 10 phenanthroline complexes was subsequently reinterpreted in terms of an interaction between two iron atoms with $S = 5/2$ spin state[65].

More recently, Fitzsimmons[39] studied the Mossbauer spectra of a few of these compounds and found that the isomer shifts were consistent with $S = 5/2$ spin state (δ values in the range 0.6 - 0.7 mm/sec w.r.t. nitroprusside). Reiff et.al[115] initially found it difficult to compromise the large quadrupole splitting in these compounds to be generated due to lattic effect alone. However, subsequent results[116] obtained from detailed magnetic, Mossbauer and spectroscopic studies on a variety of oxygen bridged binuclear compounds were consistent with a spin of $S = 5/2$ for each iron atom. It is evident from this "that whilst the Mossbauer technique looks at individual ions and provides information about the individual spin states, the measurement of the paramagnetic susceptibility over a temperature range gives information on the nett spin-state of pairs of ions".[39]

The only reports on iron chemistry on the 2 - pyridylamine ligands —— di (2 - pyridyl)amine and tri - (2 - pyridyl)amine have been confined to complexes of iron II[38,40]. There is no indication of steric objection to co-ordination with tervalent ions of the first transitional series as complexes of chromium III[87] and cobalt III are known. The ligand field strengths Δ of di - (2 - pyridyl)amine and tri - (2 - pyridyl)amine with respect to chromium III has been found to be less than ethylene diamine (en) whereas Δ of di - (2 - pyridyl)amine $\backsim$ en $<$ tri - (2 - pyridyl)amine with respect to nickel II[82]. The Δ values of the 4 - methyl and 5 - methyl derivatives of tri - (2 - pyridyl)amine have been found to be similar to the parent ligand with respect to nickel II[92]. The tris di - (2 - pyridyl)amine iron II complex has been found to be spin free whereas the bis complex of iron II with terdentate tri - (2 - pyridyl)amine is spin paired with a microsymmetry close to O_h [38].

It was of interest to see whether terdentate tri - (2 - pyridyl)amine will stabilise the ^{2}T ground state of iron III or whether the ligand field strength will be such as to permit the existence of a spin equilibrium $^{6}A_{1} \longleftrightarrow {}^{2}T_{2}$. Furthermore, the lack of information on the iron III complexes of these ligands also lent support for this investigation.

Experimental

Ion exchange studies were done using Deacidite FF as the anion exchange resin and Zeocarb 225 as the cation exchange resin.

1. Dichloro bis di - (2 - pyridyl)amine iron II

A hot solution of ferric chloride (0.3g) in acetonitrile (10 ml) and di methoxypropane (5 ml) was refluxed with a solution of di -(2 - pyridyl)amine (0.5g) in acetonitrile (10 ml) adn di methoxy propane (5 ml) for 30 minutes. On cooling a yellow crystalline precipitate was formed. This compound was filtered off washed with di methoxy propane and dried in vacuo.

2. Di bromo bis di - (2 - pyridyl)amine iron II

Ferric bromide (0.5g) in acetonitrile (10 ml) and di methoxy propane (10 ml) was heated for 10 minutes and added to a solution of di -(2 - pyridyl)amine (0.5g) in acetonitrile (10 ml) and di methoxy propane (5 ml) and refluxed for 15 minutes. A bright yellow compound was immediately precipitated. This was filtered off, washed with di methoxy propane and dried in vacuo.

3. Dichloro di - (2 - pyridyl)amine iron II

Ferric chloride (0.3g) in ethanol (10 ml) and di methoxy propane (10 ml) was refluxed for 10 minutes and added to a hot solution of di - (2 - pyridyl)amine (0.5g) in ethanol (10 ml) and di methoxy propane (5 ml). The mixture was refluxed for a further 30 minutes. On cooling a greenish yellow compound was precipitated. This was filtered off, washed with di methoxy propane and dried in vacuo.

4. Tris di - (2 - pyridyl)amine iron II perchlorate

Ferric perchlorate (0.5g) in ethanol (10 ml) and di methoxy propane (5 ml) was refluxed with di - (2 - pyridyl)amine (0.5g) in ethanol (10 ml) and di methoxy propane (5 ml) for 30 minutes. On cooling yellow-green crystals were precipitated. This was filtered off and washed with di methoxy propane.

5. Bis tri - (2 - pyridyl)amine iron II perchlorate

Ferric perchlorate (0.5g) in ethanol (10 ml) and dimethoxy propane (10 ml) was refluxed with tri - (2 - pyridyl) amine (0.5g) in ethanol (10 ml) for 30 minutes. On cooling orange-red crystals of a compound were precipitated. This was filtered off and washed with di methoxy propane.

6. Bis (di - 2 - pyridylammonium) μ - oxo - hexachlorodeferrate (III) monohydrate

Anhydrous ferric chloride (0.3g) in ethanol (10 ml) was added dropwise to a cold solution of di - (2 - pyridyl) amine (0.5g) in ethanol (10 ml). A bright yellow product wasformed immediately. This was filtered off and washed thoroughly with ethanol.

7. μ- oxo - tetra chloro tris di - (2 - pyridyl)amine di - iron III penta hydrate

Ferric chloride (0.3g) in ethanol or acetonitrile (10 ml) was refluxed with di - (2 - pyridyl)amine (0.5g) in acetonitrile or ethanol (10 ml) for 30 minutes. The bright yellow compound which was initially formed dissolved and on cooling a reddish brown compound was precipitated. This was filtered off and washed with ethanol.

8. μ- oxo - di bromo di hydroxo tris di - (2 - pyridyl)amine di - iron III bromide

Ferric bromide (0.5g) in acetonitrile (10 ml) was refluxed with di - (2 - pyridyl)amine (0.5g) in acetonitrile (10 ml) for 30 minutes. On cooling a dark brown product separated out. This was filtered off and washed with acetonitrile and dried in vacuo.

9. Bis- (isothiocyanato) bis di - (2 - pyridyl)amine iron (III) Tetra (iso thiocyanato) di - (2 - pyridyl)amine ferrate III

Ferric chloride (0.3g) in ethanol (10 ml) was added to potassium thiocyanate (1.0g) in ethanol (10 ml) was then filtered to a solution of di - (2 - pyridyl)amine (0.5g) in ethanol (10 ml). The dark red solution was refluxed for 20 minutes and on cooling violet-black crystals of a compound separated out. This was filtered, washed with ethanol and ether and dried in vacuo.

10. Bis tri - (2 - pyridyl)amine iron II tetra (isothiocyanato) ferrate (11)

To a solution of ferrous chloride (0.25g) in ethanol (10 ml) was added potassium thiocyanate (0.7g) in ethanol (10 ml) (Nitrogen was bubbled through this solution) and filtered to a solution of tri - (2 - pyridyl)amine (0.5g) in ethanol (10 ml) and refluxed for 10 minutes. On setting a side reddish brown crystals separated out. This was filtered, washed with ethanol and dried under vacuo.

11. Trichloro tri - (2 - pyridyl)amine iron III

Ferric chloride (0.3g) in ethanol (10 ml) was added dropwise to a cold solution of tri - (2 - pyridyl)amine (0.5g) in ethanol (10 ml). A bright yellow product separated out immediately. This was filtered off and washed with ethanol.

12. Bis (tri pyridyl ammonium) μ - oxo hexachloro di ferrate (III)

Ferric chloride (0.3g) in ethanol (10 ml) was heated to boiling and added dropwise to a hot solution of tri - (2 - pyridyl)amine (0.5g) in ethanol (10 ml) and refluxed for 10 minutes. A yellow product separated out on cooling. This was filtered off and washed with ethanol.

13. Di (isothiocyanato) bis tri (2 - pyridyl)amine iron (III)
tri - (2 - pyridyl)amine tetra (isothiocyanato) ferrate (III)

Potassium thiocyanate (1.0g) in ethanol (10 ml) was added to a solution of ferric chloride (0.3g) in ethanol (10 ml). This red solution was filtered into tri- (2 - pyridyl)amine (0.5g) in ethanol (10 ml) and refluxed for 20 minutes. On cooling dark violet crystals separated out. This was filtered, was with ice-cold ethanol and ether.

14. Di (isothiocyanato) bis 4 - methyl - 2 pyridyl di -(2 - pyridyl) amine iron II

Potassium thiocyanate (0.7g) in ethanol (10 ml) was added to a solution of ferrous chloride (0.2g) in ethanol. This was filtered into a cold solution of 4 - methyl 2 -pyridyl di (2-pyridyl)amine (0.5g) in acetone (10 ml) and was stirred by bubbling a stream of nitrogen. After about 30 minutes a dark brown product separated out. This was filtered and washed with ice-cold ethanol. (On warming the colour of the complex changed rapidly to reddish brown.)

15. Bis 4 methyl - 2 - pyridyl di (2 pyridyl)amine iron II tetra (isothiocyanato) ferrate (II)

Iron (II) chloride tetrahydrate (0.3g) in ethanol (10 ml) was mixed with potassium thiocyanate (0.7g) in ethanol (10 ml) and filtered into a solution of 4 - methyl - 2 - pyridyl di - (2 - pyridyl)amine (0.5g) in ethanol (10 ml) and refluxed for 20 minutes under an atmosphere of nitrogen. On setting aside reddish-brown crystals separated out. This was filtered off and washed with ethanol.

16. Tri chloro 4- methyl - 2 - pyridyl di - (2 - pyridyl)amine iron (III)

Anhydrous Iron (III) chloride (0.3g) in ethanol (10 ml) was added to an ethanolic solution (10 ml) of 4 methyl - 2 - pyridyl di - (2 pyridyl)amine (0.5g). The yellow product that separated out was filtered and washed with ethanol. An identical product was obtained even when the solutions were heated.

17. Bis 5 methyl - 2 - pyridyl di - (2 - pyridyl)amine iron (II) tetra (isothiocyanato) ferrate (II)

Iron II chloride tetrahydrate (0.3g) in ethanol (10 ml) was added to potassium thiocyanate (0.7g) in ethanol (10 ml). This solution was filtered into an ethanolic solution (10 ml) of

5 - methyl - 2 - pyridyl di - (2 pyridyl)amine (0.5g) was refluxed for 15 minutes. On setting aside a reddish brown complex separated out. This compound was filtered off and washed with ethanol.

18. Bis 5 - methyl - 2 - pyridyl di - (2 - pyridyl)ammonium, - μ - oxo - hexachloro diferrate (III)

Anhydrous iron (III chloride (0.3g) in ethanol (10 ml) was added dropwise to an ethanolic solution (10 ml) of 5 - methyl 2 - pyridyl di - (2 - pyridyl)amine (0.5g) and refluxed for 10 minutes. On cooling an orange-yellow product separated out. (This was identical with the product obtained in the cold). The product was filtered off and washed with ethanol.

Table 5.1

Physical and Analytical data of iron II complexes obtained from iron III salts

Compound	Found				Required				Λ	μ_{eff} BM	Mossbauer parameters mm/sec	
	C	H	N	Fe	C	H	N	Fe			Isomer shift*	Quad split ΔE_q
$[Fe(dipyam)_2 Cl_2]$	51.7	3.9	18.3	12.6	51.2	3.8	17.9	12.0	25^a	5.36	0.94	2.40
$[Fe(dipyam)_2 Br_2]$	43.4	3.2	15.0	10.5	43.0	3.2	15.1	10.0	85^a	5.4	0.95	2.30
$[Fe(dipyam) Cl_2]$	40.8	3.2	14.4	19.3	40.3	3.0	14.1	18.8	35^a	5.2	----	----
$[Fe(dipyam)_3](ClO_4)_2$	46.6	3.6	15.9	6.9	46.9	3.5	16.4	7.3	160^b	5.4	----	----
$[Fe(tripyam)_2](ClO_4)_2$	48.4	3.5	15.1	6.9	47.9	3.3	14.8	7.6	155^b	1.0	0.37	0.0

a - Dimethyl formamide as solvent

b nitromethane as solvent

*w.r.t. iron metal

Table 5.2

Analytical conductivity and magnetic data of some iron (II) isothiocyanato complexes of tri - 2 - pyridylamines

		Found				Required				Λ_M	μ_{eff}
No	Compound	C	H	N	Fe	C	H	N	Fe	(CH_3NO_2)	B.M
1	$[Fe\ (tripyam)_2][Fe\ (NCS)_4]$	48.2	2.8	20.0	13.0	48.6	2.8	20.0	13.4	100	3.80
2	$[Fe\ (4mpdpa)_2(NCS)_2]\ H_2O$	57.1	4.0	19.5	8.2	57.1	4.2	19.6	7.8	30	5.53
3	$[Fe\ (4mpdpa)_2][Fe(NCS)_4]\ H_2O$	48.4	3.8	18.9	13.0	48.8	3.4	19.0	12.6	100	3.86
4	$[Fe\ (5mpdpa)_2][Fe(NCS)_4]$	50.2	3.3	19.5	12.5	49.8	3.2	19.3	12.9	90	3.9

Table 5.3

Spectroscopic data of isothiocyanato iron II complexes

Compound	Colour	Electronic Spectra kK	Infra red spectra ν C≡N cm^{-1}	Mossbauer parameters mm/sec^{-1}	
				δ*	ΔEq.
$[Fe(tripyam)_2][Fe(NCS)_4]$	Red-Brown	23.0, 19.8 sh 5.6, 4.8 sh	2068 sh 20605 sp	0.37	0.0
$[Fe(4mpdpa)_2(NCS)_2]H_2O$	Brown	23.0, 18.8, 10.8	2068 s.sp	1.10	1.17
$[Fe(4mpdpa)_2][Fe(NCS)_4]H_2O$	Orange-brown	23.0, 19.6 sh 5.8. 4.8 sh	2085 sh 2057 s.sp	0.37	0.20
$[Fe(5mpdpa)_2][Fe(NCS)_4]$	Red-Brown	23.0, 19.8 sh 5.6, 4.8 sh	2090 sh 2058 s.sp	0.35	0.20

*w.r.t iron metal

Table 5.4

Analytical data of oxygen bridged binuclear iron III complexes of 2 - pyridylamines

No	Compound	Colour	Found					Required				
			C	H	N	Hal	Fe	C	H	N	Hal	Fe
1	$(\text{dipyam H})_2[(\text{Cl}_3\ \text{Fe})_2\text{O}]\ \text{H}_2\text{O}$	Yellow	34.4	2.7	11.5	29.3	16.4	34.2	3.1	11.9	30.0	15.9
2	$[\text{Fe}_2(\text{dipyam})_3\ \text{Cl}_4\ \text{O}]\ 5\ \text{H}_2\text{O}$	Red-Brown	41,0	3.6	14.0	16.0	13.3	40.9	4.2	14.3	16.1	12.7
3	$[\text{Fe}_2(\text{dipyam})_3\ \text{Br}_2(\text{OH})_2\ \text{O}]\ \text{Br}$	Brown	38.7	3.3	13.1	25.6	12.6	38.7	3.4	13.6	26.0	12.3
4	$(\text{tripyam H})_2[(\text{Cl}_3\ \text{Fe})_2\ \text{O}]$	Yellow	43.5	3.3	14.0	25.2	14.0	42.9	3.0	13.3	25.4	13.3
5	$(5\ \text{mpdpaH})_2[(\text{Cl}_3\ \text{Fe})_2\ \text{O}]$	Orange-yellow	44.4	3.7	13.1	24.9	13.3	44.3	3.5	12.9	24.6	12.9

Table 5.5

Magnetic, conductivity, infra red and Mossbauer spectroscopic data of the binuclear iron III complexes

Complex	μ_{eff} B.M	Λ_M D.M.F	Some infra red absorptions ν cm^{-1}	Mossbauer parameters I. S[*]	Q.S.
$(dipyam\ H)_2 [(Fe\ Cl_3)_2\ O]. H_2O$	2.3	100	3320 s.sp (N-H) 890 s.br(Fe-O-Fe) 375 s 369 s (Fe-Cl) 216	0.26	1.38
$[Fe\ (dipyam)_2\ Cl\ O\ Fe\ (dipyam)\ Cl_3]. 4\ H_2O$	2.2	35	3530 br (H_2O) 845 s.br (Fe-O-Fe) 360 s 355 sh 343 s (Fe-Cl)	0.33 0.33	1.36 0.66
$[Fe\ (dipyam)_2\ Br\ O\ Fe\ (dipyam)(OH)_2\ Br]\ Br$	2.1	200	800 s (Fe-O-Fe) 286 m 250 m (Fe-Br)	0.43 0.42	0.86 0.53
$(Tripyam\ H)_2 [(Fe\ Cl_3)_2\ O]$	2.0	155[a]	890 s.br (Fe-O-Fe) 360 s.br 317 s.sp (Fe-Cl)	0.20	1.19
$(5 - mpdpaH)_2\ [(Fe\ Cl_3)_2\ O]$	2.2	100[a]	863 s.br (Fe-O-Fe) 360 s.br 318 s.sp (Fe-Cl)	0.23	1.25

[*] w.r.t. natural iron [a] - nitromethane

Table 5.6

Infra red absorptions in the region (4000 - 600 cm^{-1}) of some di -(2 pyridyl)amine complexes

$[\text{dipyam H}][\text{Fe Cl}_4]$ 1	$[\text{Dipyam H}]_2[(\text{Cl}_3\ \text{Fe})_2\text{O}]$ 2	$[\text{Fe}_2(\text{dipyam})_3\ \text{Cl}_4\text{O}]5\text{H}_2\text{O}$ 3	$[\text{Fe}(\text{dipyam})_2\ \text{Cl}_2]$ 4	Assignments
		3540 br		HOH stretch
3340 s	3320 s	3280 w	3270 w	N-H stretch
3080 w	3100 w	3180 w	3180 w	C-H stretch
3060 w	3080 w	3120 w	3120 w	
3020 w	3060 w	3060 w	3060 w	
	3030 w	3000 w	3020 w	
1655 s	1660 s	1650 sh	1630 s	C = C and C = N stretch
1640 sh	1640 sh	1630 s	1615 sh	
1620 sh	1620 sh	1600 s	1590 sh	
1605 s	1608 s	1585 s	1580 s	
1590 sh	1590 sh	1565 sh	1560 sh	
1560 s	1565 s	1560 s	1522 s	
1535 s	1540 sh	1520 w		
1490 w	1500 m	1505 w		
1450 s	1485 w	1470 s	1470 v.s	
1345 s	1458 s	1450 s	1430 s	
1315 m	1310 m	1410 s	1410 s	
	1310 m	1360 s	1365 s	

continued....

Table 5.6 continued

1	2	3	4	Assignments
1270 s	1270 m	1265 m	1270 m	
1245 s	1245 s	1235 s	1233 s	
1220 sh	1210 sh	1200 sh		
1170 s	1170 s	1165 sh	1210 sh	C-H bend in plan
1155 sh	1157 s	1160 s	1172 sh	
1040 w	1090 w	1120 sh	1160 s	
1010 m	1050 w	1055 w	1120 sh	
	1005 m	1012 m	1058 w	
		1005 sh	1010 m	
			1005 sh	
990 m	990 m	990 sh	960 w	
938 m	935 m	908 m	910 w	
			890 w	C-H bend out of plane
902 m	895 s br*	845 s br*	875 w	
865 w	845 w		865 w	
773 v.s	770 v.s	780 sh	840 w	
740 w	738 m	770 v.s	790 s	
725 w	725 m	745 m	770 v.s	
		740 sh	745 m	
		722 w	722 w	
670 w	675 w	643 m	650 sh	C-C deformation
640 sh	640 w	630 sh	640 w	
630 m			630 w	

* ν (Fe - O - Fe)

Table 5.7

Analytical data of some iron III complexes

No	Compound	Colour	Found					Required				
			C	H	N	Cl	Fe	C	H	N	Cl	Fe
1	$Fe_2(dipyam)_3(NCS)_6$	Violet-black	44.9	3.4	23.2	--	12.1	44.4	3.4	23.6	--	11.6
2	$Fe_2(tripyam)_3(NCS)_6$	Deep violet	50.4	3.2	21.4	--	10.0	50.8	3.0	21.0	--	9.5
3	Fe (tripyam) Cl_3	Yellow	44.4	3.1	13.6	25.7	14.1	43.9	3.0	13.6	25.8	13.6
4	Fe (4-mpdpa) Cl_3	Yellow	44.9	3.6	13.1	24.9	13.2	45.2	3.3	13.2	25.2	13.1

Table 5.8

Magnetic, conductivity, infra red and Mossbauer spectroscopic data of some iron III complexes

Complex	μ_{eff} B.M	Λ_M	Some infra red absorptions ν cm^{-1}	Mossbauer parameters I.S*	Q.S
$[Fe\ (dipyam)_2(NCS)_2][Fe\ (dipyam)(NCS)_4]$	5.7	94^a	2070s, 2035s, 2013 v s.1995 sh ($C \equiv N$); 295 285 sh	0.37	0.62
$[Fe\ (tripyam)_2(NCS)_2][Fe\ (tripyam)(NCS)_4]$	5.8	95^a	2065s sp 2050 sh. 2030 v s br ($C \equiv N$) 310 sh 295 v s	0.35	0.66
$[Fe\ (tripyam)\ Cl_3]$	5.6	25^b	354m, 310 v s.br 292 s sh (Fe-Cl) 221 s sp (Fe-N) ?	0.33	0.0
$[Fe\ (4\text{-}mpdpa)\ Cl_3]$	5.8	35^b	360 m br 310 v s br 295 sh (Fe-Cl) ; 218 s sp (Fe-N)?	0.35	0.20

[a] - D.M.F [b] - nitromethane * w.r.t natural iron

Results and Discussion

Iron II complexes obtained from iron III salts

The formation of the complexes tabulated in Table 5.1. was very puzzling. All available data suggested that these compounds were iron II complexes and the Mossbauer parameters unequivocally supported this. The values of the isomer shift $\delta = 0.95$ mm sec^{-1} (w.r.t. Fe metal) and the large quadrupole splitting $\Delta Eq > 2$ mm sec^{-1} characteristic of spin free iron II supported by the analytical, conductivity and magnetic data indicated that these complexes were identical to those reported previously by McWhinnie[38] and Goodgame[40]. The spin paired bis tripyridylamine iron II perchlorate has also been reported previously[38].

The only common factor in the preparation of all these complexes was the use of dimethoxy propane as a dehydrating solvent. There has been previous experience of the reducing ability of this solvent. Solutions of zirconium IV when refluxed with dimethoxy propane have been found to produce intensely violet coloured products which are characteristic of zirconium III[117]. Since one of the hydrolytic products of dimethoxy propane is methanol, the preparation of the above complexes were carried out with methanol as solvent but this did not bring about the reduction of iron III to iron II. Perhaps, the composition of the solvent medium influences the reduction iron III $\longrightarrow$ iron II, possibly due to the oxidation/reduction potential E_0 of iron being a function (amongst other factors) on the solvent medium. However, subsequent attempts to exploit these observations for the preparation of iridium III complexes were not very promising[118].

Iron II isothiocyanato complexes

The thiocyanate group is a bifunctional ligand and the positions of ν_1, C $\equiv$ N stretch ν_2, N-C-S bend and ν_3, C-S stretch depend on whether this ligand is attached to the metal ion through the nitrogen (isothiocyanato) or sulphur atom (thiocyanato). For the isothiocyanato complexes the following absorption ranges have been proposed ν_1, 2040 - 2080, ν_2, 465 - 480 and ν_3, 780 - 800 cm^{-1} whereas for the thiocyanato complexes the ranges are ν_1, 2080 - 2120, ν_2, 410 - 470 and ν_3, 690 - 720 cm^{-1} [7,93]. The ν(C $\equiv$ N) stretching frequencies of the iron II complexes of the tripyridylamines (Table 5.3) indicates that the thiocyanate is N bonded in all the complexes. ν_2 N-C-S and ν_3 C-S vibrations coincide with some of the absorption bands of the ligands.

Compounds 1. 3 and 4 (Table 5.2) are analogous to one another. The infra red spectra of these complexes indicate that the pyridylamine ligand is terdentate. The electronic spectrum in the visible region (Fig. 5.1) closely resembles that of the corresponding bis ligand iron II perchlorates[38, 92], the shoulder around 19.6 - 19.8 kK arising most probably from the first spin allowed transition $^1A_{1g} \longrightarrow {}^1T_{1g}$, and the band at 23 kK being more likely of charge transfer origin. The Mossbauer spectrum shows the presence of a singlet with an isomer shift δ = 0.35 - 0.37 mm sec^{-1} which is consitent with that reported for the spin paired iron II complexes (δ = 0.37 - 0.40 w.r.t. Fe metal). The infra red, electronic and Mossbauer

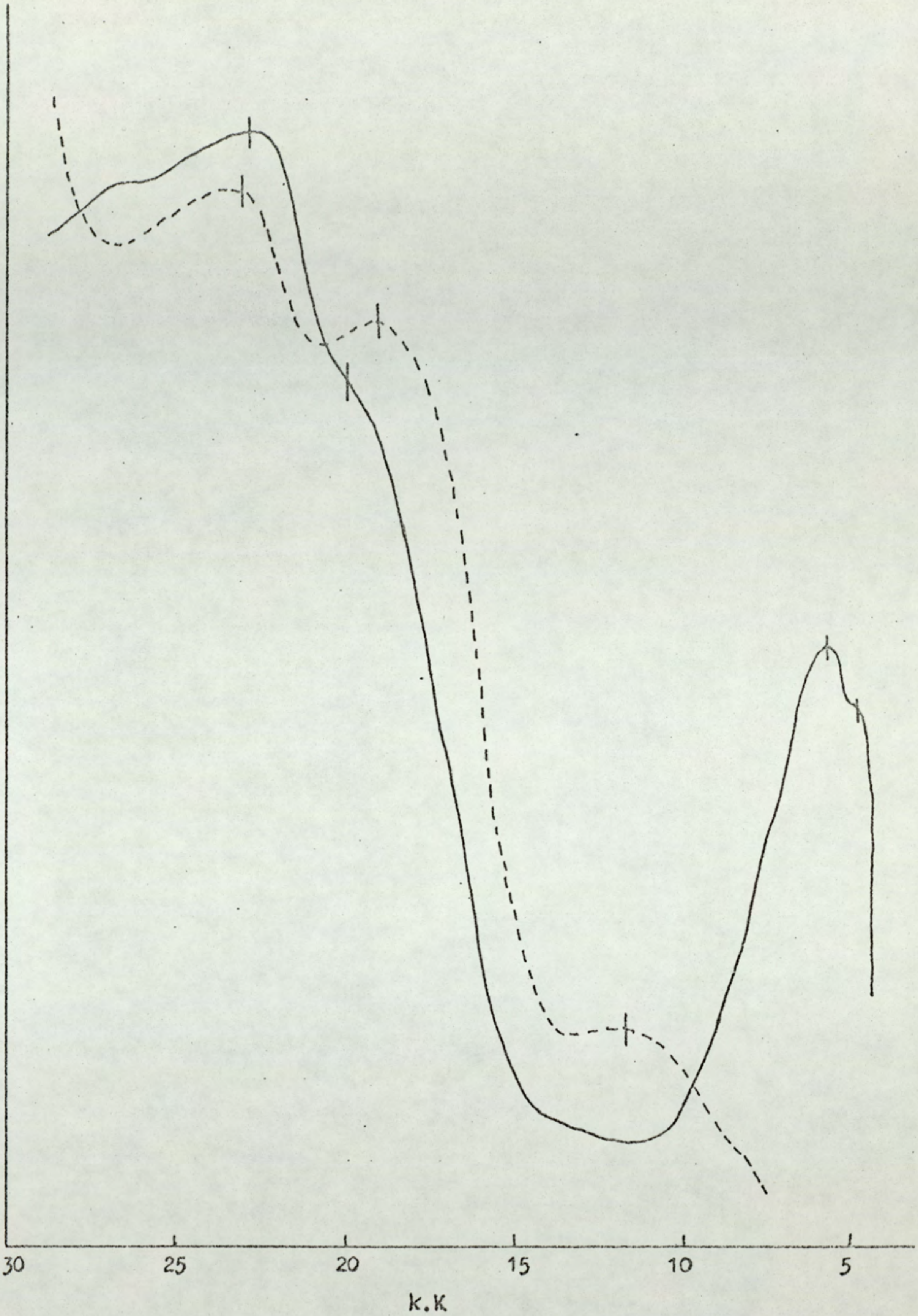


Fig.5.1 Diffuse reflectance spectra of

———— $[Fe(tripyam)_2][Fe(NCS)_4]$
- - - - - $[Fe(4mpdpa)_2(NCS)_2]$

spectral data are therefore compatible with the presence of the spin paired bis tripyridylamine iron II cation. However, the electronic spectrum in the near infra red region shows the presence of a strong absorption band with peaks at 5.6 - 5.8 kK and 4.8 kK (Fig 5.1). This is very similar to that reported for the spin free tetrahedral tetraisothiocyanato ferrate II which has bands at 5.8 and 4.8 kK[119].

The magnetic data obtained for these compounds (3.8 - 3.9 B.M) is consistent with the presence of a spin-paired cation and a spin free anion. The conductivity data also supports a 1 : 1 formulation. The appearance of only a singlet in the room temperature Mossbauer spectrum (Fig 5.2) is understandable as the quadrupole doublet of tetrahedral iron II is known to be temperature dependent[120]. The Mossbauer spectrum at low temperatures will very likely reveal the presence of a singlet due to the spin paired cation and a doublet due to the spin free T_d anion (c.f. bis tri-(2 - pyridyl)amine iron II tetrachloro ferrate II).

In contrast to the above complexes Compound 2 (Table 5.2) is of a different type. The infra red spectrum reveals that the ligand 4-methyl 2 - pyridyl di - (2 - pyridyl)amine is distinctly bidentate and that the thiocyanate groups are N - bonded. These characteristics makes this compound analogous to the bis 2. 2$'$ bipyridyl and 1 :10 phenanthroline isothiocyanato complexes of iron II[26,28]. The magnetic data obtained are consistent with the presence of a spin free environment for iron II. A single concentration conductivity measurement supports the formulation as a non-electrolyte though there is evidence of slight dissociation. The electronic spectrum

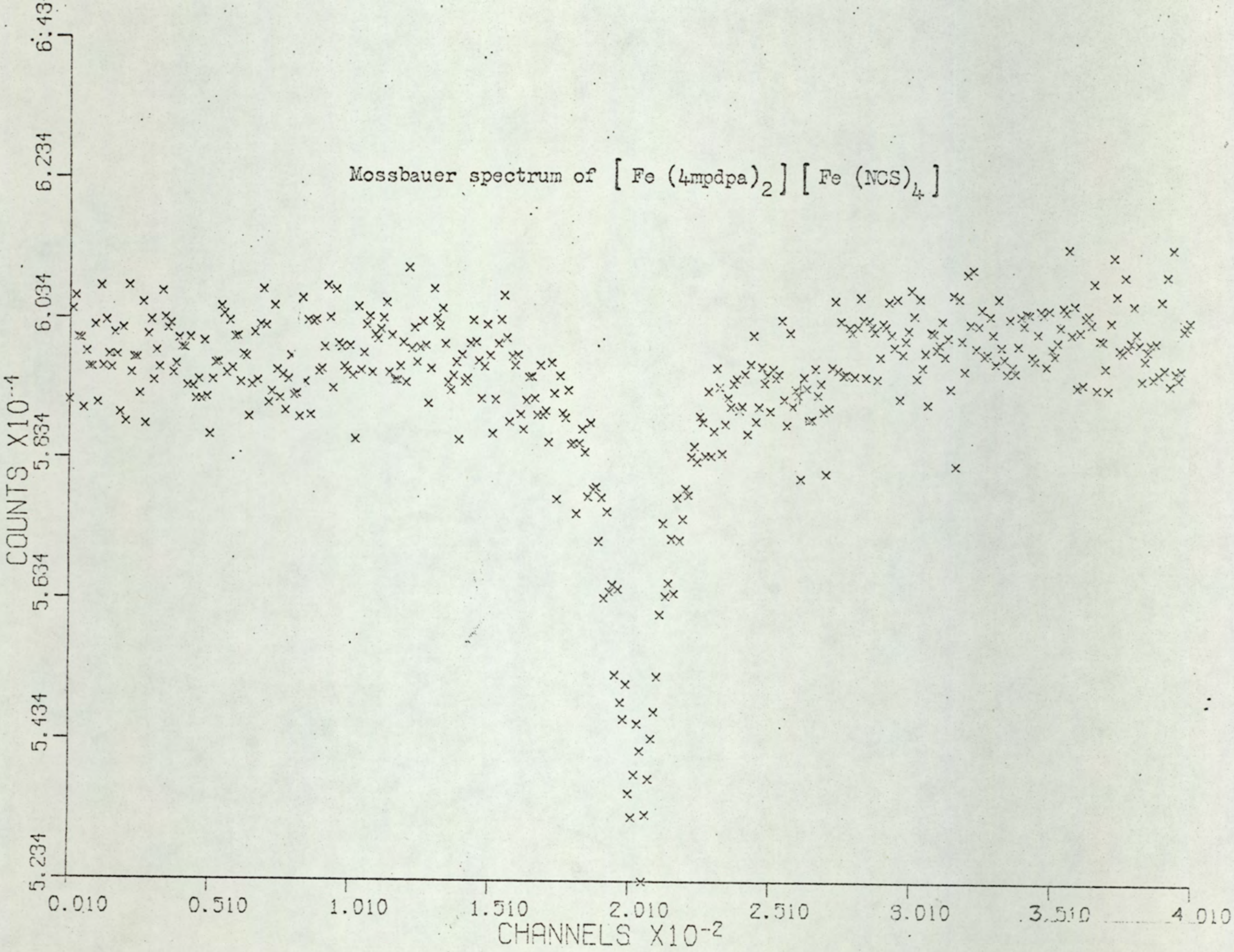

Mossbauer spectrum of $[Fe(4mpdpa)_2][Fe(NCS)_4]$

Fig. 5.2

(Fig. 5.1) shows a close resemblance to that of the bipyridyl and phenanthroline complexes[27.28]. The lowest frequency band at 10.8 kK probably corresponds to the $^5T_2 \longrightarrow {}^5E$ transition while the more intense bands at higher energies viz. 18.8 and 23 kK are more likely due to metal - ligand and internal ligand charge transfer transitions ($[Fe(phen)_2(NCS)_2]$ 11.9, 18.0 and 19.0 kK; $[Fe(bipy)_2(NCS)_2]$ - 11.2 and 18.4 kK). The bipyridyl and phenanthrodine complexes have been shown to have the ligands in a cis configuration[80] and this is to be expected in the bipyridyl case on steric grounds alone[51]. The above data on the other hand, does not permit the confident assignment of the stereochemistry of the molecule though the presence of a single band in the $\nu C \equiv N$ region is that expected for a trans complex.

The Mossbauer spectrum shows the presence of a well resolved quadrupole doublet with an isomer shift $\delta = 1.10$ mm sec^{-1} which is consistent with spin free iron II. Since the largest contribution to the electric field gradient generally arises from incompletely filled d electron shells, a substantial value of ΔEq is expected for spin free iron II. The quadrupole splitting ΔEq obtained for $[Fe(4mpdpa)_2(NCS)_2]$ i.e. 1.17 mm sec^{-1}, is smaller in magnitude that that reported for other spin free iron II complexes of chelating nitrogen ligands (2.0 - 3.3 mm sec^{-1}). However, this magnitude for the quadrupole splitting is not uncommon among other spin free octahedral iron II complexes[121].

An interesting feature about this compound is that the action of heat converts it to the tetraisothiocyanato ferrate II salt (Compound 3)

$$2\left[\mathrm{Fe}\,(4\mathrm{mpdpa})_2\,(\mathrm{NCS})_2\right] \rightleftharpoons \left[\mathrm{Fe}\,(4\mathrm{mpdpa})_2\right]\left[\mathrm{Fe}\,(\mathrm{NCS})_4\right] + 2\,(4\mathrm{mpdpa})$$

bidentate ligands terdentate ligands

Brown Orange-brown.

Perhaps, the large ligand field strength of the terdentate ligand favours the formation of $[\mathrm{Fe}\,(4\mathrm{mpdpa})_2]^{2+}$ cation which under the reaction conditions comes down as the tetraisothiocyanato ferrate II salt. A similar disproportionation is known to take place with the corresponding cobalt II tripyridylamine complex[90].

Iron III complexes of dipyridylamine.

The direct reaction of iron III salts with pyridyl ligands is known to lead to the formation of brown binuclear products. However, when ethanolic solutions of iron III chloride and dipyridyl amine were mixed a bright yellow product was immediately precipitated. (Compound 1 Table 5.4). The infra red spectrum of this compound showed that the ligand absorptions especially in the ν (C = N) and γ(C - H) regions closely resembled that of the tetrachloro ferrate III salt and differed markedly from that of the co-ordinated ligand (Table 5.6) indicating that the ligand dipyridylamine in compound 1 is not co-ordinated. Furthermore, the presence of a strong absorption band around 3320 cm^{-1} characteristic of the protonated pyridyl ring suggests that compound 1 is very likely the dipyridylammonium salt. A strong broad band at 895 cm^{-1} characteristic of iron-oxygen-iron vibration was also seen in the infra red spectrum. The iron-chlorine stretching vibrations at 375 and 369 cm^{-1} are compatible with an anionic chloro complex as νFe - Cl in $[\mathrm{Fe\,Cl}_4]^-$ is known to absorb at 378 cm^{-1} [122]. There is also an additional band at 216 cm^{-1} which may be assigned to an Fe - Cl bending mode. The magnetic data obtained are suggestive of a spin-paired environment but this is not unusual for an oxygen bridged complex where two spin free species are capable of antiferromagnetic interaction whereby the nett spin state becomes $\leq$ 1 unpaired electron. The Mossbauer spectrum consisted of a well resolved quadrupole doublet $\Delta Eq = 1.38$ mm sec^{-1} with an isomer shift of 0.26 mm sec^{-1} (w.r.t natural iron). This magnitude of isomer shift for an iron III species is within the range of that expected for a four co-ordinate complex viz δ of $[Fe\,Cl_4]^-$ = 0.23 mm sec^{-1} [39]. The above data is compatible with the suggested formulation (Table 5.5) where two four co-ordinate iron III species are bridged by oxygen forming a divalent anion with protonated dipyridylamine as the cation.

An interesting feature about this complex is that on heating an ethanolic solution with dipyridylamine it very readily forms compound 2 which is a red-brown complex with co-ordinated dipyridylamine (Table 5.6). Compound 2 (Table 5.4) can also be prepared by refluxing ethanolic or acetonitrilic solutions of iron III chloride and dipyridylamine. When an ethanolic solution of compound 2 is treated with excess ferric chloride it regenerates the yellow complex 1.

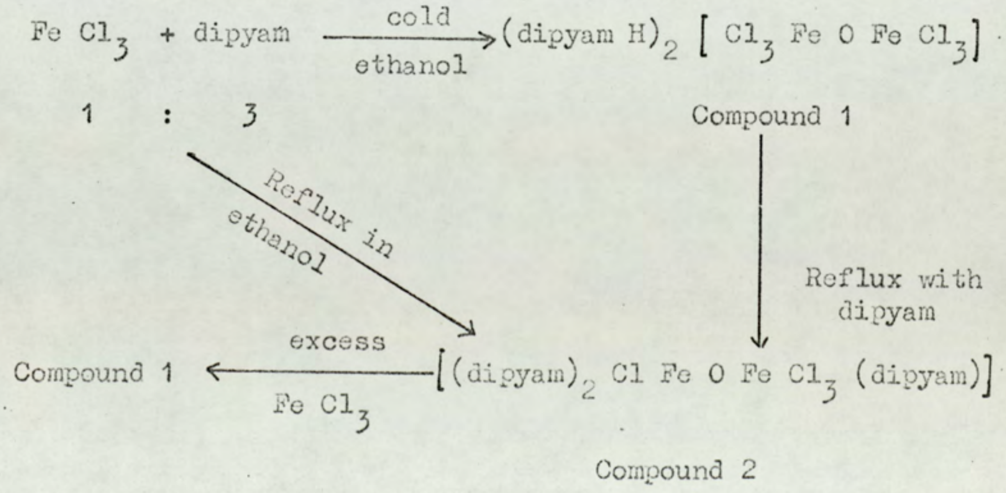
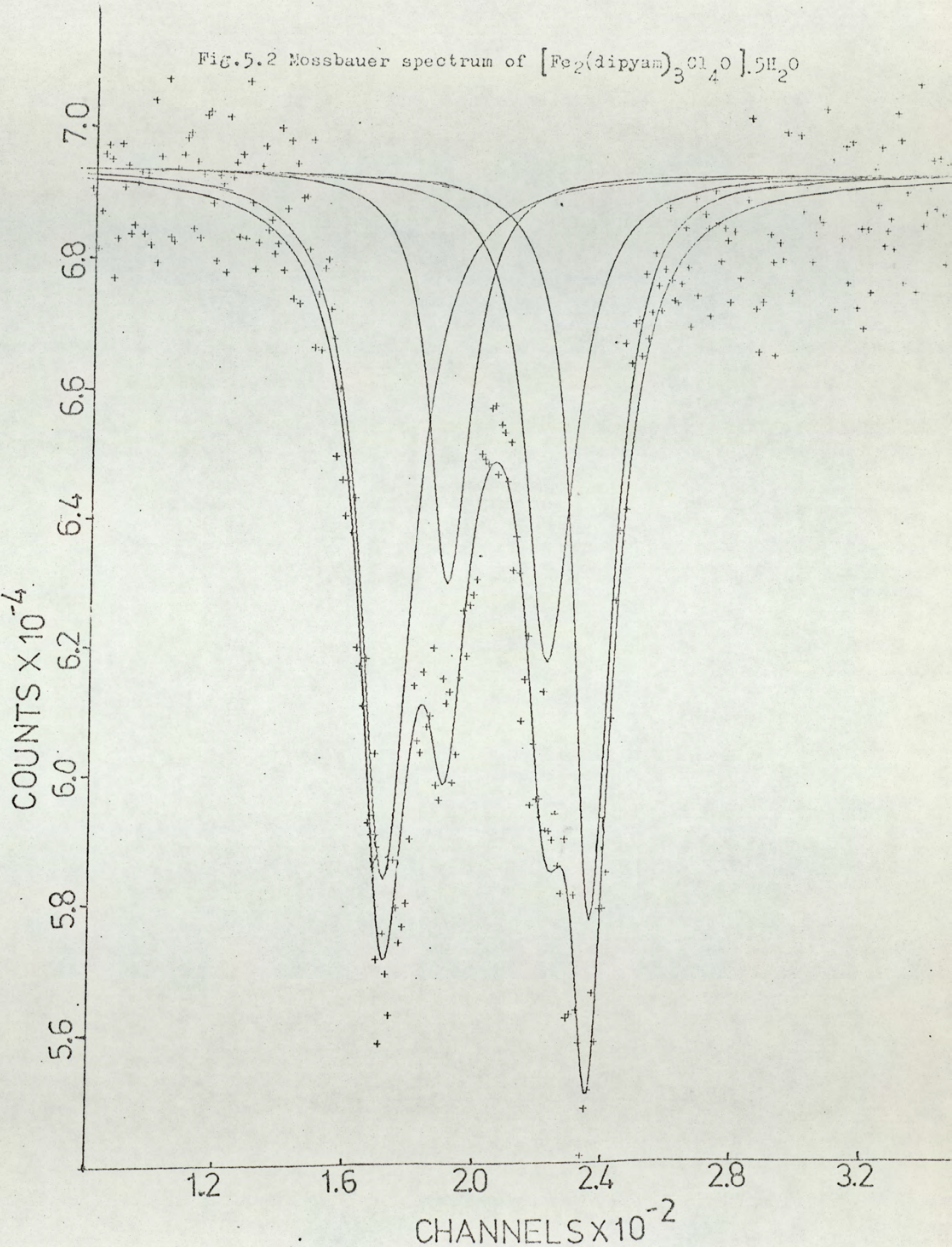


Fig.5.2 Mossbauer spectrum of $[Fe_2(dipyam)_3Cl_4O].5H_2O$



The infra red spectrum of compound 2 shows the presence of a very prominant band at 845 cm^{-1} due to an Fe - O - Fe vibration. There are three bands in the far infra red region at 360. 355 and 343 cm^{-1} due to iron-chlorine vibrations. The lowering of the frequency of the bands being compatible with increase in co-ordination number[122]. The conductivity data are suggestive of a non electrolytic formulation though there is evidence of slight dissociation. The Mossbauer spectrum is rather complex (Fig 5.3). Resolution of the spectrum with a curve fitting programme clearly indicates the presence of four peaks due to two pairs of quadrupole doublets. The parameters obtained are consistent with the presence of two different iron sites in the complex with both iron atoms in $S = 5/_2$ spin state. The magnetic data obtained though closer to a spin only value for one unpaired electron is the resultant moment due to antiferromagnetic interactions of two spin free iron atoms via the oxygen bridge.

The infra red spectrum of the bromo complex (compound 3 Table 5.4) shows the Fe - O - Fe band at lower energy (800 cm^{-1}) being incorporated as a broad composite band with the γ C - H vibrations of the ligand. The far infra red spectrum shows two conspicuous bands at 286 and 250 cm^{-1} which judging from the positions of the iron-chlorine vibrations of compound 1 may be assigned as due to iron-bromine vibrations.

The Mossbauer spectrum is as complex as that of compound 2 with four peaks due to two pairs of quadrupole doublets. The parameters obtained (Table 5.5) indicate that the isomer shifts are slightly higher than those of the chloro complex but they are nevertheless, compatible with spin free iron III. The magnetic data is that expected for an oxo bridged complex confirming an interaction between the two iron atoms. The conductivity data, however, indicates a considerable degree of dissociation of the complex in dimethyl formamide.

The above data are consistent with the presence of an unsymmetrically oxygen bridged binuclear complex of iron III. The iron atoms are both six co-ordinated and one iron atom has two dipyridylamine molecules co-ordinated to it

$$[L_2 X \text{Fe} O \text{Fe} L X_3] \quad \text{where } L - \text{dipyridylamine}$$
$$X - \text{Cl, Br or OH.}$$

The data obtained however do not permit the definite assignment of the stereochemistry of the molecule though it is very likely that the iron atom with the bis dipyridylamine will have a cis geometry.

Binuclear iron III complexes of the tripyridylamines

The formation of the μ- oxo complex compound 4 when iron III chloride was treated with tripyridylamine was very surprising especially because of the ease with which the mononuclear complex was precipitated (see later). This compound is analogous to the dipyridylamine complex (Compound 1). The infra red spectrum shows the presence of a strong broad band at 890 cm^{-1} due to Fe - O - Fe vibration. The ligand absorptions in the ν (C = N) and γ (C - H) region indicate that it is not co-ordinated. The magnetic data are consistent with an oxo bridged complex. The Mossbauer parameters (Table 5.5) supports the presence of four co-ordinate spin free iron III.

Subsequent attempts to prepare this complex always resulted in the formation of a mixture of the mononuclear and binuclear species. Although the analytical data was compatible

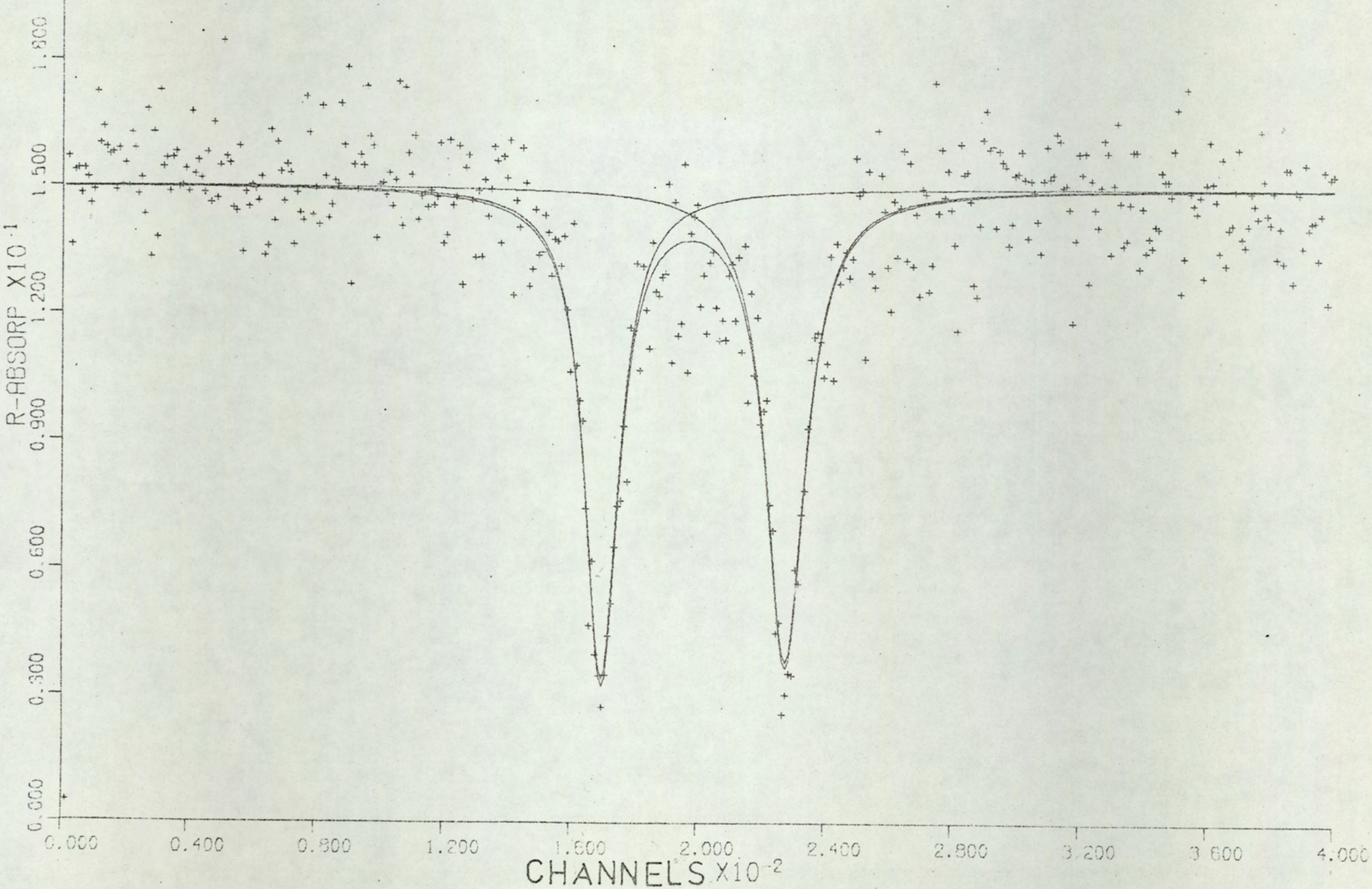


Fig.5.4 Mossbauer spectrum of $(5mpdpaH)_2[(FeCl_3)_2O]$

for a pure complex, the magnetic and Mossbauer data provided evidence for the existence of a mixture.

In contrast to tripyridylamine the reaction of iron III chloride with 5 - methyl 2 - pyridyl di -(2 pyridyl) amine always resulted in the formation of a binuclear complex (Compound 5. Table 5.4). The presence of an oxo bridge is confirmed by the broad absorption band at 890 cm^{-1} in the infra red spéctrum. The magnetic data is consistent with the occurrence of antiferromagnetic interaction between the two iron atoms. The Mossbauer data (Fig 5.4 Table 5.5) supports the presence of spin free four co-ordinate iron III. The far infra red bands at 360 and 317 cm^{-1} may be assigned to iron-chlorine vibrations.

The formation of the binuclear pyridylammonium salts could be explained as follows where the base induces hydrolysis

$$\underset{\text{base}}{L} + HOH \rightleftharpoons LH^+ + OH^-$$

$$Fe\,Cl_4^- + OH^- \rightleftharpoons Fe\,Cl_3\,OH^- + Cl^-$$

$$2\,Fe\,Cl_3\,OH^- \rightleftharpoons [Cl_3\,Fe\,O\,Fe\,Cl_3]^{2-} + H_2O$$

The precipitation of the pyridylammonium salt at this stage is probably due to a solubility effect. In the case of dipyridylamine the reaction proceeds further

$$Fe\,Cl_3\,OH^- + L \rightleftharpoons Fe\,L\,Cl_3\,OH^-$$

$$Fe\,L\,Cl_3\,OH^- + L \rightleftharpoons Fe\,L_2\,Cl\,OH^+ + 2\,Cl^-$$

$$Fe\,L\,Cl_3\,OH^- + Fe\,L_2\,Cl\,OH^+ \rightleftharpoons [Cl_3LFeOFeL_2Cl] + H_2O$$

with the formation of the red-brown binuclear complex similar to that reported with bipyridyl and phenanthroline.

Isothiocyanato complexes of iron III

The bright red complex species formed by mixtures of ferric and thiocyanate ions has been used as a method of determining iron colorimetrically[123]. The reaction of iron III thiocyanate with dipyridylamine and tripyridylamine resulted in the formation of dark violet coloured products (Compounds 1 and 2 Table 5.7). These two pompounds are similar to each other in many respects. The analytical data suggest a stoichiometry of $Fe\,L_{1.5}\,(NCS)_3$ (L - dipyridylamine or tripyridylamine) so that the molecular formula is very likely $Fe\,L_2\,(NCS)_6$. The complexity of the infra red spectrum of compound 2 below 600 cm^{-1} clearly suggests that tripyridylamine is acting as a bidentate ligand. The following structures are possible for both complexes viz. $[Fe\,L_3][Fe\,(NCS)_6]$, $[Fe\,L_2(NCS)_2][Fe\,L\,(NCS)_4]$ and $[L_2Fe(NCS)_2FeL\,(NCS)_2](NCS)_2$. The $\nu(C\equiv N)$ stretching region of both compounds is rather complex (Table 5.7) which could arise from any three of the above structures. The conductivity data support the dissociation of the complexes in solution as 1 : 1 electrolytes. The magnetic data is that expected for a high spin iron III complex. The diffuse reflectance spectra (Fig. 5.5) show a very broad change transfer band at 17 - 18 kK and a weak band appears around 9.0 kK which may be due to a spin forbidden transition $^6A_1 \longrightarrow {}^4T_1\,(G)$.

Aqueous-ethanolic and acetone solutions of these complexes are bright red coloured. The visible absorption spectra of solutions of these complexes and that of the potassium salt of hexa isothiocyanato ferrate III showed the presence of absorption bands at 19.8 kK and 20.6 kK respectively.

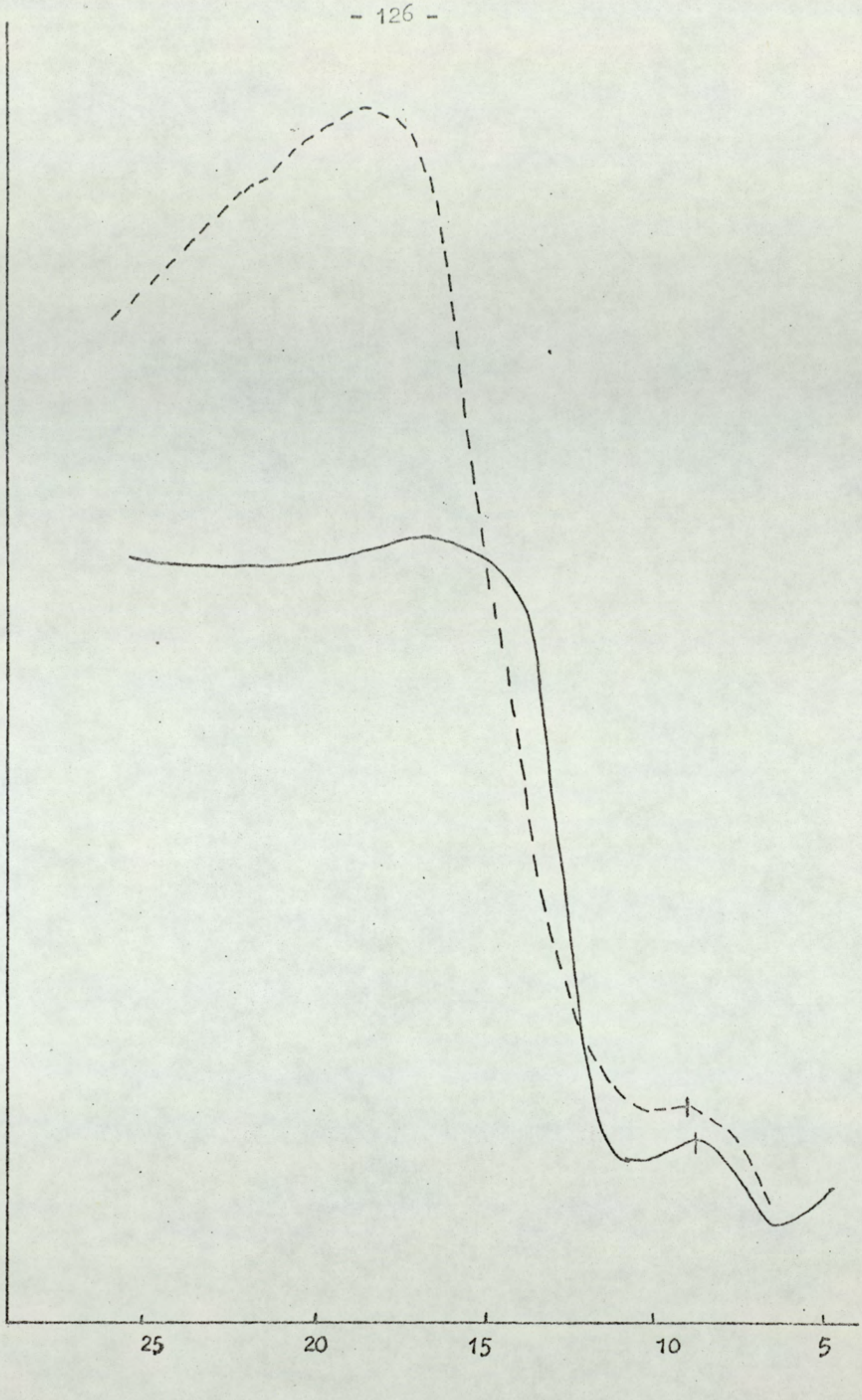


Fig.5.5 Diffuse reflectance spectra of

$[Fe(dipyam)_2(NCS)_2][Fe(dipyam)(NCS)_4]$

$[Fe(tripyam)_2(NCS)_2][Fe(tripyam)(NCS)_4]$

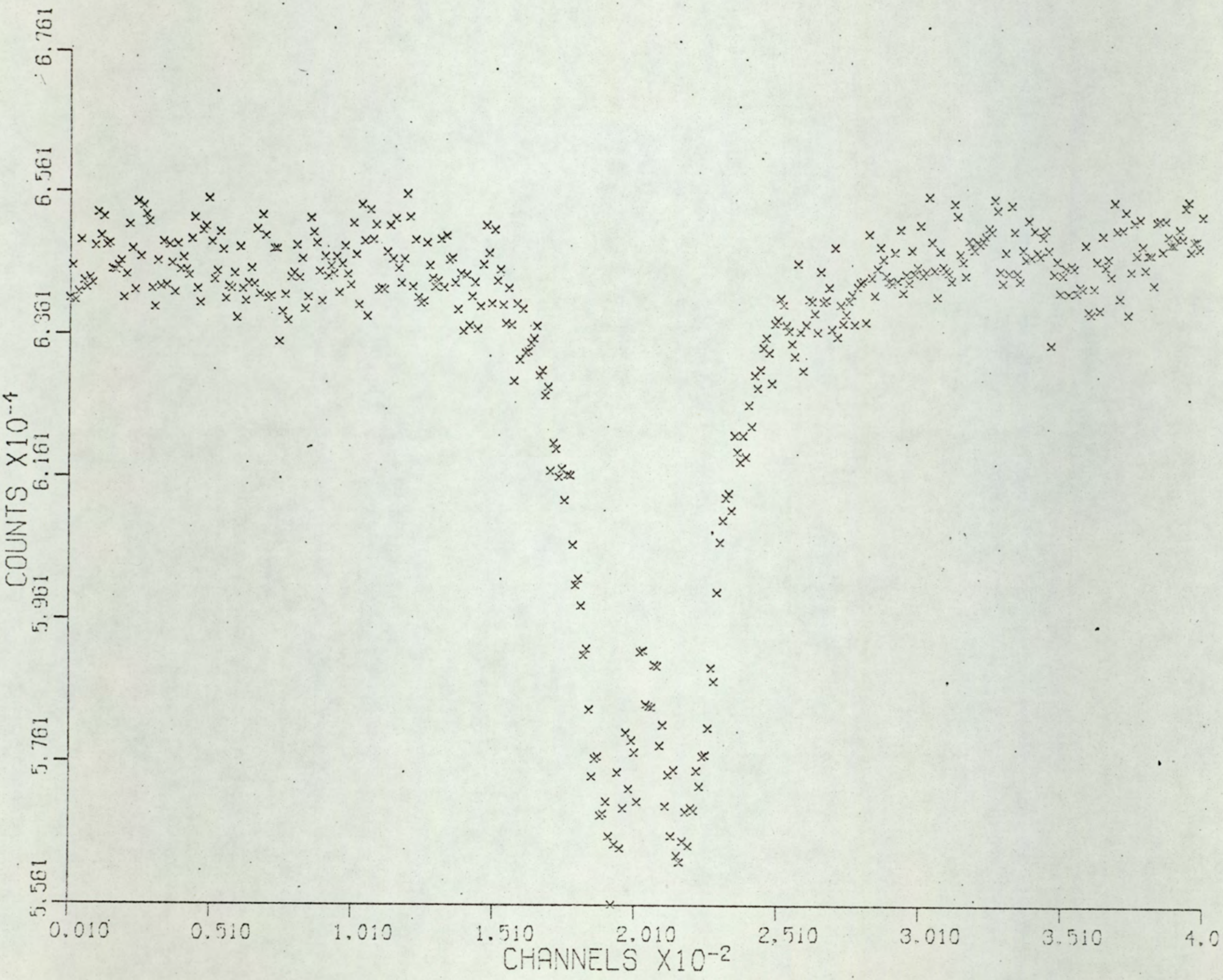


Fig. 5.6 Mossbauer spectrum of [Fe (dipyam)$_2$(NCS)$_2$] [Fe (dipyam) (NCS)$_4$]

Ion exchange studies showed that the hexa isothiocyanato ferrate III solution passed through a cation exchange resin without any change in the absorption spectrum but neither the anion nor the cation exchanged extracts of the two complexes showed any bands in the visible region of the spectrum. Furthermore, the infra red spectra of both the cation and anion exchanged extracts of the two complexes revealed the presence of thiocyanate in both the anion and the cation thereby very conclusively excluding the existence of $[Fe(NCS)_6]^{3-}$ species in the two complexes. The infra red spectra of the ion exchanged extracts also showed the presence of the pyridylamine ligand in both the cation and the anion which also supports the above conclusion and excludes the presence of ionic thiocyanate as the anion.

The Mossbauer spectra are very similar showing the presence of quadrupole splitting $Eq = 0.6 - 0.7$ mm sec^{-1}. This magnitude of the quadrupole splitting generally arises due to inequivalencies of the ligand atoms or to lattice effects. The isomer shift is consistent with spin free iron III. The magnitude of the half width suggests an overlap of two definite resonances with similar quadrupole splittings indicating the presence of two definite iron sites in the complex. The above data supports the formulation $[Fe\,L_2(NCS)_2][Fe\,L(NCS)_4]$ for the two complexes.

Fe (tripyam) Cl_3 and Fe (4mpdpa) Cl_3

In contrast to the oxygen-bridged complexes that were formed, the addition of iron III chloride to an ethanolic solution of tripyridylamine and 4 - methyl 2 - pyridyl dipyridyl amine resulted in the immediate precipitation of bright yellow coloured complexes (Compounds 3 and 4 Table 5.7). There is no doubt that these are simple, monouclear high spin iron III compounds. The magnetic moment of 5.6 - 5.8 B.M is compatible with a high spin environment for iron III. The lowish moment of 5.6 B.M for Fe (tripyam) Cl_3 may be attributed to the presence of a low spin contaminant which very likely is the oxo bridge binuclear complex (see page 122). The infra red spectral data show that the pyridylamine ligand is terdentate in both complexes and there is no evidence for the presence of an oxygen bridge. The far infra red spectrum shows the presence of three bands 350 - 360, 310 and 290 - 295 cm^{-1} (Table 5.8) which may be assigned to iron-chlorine vibrations. This is in agreement with the results of Clark who observed that increase in co-ordination decreases the metal-halogen frequency[122]. However, the presence of three bands due to iron-chlorine vibrations is not that anticipated for a complex of C_{3V} symmetry. Hudman, Patel and McWhinnie also observed three bands in the analogous thallium III complex. They attributed this to the splitting of the degenerate E mode in C_{3V} symmetry by crystal effects. The two compounds are probably isomorphous, but x-ray diffraction studies did not prove very useful as the iron III complex was not sufficiently crystalline. The electronic spectra of these compounds do not show any discernible d - d bands, this is to be expected as all possible d - d transitions for a $^6A_1$ ground state are spin forbidden.

The Mossbauer spectra show the presence of a singlet with an isomer shift consistent with spin free iron III (Fig 5.7). Since the ligand atoms (3 chlorines and 3 pyridyl nitrogens) are chemically nonequivalent an electric field gradient is expected to be generated and therefore a measur able quadrupole splitting is

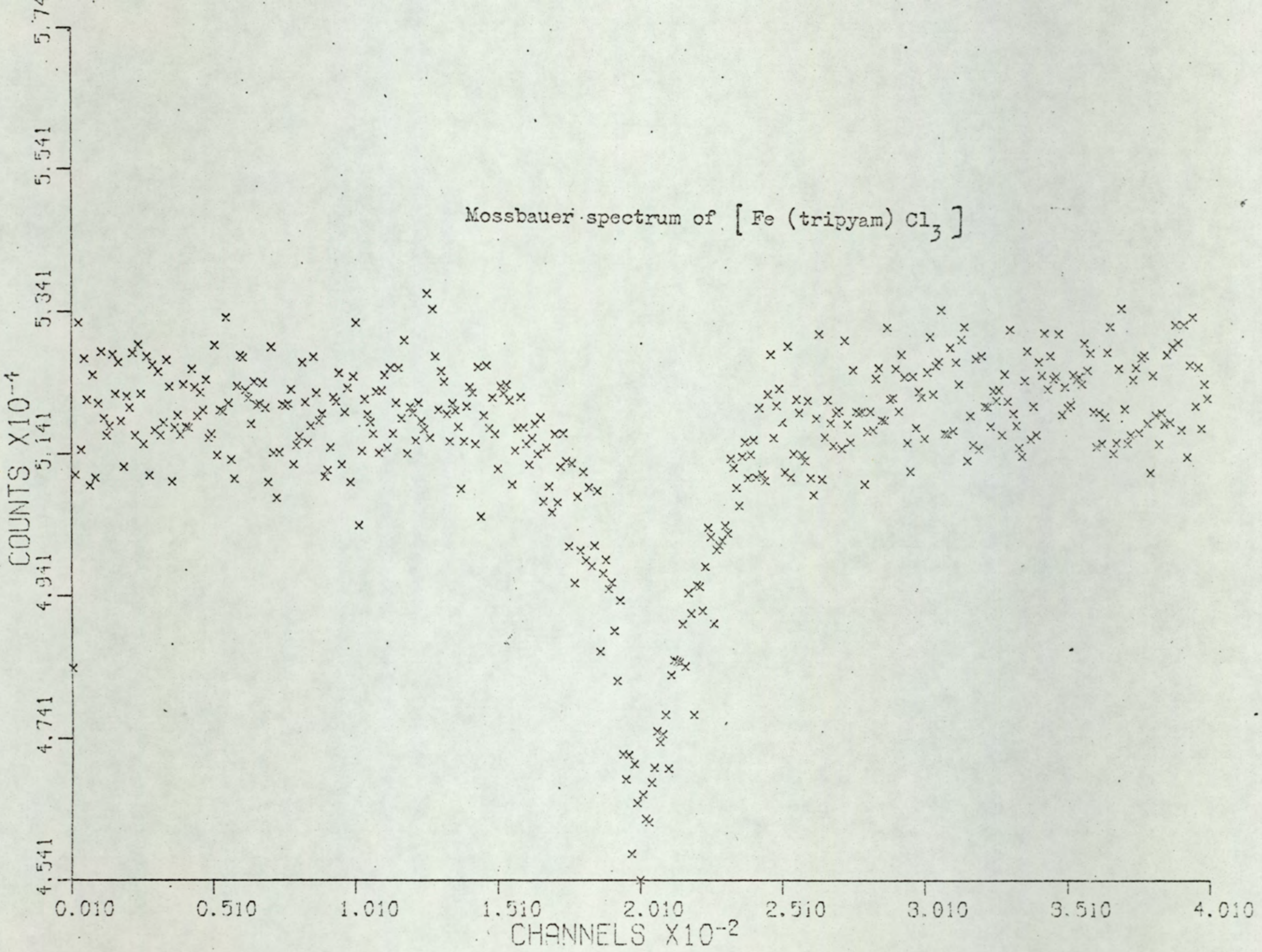

Mossbauer spectrum of $[Fe\ (tripyam)\ Cl_3]$

Fig. 5.7

anticipated in the Mossbauer spectrum. However, the spectrum obtained suggests that chlorine and pyridyl nitrogen atoms are electrically equivalent so that the iron atom is essentially in an electrically cubic environment c.f. $[Fe(III)(phen)Cl_4]^-$ — the Mossbauer spectrum of which also shows zero quadrupole splitting. The small quadrupole splitting observed in $Fe(4mpdpa)Cl_3$ may be attributed to the non-cubic micro symmetry arising as a consequence of the presence of the methyl substituent in one of the rings.

Conclusions.

The use of dimethoxy propane as a dehydrating solvent for the preparation of iron III complexes resulted in the reduction of iron III - iron II.

The tripyridyl ligands reacted with iron II thiocyanate forming the bis ligand complexes as the tetra isothiocyanato ferrate II salts. 4 methyl - 2 - pyridyl di - (2 pyridyl)amine also formed the diisothiocyanato bis (4 mpdpa) iron II complex.

Dipyridylamine formed four and six co-ordinated oxygen bridged binuclear complexes of iron III. Tripyridyl amine and 5 - methyl 2 - pyridyl di (2 pyridyl)amine formed only the four co-ordinated binuclear complexes as the pyridylammonium salts.

Dipyridylamine and tripyridylamine reacted with iron III thiocyanate producing dark violet coloured complexes of the following structure $[Fe\ L_2(NCS)_2]\ [Fe\ L\ (NCS)_4]$

Tripyridylamine and 4 mpdpa formed mononuclear complexes with iron III chloride.

None of the above complexes exhibited high spin - low spin equilibria at the temperatures of investigation. The lack of the necessary equipment in the premises did not permit the low temperature magnetic and Mossbauer studies of these complexes. Such data will be of great interest especially that of the iron II isothiocyanato complexes.

The Mossbauer spectral study of the magnetically anomalous compounds has demonstrated unequivocally the use of this technique for the study of the environment of individual atoms. This work has also showed that the correlation of data from different physical techniques is necessary for the correct interpretation of the structure of a compound.

Some attempts in the preparation of a tellurium containing chelate ligand.

Mossbauer spectroscopy has established itself as an invaluable tool in the elucidation of the structure and bonding of compounds containing iron and/or tin. Ligands containing tin are not uncommon and therefore it is not surprising that some organotin compounds with tin - transitional metal bonds have been examined using Mossbauer spectroscopy. Furthermore, with iron as the transitional element the facility to use both ^{57}Fe and ^{119}Sn resonances for the study of the detailed stereochemistry and the nature of the iron-tin bond has also been exploited[124-125].

Most of the work on Mossbauer spectroscopy has been confined to iron and tin mainly because of the more severe experimental conditions required for the study of the other Mossbauer elements. Nevertheless, one of the more promising nuclides for further development is tellurium - 125. A few workers[126,127] have recently reported the study of some tellurium complexes thereby paving the way for the utilisation of this versatile tool for the detailed study of tellurium containing complexes.

It was thus considered worth while to prepare some tellurium containing ligands whereby the complexes formed with transitional metals could be studied using ^{125} Tellurium Mossbauer. This would necessarily lead to the preparation of complexes with iron as the transitional metal, so that resonances of both ^{125}Te and ^{57}Fe could be utilised for a study of the detailed stereochemistry and the nature of the tellurium-iron bond in these complexes.

It is well known that chelating ligands form very stable complexes and among the most extensively studied are the pyridyl containing ligands. To keep to the theme of the work reported in the rest of this thesis, it was a natural extension to attempt the preparation of a ligand with tellurium and pyridyl nitrogen as the donor atoms.

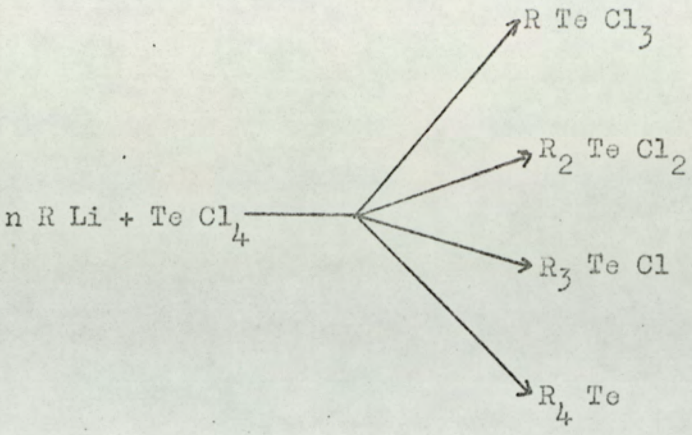
Results and Discussion

The formation of tellurium derivatives by the interaction of tellurium tetrachloride with Grignard reagents has been studied by several workers. The method of Rheinboldt and Petragnani[128] for the preparation of bis (organo) tellurides was

$$\mathrm{Te\,Cl_4 + 4\,RMgBr \rightleftharpoons R_2\,Te + R_2 + 4\,Mg\,Cl\,Br}$$

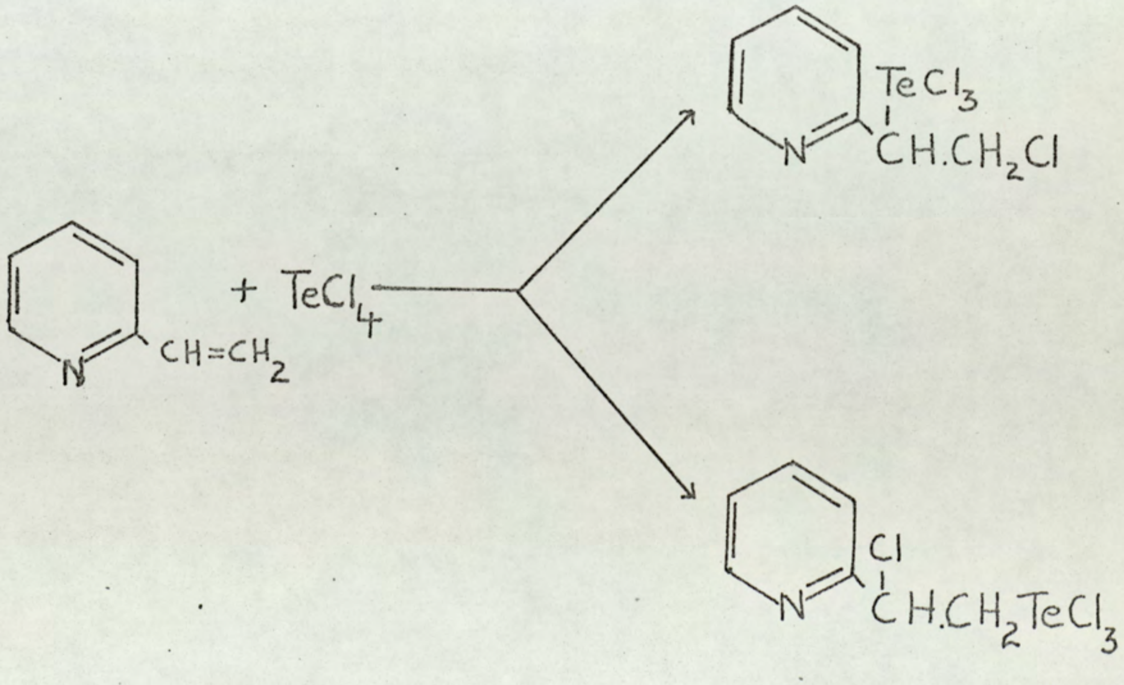
adopted using picolyl magnesium bromide as the starting material. Unfortunately, black elemental tellurium was deposited under varying experimental conditions.

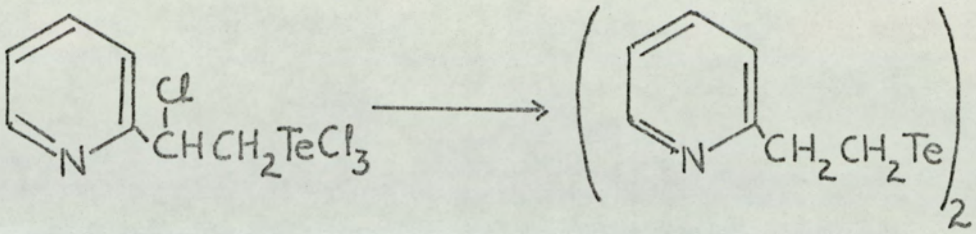
Aromatic and aliphatic lithium compounds have served as reagents in the preparation tellurides tetra organo tellurium compounds and heterocyclic tellurium derivatives[129]. The primary products in the reaction of an aryl lithium compound with tellurium tetrachloride would be the organo tellurium chlorides and tetra organo tellurium compounds[128].



Picolyl lithium was prepared and treated with tellurium tetrachloride in ether in the hope of obtaining the desired telluride. A yellow product was formed which decomposed almost immediately to black tellurium. An extension of this method to the lithio derivative of 2 - ethyl pyridine also gave a yellow product but it was too unstable for further study.

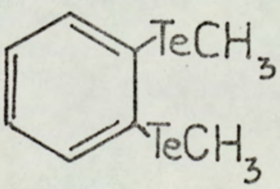
The addition of tellurium tetrachloride across olefinic double bonds is reported to yield the corresponding trichloride[131.132] 2 - vinyl pyridine was prepared by the dehydration of 2-pyridyl ethanol[133] and treated with tellurium tetrachloride in benzene.





A bright yellow product was obtained but this compound was insoluble in all the common organic solvents. Elemental analysis indicated the presence of tellurium, chlorine, carbon, hydrogen and nitrogen and supported a stoichiometry of $C_7 H_7 N Cl_3$ Te, but no definite structure could be formulated. The action of reducing agents such as sodium sulphide, potassium metabisulphite, zinc/acetic acid and even zinc/benzene (which are generally used for the reduction of tellurium compounds), resulted in the immediate deposition of black elemental tellurium. Water andethanol caused hydrolysis to tellurim oxide. The inability to recrystallise this compound and get some meaningful data prevented further study.

Finally, an attempt was made to prepare a ditellurium chelate of the type,



following the method of Petragnani[134], but this too did not yield any valuable products.

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