THE SYNTHESIS, CHARACTERIZATION AND COMPLEX FORMING ABILITY OF SEVERAL -2-PYRIDYLAMINE LIGANDS

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ABSTRACT

Several substituted tri-2-pyridylamines have been synthesised and their complexing potential with transition metal ions studied.

The synthesis of 6-methyl-2-pyridyl-(2-pyridyl)amine (6mpdpa), 5-methyl-2-pyridyl-(2-pyridyl)amine (5mpdpa), 4-methyl-2-pyridyldi-(2-pyridyl)amine (4mpdpa), 5-nitro-2-pyridyldi-(2-pyridyl)amine (5npdpa) and tri-(4-methyl-2-pyridyl)amine (tri-4m-pyam) are discussed in terms of difficulties experienced and of modifications to the Wibaut and La Bastide synthesis for tri-(2-pyridyl)amine (tripyam). Attempts to prepare a pentapyridyl ligand [2,6 di(di-2-pyridylamine) pyridine] are discussed together with a possible explanation for the failure to isolate the ligand under the conditions used. The infra red and nuclear magnetic resonance spectra of the pyridylamines were analysed and the effect of the substituent on absorption position was noted. Nuclear magnetic resonance data were used in an attempt to explain earlier observations by Watson and Mann for the protonation of tri-2-pyridylamine.

Complexes of the above ligands were synthesised with iron (II), Cobalt (II), nickel (II), copper (II) and molybdenum (0). The infra red and electronic spectra of the nickel complexes and the Mössbauer spectra of the iron complexes were studied. The single absorption in the Mössbauer spectrum of $[Fe(tripyam)_2](ClO_4)_2$ is split for $[Fe(5mpdpa)_2](ClO_4)_2$ and $[Fe(4mpdpa)_2](ClO_4)_2$ indicating that the metal ion is sensitive to the effect of the substi-

tuent present in one of the pyridine rings. The electronic spectra of the nickel complexes and the Mössbauer spectra of the iron complexes were analysed to determine the extents of σ and π bonding in the complexes.

Isomeric complexes with copper(II) (e.g. $[Cu(6mpdpa)_2](ClO_4)_2$ and $[Cu(6mpdpa)_2(ClO_4)_2]$), were studied and data obtained analysed to determine the morphology of the complexes. Infra red, electron spin resonance and electronic spectra were analysed and a tetragonally distorted octahedral environment was suggested for complexes of the type $[Cu(L)_2](ClO_4)_2$ where L = 6mpdpa and 4mpdpa. Complexes of the type $[CuL_2(ClO_4)_2]$ where L = 6mpdpa, 4mpdpa and 5npdpa were considered to have a trans stereochemistry.

The isotropic nature of several of the esr spectra presented the problem of determining whether a static or dynamic Jahn Teller distortion existed for the complexes concerned. Electron spin resonance studies were extended to cover related copper(II) systems, the ligands involved being di-2-pyridylamine and pyridine.

An exploratory examination of complexes with cobalt(II) was undertaken, with an emphasis on magnetic behaviour, in an attempt to ascertain whether earlier observations for $[Co(tripyam)_2](ClO_4)_2$ were common to the tri-2-pyridylamine type ligand in general. Data obtained suggested that the detailed behaviour of $Co(tripyam)_2(ClO_4)_2$, which undergoes a change of spin multiplicity between $100^{o}K$ and $200^{o}K$, was not general for the series. Although the new complexes with substituted tri-2-pyridylamines give room temperature magnetic moments remarkably close to the spin only value for 3 unpaired electrons, the Curie-Weiss Law is obeyed to 77°K, the limit of the measurements.

Finally, the use of physical techniques for studying structural variations in silver(II) complexes was considered. The techniques used were found to yield limited information.

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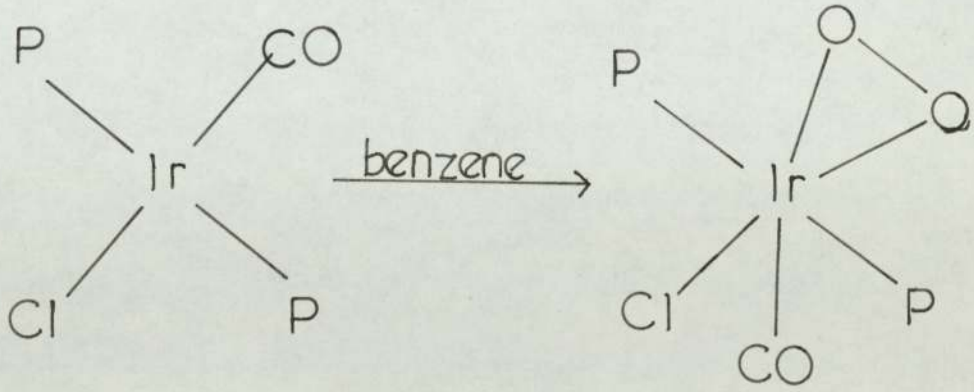
INTRODUCTION

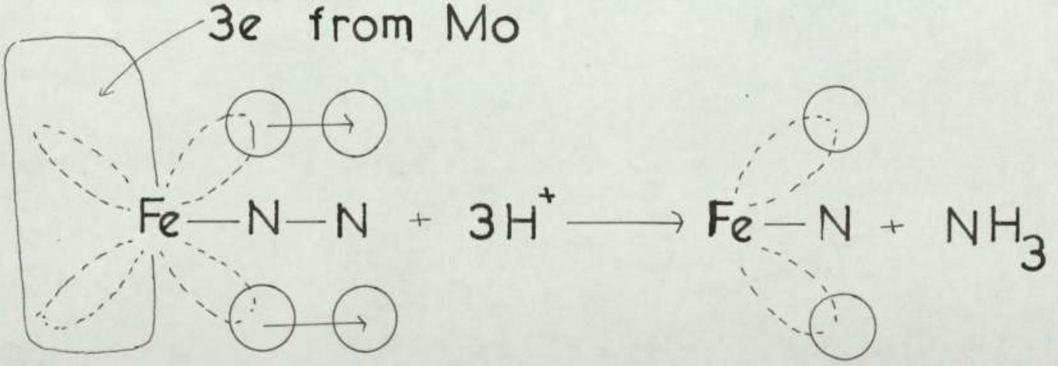
The availability of vacant low energy orbitals on transition metal ions enables a variety of donor molecules, ligands, to co-ordinate to the metal ions, affording complexed products of metal salt and ligand. This ability to accommodate ligands has opened up the vast field of co-ordination chemistry.

This particular area of chemistry is of importance for several reasons, the following being some of the more interesting. The ability of chlorocarbonyl bis(triphenylphosphine)iridium to take up gases was observed by Vaska[1]. He observed that, in benzene as solvent, $IrCl(CO)(Ph_3P)_2$ takes up one molecule of oxygen per metal atom. He also found that the gas uptake is reversible when the oxygen pressure above the solution is reduced.

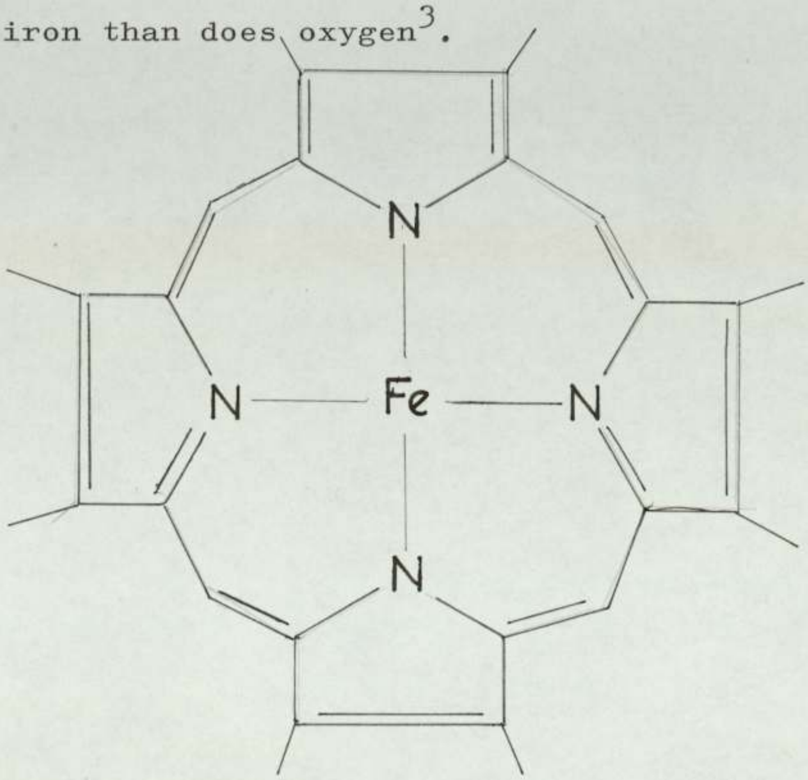


De-oxygenation is fairly rapid in boiling benzene but is also observed at 25°C. The oxygen adduct is best formulated as a molecular peroxide of tervalent iridium with both oxygens bonded to the same central atom. This discovery promptly stimulated interest in the potential of transition metal complexes as catalysts.

Nitrogen fixation has been studied by biologists and chemists alike in attempts to gain insight into bacterial nitrogen fixation. Breaking of the N-N bond of molecular nitrogen is achieved on route to ammonia formation. It is thought that the natural enzyme contains an iron atom in such an electronic state (determined by the protein ligand) that it picks up nitrogen very easily. Molybdenum is thought to be concerned with the reducing action, acting as a cource of electrons, energy being produced by the hydrolysis of A.T.P. Electrons from the reducing source are fed to the iron atom and then to the anti-bonding orbitals on the complexed nitrogen via the d and π system[2].



The oxygen carrier in the bloodstream, haemoglobin, is a protein, which, on hydrolysis with HCl, is cleaved into two fragments, haemin and globin. Haemin contains an iron centre surrounded by four nitrogen heterocycles, the actual passage of oxygen being a function of the metal ion. The poisonous property of carbon monoxide stems from its ability to complex more strongly with the iron than does oxygen[3].



In order to enable studies to be carried out in more specialist fields such as those mentioned above, more fundamental research is necessary to study bonding and stereochemistry (which is often very important in enzymic functioning). Research into the adaptability of physical techniques to aid in solving problems is also of great importance. It is, however, important to stress that it is not always possible to extrapolate from the behaviour of one compound to determine what is happening in another compound.

The co-ordination of nitrogen heterocycles to transition metals has been studied, complexes with ligands such as pyridine, bipyridyl[4,5,6] and di-2-pyridylamine [7,8,9,10] having been extensively studied. Emphasis has been placed on studying variations in co-ordination behaviour and so a section of this work has been devoted to a study of the bonding of ligand to metal in tri-2-pyridylamine complexes. Tri-2-pyridylamine is a useful ligand to study because of the high degree of symmetry it enforces on the metal ion[11]. Basically, there are two possible contributory factors to the strength of the metal-nitrogen bond in tri-2-pyridylamine complexes, σ bonding involving overlap of the lone pair on the ring nitrogen with vacant low energy orbitals of correct symmetry on the metal and π bonding involving overlap of the filled d orbitals on the metal with the delocalised π cloud above and below the aromatic ring. It is feasible that either one of these factors or more probably a combination of both is responsible for the strength of metal-ligand bonding.

A brief survey of the co-ordination behaviour of tri-2-pyridylamine will be useful at this stage. Tri-2-pyridylamine was first synthesised in 1927 by Wibaut and La Bastide[12], who found that it was less basic than 2-aminopyridine and di-2-pyridylamine[13]. In hydrochloric acid it was found to form an adduct with mercuric chloride. In 1948 Watson and Mann[14] attempted to protonate and methylate the three pyridine ring nitrogen atoms. They were, however, only able to protonate two of the rings, the third ring being reluctant to accept a proton or methyl group. Reduction of the base, by the same workers, with tin and hydrochloric acid resulted in the formation of di-2-pyridylamine, a free radical mechanism being suggested. Kulasingam and McWhinnie studied the co-ordination to transition metal ions[15,16,17,18]. As in the case of di-2-pyridylamine it was found to co-ordinate to transition metal ions via the ring nitrogens rather than the amino nitrogen. The base was found to co-ordinate either bidentate or terdentate, there being no evidence to date of unidentate co-ordination. The preference for bidentate co-ordination in many cases is difficult to understand in terms of the considerably lower ligand field strength for bidentate co-ordination (11,000 cm^{-1}) compared to that for terdentate co-ordination (12,800 cm^{-1}). The co-ordination behaviour will now be discussed in more detail.

The perchlorates of iron(II), cobalt(II), nickel(II) and copper(II) yielded bis terdentate complexes. In the diffuse reflectance spectrum of $Ni(tripyam)_2(ClO_4)_2$, the Δ band ($^3A_{2g} \rightarrow {}^3T_{2g}$) occurred at 12,800 cm^{-1} indicating that terdentate tripyam is a strong field ligand. The three absorptions in the electronic spectrum of the Ni(II) complex are consistent with an octahedral (O_h) stereochemistry. $Fe(II)(tripyam)_2(ClO_4)_2$[11,62] was found to be low spin, as indicated by the low magnetic susceptibility (0.9 B.M.) and position of absorption in the Mössbauer spectrum. The single sharp peak at δ = 0.63 mm/sec (sodium nitro-prusside) indicated a microsymmetry around the metal very close to O_h. X-ray data showed the bis terdentate tri-2-pyridylamine iron(II), nickel(II), cobalt(II) and copper(II) perchlorate complexes to be isomorphous, indicating microsymmetry close to O_h in all four complexes.

The study of cobalt(II) complexes with tri-2-pyridylamine revealed that the magnetic moment of $Co(tripyam)_2(NO_3)_2$ is 5.15 B.M. whereas $Co(tripyam)_2(ClO_4)_2$ exhibited a moment of 4.8 B.M. The low moment for the perchlorate complex could possibly be due to deviations from true O_h symmetry, which would result in a quenching of the orbital contribution to the magnetic moment. However, X-ray powder photography indicated that $Co(tripyam)_2(ClO_4)_2$ is isomorphous with $Fe(tripyam)_2(ClO_4)_2$. This suggests that lattice spacings of the heavier elements are similar in both complexes. The $^{57}Fe(II)$ Mössbauer spectrum of $Fe(tripyam)_2(ClO_4)_2$ consisted of a single sharp isotropic peak indicating a truly O_h microsymmetry around the iron metal. This evidence, together with X-ray powder data, indicates O_h symmetry around the cobalt ion; there is no evidence for a trigonal distortion along the C_3 axis. Kulasingam[69], therefore, suggested the presence of spin doublet$\rightleftharpoons$spin quartet isomerism with a Boltsman distribution between the spin states. The presence of $^4T \rightleftharpoons {}^2E$ equilibrium has since been confirmed[19]. Previously, spin isomerism in Co(II) complexes has only been experienced for complexes where π delocalization is possible. The presence of an insulating group on tri-2-pyridylamine inhibits electron delocalization via the π network. The availability of substituted tri-2-pyridylamines prompted the synthesis of $CoL_2(ClO_4)_2$ complexes in an attempt to ascertain whether the spin isomerism is common to the tri-2-pyridylamine class of ligand generally. It is, however, noted that the presence of a substituent in one of the rings enforces a microsymmetry lower than O_h and presence of spin equilibrium can only be confirmed by determination of magnetic susceptibilities at various temperatures.

Hogg and Wilkins[75] studied some cobalt(II) complexes with 2,2',6',2"-terpyridyl and they noticed that values of the magnetic moments have an unusual dependence on the anion present, ranging from 4.3 B.M. for the perchlorate to 2.1 B.M. for the chloride (only slightly higher than the value expected for a low spin complex). A temperature-dependence study on the bromide complex indicated the possibility of a spin equilibrium.

Stoufer and co-workers[76] also noted that the occurrence of spin isomerism was dependent on the anion present and this was confirmed by Barnard et al. $Co(tripyam)_2(PF_6)_2$ was found to obey the Curie-Weiss Law at low temperatures.

The tendency for Co(II) complexes to distort in the low spin state resulted in alteration of the infra red spectrum for $Co(tripyam)_2(ClO_4)_2$ on cooling. The spectrum of $Co(tripyam)_2(PF_6)_2$ remained unaltered on cooling, apart from a small shift of 4 cm^{-1} of the whole spectrum.

Copper(II) perchlorate was found to yield two interconvertible isomers[69], one containing bis terdentate tri-2-pyridylamine and ionic perchlorate anions, the other containing bis bidentate tri-2-pyridylamine with co-ordinated perchlorate anions.

Complex formation with nitrates, thiocyanates was subsequently studied[17,77]. Cobaltous nitrate preferentially forms a bis bidentate dinitrate complex with tri-2-pyridylamine but it was possible to effect isomerization to the bis terdentate complex analagous to the perchlorate complex prepared previously. The diffuse reflectance spectra of the perchlorate and nitrate complexes were superimposable. In solution the tendency for one ring to break loose to enable solvent co-ordination is evident. Copper (II) nitrate forms a dinitratobis tri-2-pyridylamine copper(II) in the solid but in solution there is evidence for a tetragonal species $[Cu(tripyam)_2(NO_3)S]^+$ where S represents a co-ordinated solvent molecule. Metal nitrate complexes with tri-2-pyridylamine where metal: ligand ratio is 1:1 have been obtained for M = Co, Ni, Cu. $[Ni(tripyam)(H_2O)_2NO_3]NO_3$ was shown to be octahedral, conductivity data indicating a uni-univalent electrolyte. The postulated formulation of bis(tri-2-pyridylamine)Cobalt(II)tetranitratocobaltate for the cobalt(II) nitrate complex was suggested after comparison with the corresponding halide complex. In the solid state $Cu(tripyam)(NO_3)_2$ contains bidentate ligand and co-ordinated nitrate groups.

Thiocyanate groups can function as unidentate ligands bonding to the metal via the nitrogen atom (iso-thiocyanate) or via the sulphur atom (thiocyanate). It is also possible for thiocyanate to act as a bridging ligand between two adjacent metals. $Co(tripyam)_2(NCS)_2$ contains bidentate tri-2-pyridylamine, thiocyanate bonding via the nitrogen, octahedral stereochemistry being indicated. In the absence of excess ligand, solutions give rise to $Co(tripyam)_2Co(NCS)_4$ containing both octahedral and tetrahedral Co(II). Nickel forms complexes of the form $Ni(tripyam)_2(NCS)_2$ and $Ni(tripyam)(NCS)_2$. Both complexes have been shown to possess octahedral stereochemistry, the bis tripyam complex containing bidentate tri-2-pyridylamine but $Ni(tripyam)(NCS)_2$ possesses terdentate tri-2-pyridylamine with at least one bridging thiocyanate. Copper thiocyanate forms complexes $Cu(tripyam)(NCS)_2$, three distinct forms having been prepared, Cu(tripyam)(NCS)(CNS), $Cu(tripyam)(NCS)_2$ and $Cu(tripyam)(CNS)_2$, tri-2-pyridylamine co-ordinating bidentate in all cases.

Cobaltous halides[16] tend to form complexes containing tetrahedral Co(II) due to the presence of the tetrahalocobaltate anion. Copper halides complex similarly but data obtained for complexes with Ni(II) halides are consistent only with the formulation of an octahedral environment around the metal. $[Ni(tripyam)(H_2O)_2X]$ is the suggested formulation. Rhodium and iridium halides also form octahedral complexes with tri-2-pyridylamine of the form $Rh(tripyam)Cl_3$. The cis complexes of the type $Pd(tripyam)_2Cl_2$ are thought to possess a cis dihalo planar structure with bidentate ligand.

It is obvious that a large number of variations in co-ordination behaviour of tri-2-pyridylamine to transition metal ions occur. For this reason, present work concentrated on the relatively straightforward perchlorate complexes. Several substituted tri-2-pyridylamines were synthesised, the role of the substituent being to alter the relative extents of σ and π bonding on co-ordination to transition metal ions. Methyl substituents were introduced due to their electron donating properties as a result of hyperconjugation; the nitro substituent was chosen as a result of its ability to withdraw electrons both inductively and mesomerically. Characterization of the bases involved microanalysis, infra red spectroscopy and nuclear magnetic resonance spectroscopy. As the nuclear magnetic resonance data are discussed in detail later, a brief survey of the application of nmr to related nitrogen heterocycle systems will be useful.

The simplest related heterocycle, pyridine, has been extensively studied by Pople, Bernstein and Schneider[20]. The marked difference between chemical shifts for ortho, para and meta protons was noted. Partial deuteration of pyridine enabled coupling constants to be obtained (from the spectra of 2.6D_2 pyridine, 3D pyridine and 4D pyridine). Elimination of certain spin interactions by deuteration is justified in view of the absence of any electronic effect on deuteration.

1,10-phenanthroline and its complexes with Fe(II), Co(II), Ru(II) and Zn(II) have been studied[78] in terms of $AA'MM'SS'X_2$ system. A high field shift for protons 2 and 9 was observed on complex formation, postulated as being due to a metal-non-bonded proton interaction. The single absorption for protons 5 and 6 is due to their equivalence and is also indicative of their inability to interact with any other protons.

Cox and Bothner-By[21] studied the nuclear magnetic resonance spectra of tautomeric substituted pyridines and their conjugate acids. The spectra of 2-pyridone, 2-chloro, 2-amino and 2-methoxy pyridine were studied. A marked substituent effect on the chemical shift of the ring protons was observed. In general, the chemical shifts of substituted pyridines appear to low field as the electronegativity of the substituent is increased. A comparative study of coupling constants was also made. For normal 2-substituted pyridines, J_{34} is 7.98 - 8.38H_z and increases to 9.20H_z in 2-pyridone. Similarly, J_{56} is greater in 2-pyridone compared with other 2-substituted pyridines. This has been attributed to the greater double bond character between these positions in 2-pyridones over normal 2-substituted pyridines.

Griffin and Thomas[22] recently studied the nmr spectrum of tri-2-pyridylphosphine, chemical shifts observed for protons 3, 4, 5 and 6 being 2.60, 2.30, 2.82 and 1.30τ respectively.

Nuclear magnetic resonance spectra of the substituted tri-2-pyridylamines were of particular interest in that they provided a possible explanation for various observations of previous workers. Watson and Mann's[14] inability to protonate all three rings of tri-2-pyridylamine was hard to understand in terms of the apparent equivalence of the three rings. Secondly, preference for bidentate co-ordination despite the more favourable ligand field strength on terdentate co-ordination was not easy to explain in the absence of any steric hindrance.

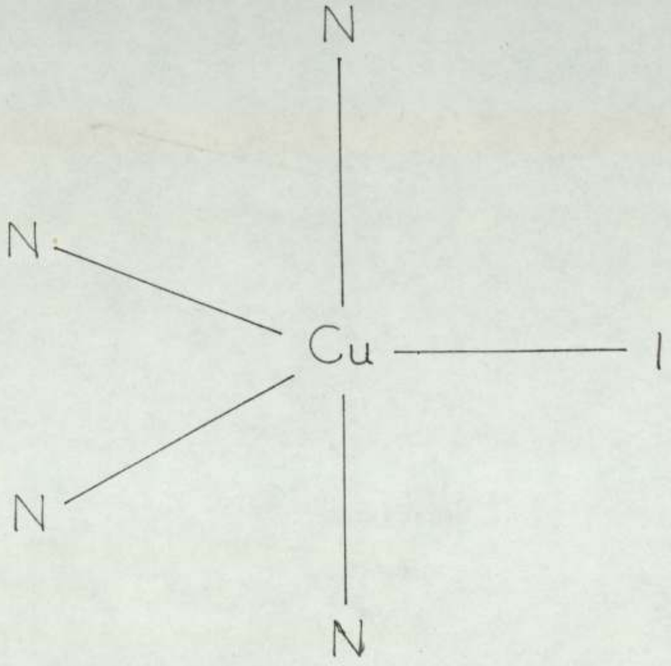
A study of the co-ordination behaviour of the ligands and the complexes formed was also undertaken, the effect of the substituents on the microsymmetry around the metal being examined. In the search for novel complexes co-ordination with copper(II) ion was examined, the ability of tri-2-pyridylamine to form two interconvertible isomers with copper perchlorate having been mentioned previously. A summary of the more common stereochemical environments experienced by copper(II) will be useful.

The copper(II) ($3d^9$) ion is susceptible to Jahn Teller distortion in which the degeneracy of the e_g orbitals is removed in the presence of an electrostatic field. The Jahn Teller theorem requires that any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some kind of distortion which will lower its symmetry and split the degenerate state. In copper(II) systems, the unpaired electron occupies one of the e_g orbitals, [e_g $d(x^2 - y^2)$]. In this case the dz^2 orbital is doubly occupied and ligands on the z axis are more screened from the electrostatic attraction of Cu^{2+} ion than are ligands in the xy plane. This will result in ligands in xy plane being held more closely to the metal ion.

Consequently, a regular octahedral stereochemistry is uncommon for copper(II) systems $K_2PbCu(NO_2)_6$ contains six equivalent Cu-N bonds[23] (2.11 A^o) and the electron spin resonance[24] spectrum consists of a single isotropic absorption, consistent with a regular octahedral environment. However, the electronic spectrum is consistent with an elongated tetragonal octahedral CuN_6 environment. The isotropic electron spin resonance spectrum has been explained in terms of a dynamic or pseudo rotational[26] Jahn Teller rather than a static distortion, which is observed in the majority of copper complexes.

Tris-ethylenediamine copper(II) sulphate contains six equivalent Cu-N bonds (2.17 A^o) but the symmetry is lowered from true octahedral (O_h) to trigonal D_3 due to the methylene groups of the ligands. The occurrence of a dynamic distortion is considered likely in this compound. A dynamic distortion results from distortion along the equivalent x, y and z axes. Cooling the sample results in 'freezing' the complex into one of its potential minima and in this state it is possible to detect the distortion.

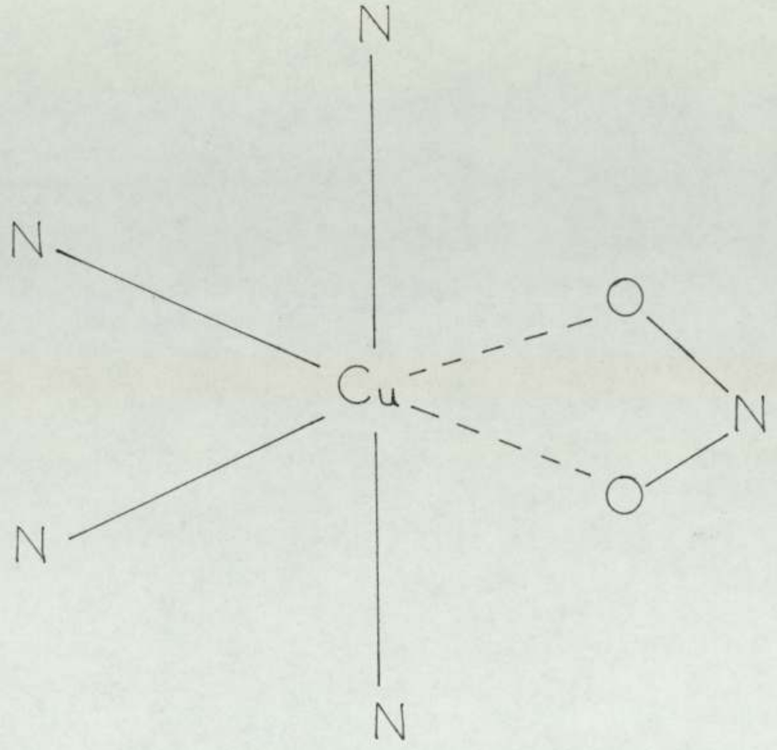
There is no evidence for the occurrence of a regular tetrahedral stereochemistry. The most common stereochemistry around copper(II) is elongated tetragonally distorted octahedral which contains four short bonds in the plane of the copper(II) ion and two longer bonds in the axial direction. This is experienced in $Cu(NH_3)_4(SCN)_2$[27], $Cu(NH_3)_4(NO_2)_2$[25] and $Cu(en)_2(BF_4)_2$. The spectra of these complexes are consistent with D_{4h} stereochemistry with a $dx^2 - y^2$ ground state. An effectively square coplanar stereochemistry, involving bonding ligands is believed to exist in $Na_4Cu(NH_3)_4[Cu(S_2O_3)_2]H_2O$[28]. Polarised single crystal spectra[29] and the esr spectrum[30] indicate a stereochemistry approximating to trigonal bipyramidal although stereochemistry is not regular D_{3h}. Polarised single crystal spectra of $[Cu(bipy)_2I]I$ indicate a distorted trigonal bipyramidal stereochemistry.



$[Cu(bipy)_2I]I$

Square based pyramidal stereochemistry is more common, examples being $[Cu(NH_3)_4(H_2O)]SO_4$[31] and $[Cu(1, 3\ pn)_2H_2O]SO_4$[32]. In most cases the copper(II) ion is displaced about 0.2 A° out of the plane of the four in plane ligands, towards the fifth ligand.

In contrast with the common occurrence of the elongated tetragonal octahedral stereochemistry a cis distorted octahedral stereochemistry has only been established for a few complexes, one example being $[Cu(bipy)_2ONO]NO_3$[33]. The esr spectrum is considered to be indicative of a dz^2 ground state.



$[Cu(bipy)_2ONO]NO_3$

Elucidation of structural details of copper(II) complexes involves use of techniques including infra red, diffuse reflectance and electron spin resonance spectroscopy, together with X-ray powder and diffraction data. The copper(II), i.e. with a d^9 configuration has an effective spin of $\frac{1}{2}$ with an associated spin angular momentum of $Ms = \pm\frac{1}{2}$ leading to a doubly degenerate spin state in the absence of a magnetic field. In a magnetic field this degeneracy is removed and the energy difference between these two states is given by

$$h\,v = g\,\beta\,H$$

where h is Planks constant, v is the frequency, g is the Lande splitting factor, β is the electronic Bohr Magneton and H is the magnetic field. For the free copper(II) ion there is also an interaction with the magnetic field due to the orbital angular momentum (L) of the electron.

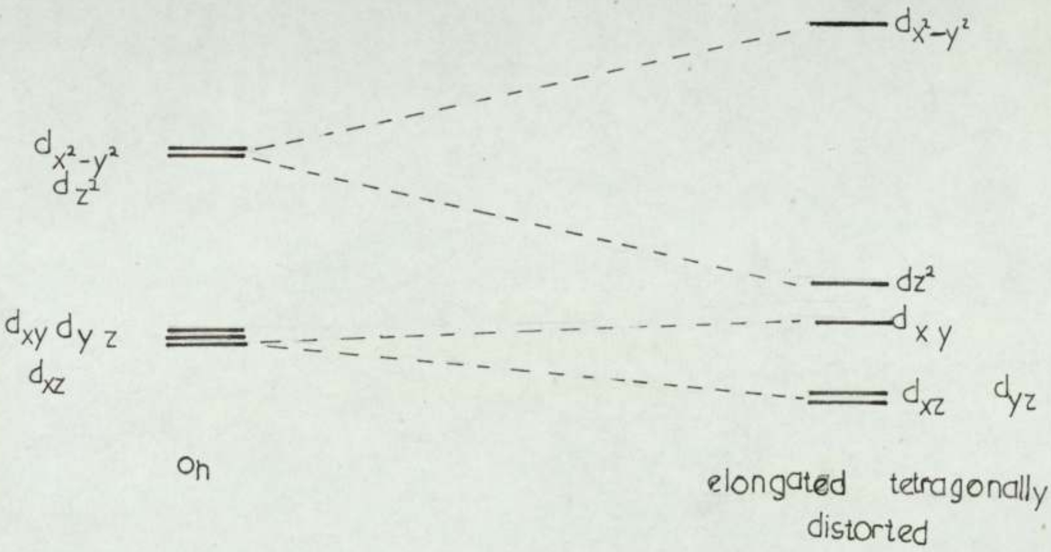
In practice the esr spectra of polycrystalline samples of copper complexes are displayed as first derivative absorption curves. Hathaway and co-workers[34] consider the esr spectra of axial complexes, in particular the precise value of $g_\perp$, useful for distinguishing between $dx^2 - y^2$ and dz^2 ground state. Axial compressed complexes, where the unpaired electron is in the dz^2 orbital, are considered to exhibit a considerably lower g value ($g \nless 2.004$) than for axially elongated ($dx^2 - y^2$ ground state) complexes ($g \nless 2.056$). It is emphasised that such simple interpretations of the esr spectra only apply if all the tetragonal axes of the local copper(II) ion environment are aligned parallel to the unit cell. However, Hitchman[54] has recently suggested that for low symmetry complexes the ground state can only be described in terms of a hybrid orbital, possibly involving contributions from all five d orbitals. It seems dangerous, therefore, to interpret the lowest g factor in terms of a pure $dx^2 - y^2$ or dz^2 ground state.

Recent publications by Hathaway illustrate the shortcomings of the original suggestion. The lowest g factor for dichloro bis-(2-methylpyridine)copper(II)[55] was found to be 2.033 but the complex was discussed in terms of a $dx^2 - y^2$ ground state, rather than dz^2 ground state. The same workers[56] have suggested a dxy ground state for 2,2'bipyridylbis(hexafluoroacetylacetonate)copper(II) despite a value of 2.029 for the lowest g factor.

In many cases, an isotropic esr spectrum is obtained.

This, however, does not indicate the presence of a regular octahedral or tetrahedral environment but can result from either a dynamic Jahn Teller distortion or misalignment of molecular axes within the crystal.

Electronic spectra provide information about electronic transitions between the ground state and excited state of the crystal field levels.



These transitions occur in the range 4.0 - 30.0 kK. The number of bands and relative intensities of the bands afford information as to the precise structure of the complex.

In fact, Hathaway and co-workers have suggested that there are certain characteristic spectra for particular stereochemical environments around the copper(II) ion. A spectrum involving a single sharp band at 12.0 - 12.5 kK is considered[57] to be characteristic of a trigonal bypyramidal environment, whereas square pyramidal structure is indicated by a single band in the region

15.0 - 18.0 kK. The presence of two bands of equal intensity in the regions 9.2 - 10.8 kK and 14.3 - 15.6 kK has been assigned[33,34] by the same workers to a cis distorted octahedral stereochemistry. A single broad band in the region of 14.4 - 15.2 kK, suggesting more than one transition under the band envelope, has been assigned for $Cu(bipy)_2(ClO_4)_2$ to a stereochemistry involving twisting of the pyridyl rings out of the xy plane towards a tetrahedral stereochemistry.

However, McKenzie[58] has examined the electronic spectra of a number of closely related $[CuN_5]^{2+}$ and $[CuN_6]^{2+}$ chromophores to assess the validity of using electronic spectra to assign structures to copper(II) compounds. He noted that the spectra of many of the $[CuN_5]^{2+}$ chromophores are well within the range which Hathaway regards as characteristic of a cis distorted octahedral stereochemistry. In all cases the $[CuN_5]^{2+}$ chromophores have at least two absorption bands separated by > 3kK, although they are not always resolved. In some cases there are two well defined peaks separated by 5kK.

It is also interesting to note that recent publications by Hathaway discussing the electronic spectra of $[Cu(NH_3)_3]Ag(SCN)_3$ and $[Cu(bipy)_2I]I$[59] are reported. Three absorptions are shown in the spectra for both, which is not consistent with his earlier data, where one maximum was indicated in both cases.

However, McKenzie noted that comparison of electronic data within closely related series of compounds was still valuable and in this respect Hathaway's work is useful.

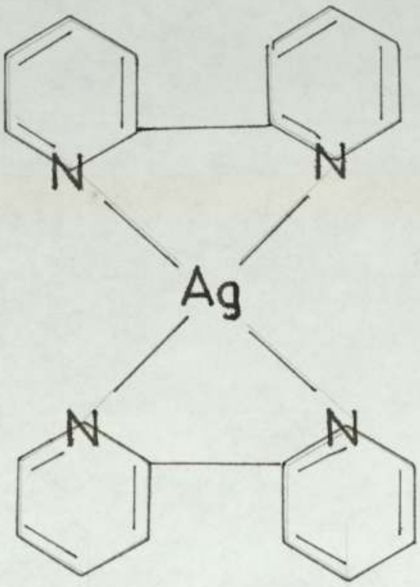
It was hoped to extend the co-ordination study of the copper complexes to those of silver(II), little work having been done of a comparative nature. Unfortunately, it was not found possible to stabilize Ag(II) with tri-2-pyridylamines as ligands.

However, it was decided to undertake a comparative study of the bis(2,2'-bipyridyl) and bis(1,10-phenanthroline) complexes of copper(II) and silver(II). With this in mind, a summary of previous work with Ag(II)bipy and phenanthroline complexes will serve as a background to future discussion.

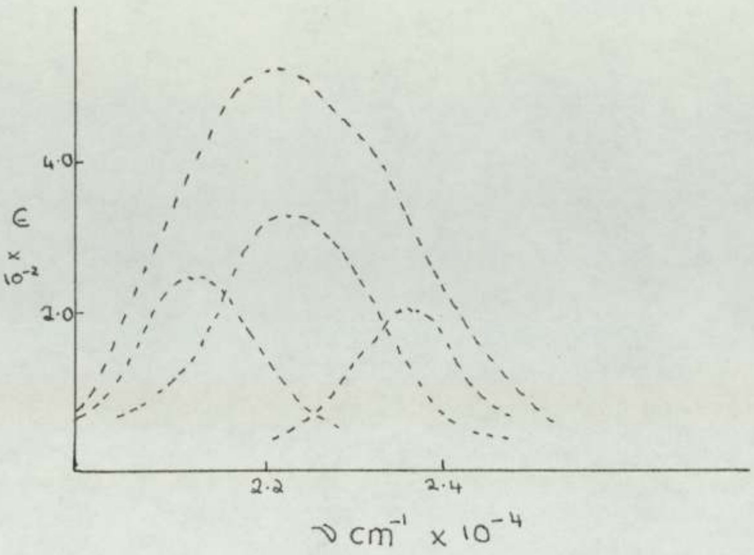
Bivalent silver is stabilized by co-ordination with some nitrogen containing heterocycles, co-ordination occurring in most cases by formation of four dsp^2 hybrid bonds[35] although compounds of higher co-ordination are known[36]. The oxidation potential of Ag(II)/Ag(I) is strongly reduced from 1,914 volts in nitric acid solution[37] to 1.453 volts on complexing with dipyridyl[38]. Many of these complexes are stable in the solid state. Pyridine forms a tetrapyridine complex $Ag(Py)_4S_2O_8$[37,40] which is considered to be isomorphous with the corresponding cupric complex. Compounds with di-2-pyridyl[41], ter-2-pyridyl[42] and o- phenanthroline[43] have also been prepared, by oxidation of the corresponding Ag(I) complex. Solutions of silver iodide in the presence of excess ligand molecule are oxidized by means of potassium persulphate or ammonium persulphate. The silver(II) persulphate complexes are then precipitated as yellow to dark red crystalline powders, sparingly soluble in water. By further double decomposition, different salts can be obtained, a series of salts $Ag(1,10\text{-}phen)_2X_2$, (where $X = \frac{1}{2}S_2O_8$, HSO_4, NO_3, ClO_3 and ClO_4) having been prepared[43]. Various bipyridyl complexes have also been obtained by oxidation with persulphate followed by double decomposition, e.g. $Ag(bipy)_2S_2O_8$, $Ag(bipy)_2(HSO_4)_2$, $Ag_2(dipy)_3(NO_3)_2$, $Ag(dipy)_3(ClO_4)_2$[41].

Because of the considerable lowering of oxidation potential on complex formation, it is possible to use oxidizing agents such as PbO_2, BaO_2 and CeO_2[44]. Ozone can also be used but care must be taken to avoid oxidation of the ligand.

A more common route to complexes of Ag(II) is via anodic oxidation in a divided cell[45]. In the presence of dilute nitric acid, $Ag(terpy)NO_3$ is oxidized readily at the anode of an electrolytic cell forming $[Ag(terpy)NO_3]NO_3$. Other complexes with terpy can be prepared via anodic oxidation or double decomposition. There is no evidence for the formation of an argentic complex with more than one molecule of terpyridyl co-ordinated. There is little detailed structural data available on the complexes formed, a square coplanar stereochemistry having been postulated in the case of bipy, o-phen and terpy complexes.



The visible and ultra violet[60] spectra of several $Ag(bipy)_2^{++}$ complexes were found to contain two absorption bands, a weak absorption at about 460 mm and an intense band near 360 mm. It was suggested that the high extinction coefficient of the shorter wavelength band indicated that it was caused by a charge transfer process. Similarly, the higher wavelength band was assigned to a d-d transition of the metal. The higher wavelength band is shown below.

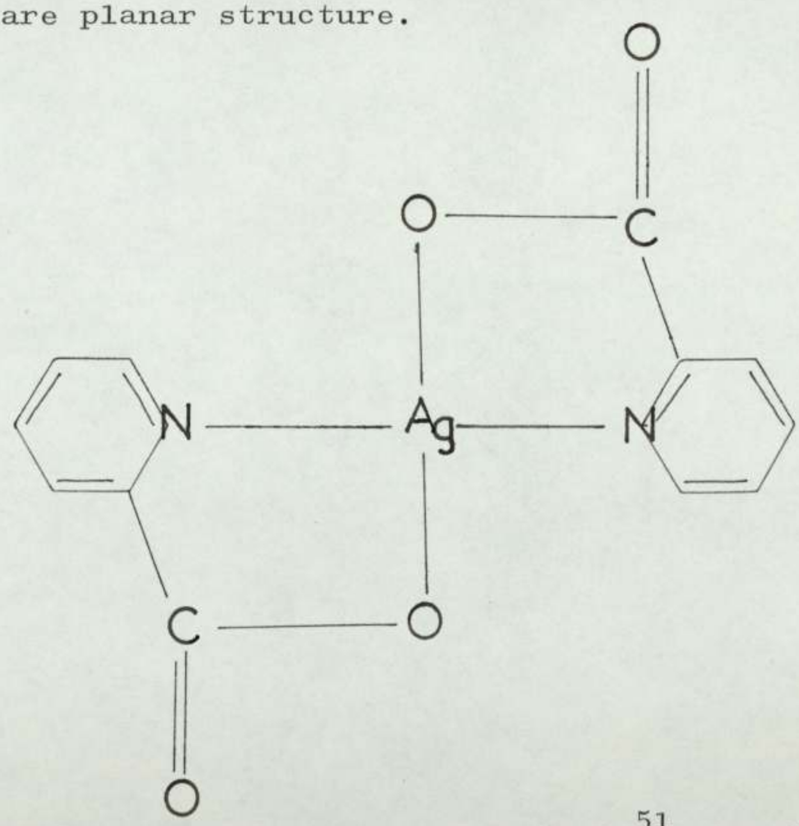


In all three complexes studied, the bivalent silver was tetraco-ordinated. It was then argued that the stereochemistry of the complexes is <u>either</u> planar or tetrahedral, intermediate stereochemistries not being considered. As the above absorption band on gaussian analysis was considered to contain three components, it was deduced that these corresponded to the transitions between the four energy levels present in a planar environment dxy, dz^2, $dx^2 - y^2$ and dxz, dyz.

Recent work by Harris[61], where the solution spectrum of $Ag(terpy)S_2O_8(10^{-3}M)$ in aqueous $(NH_4)_2[Ce(NO_3)_6]$ $(4 \times 10^{-3}M)$ was obtained, showed that the extinction coefficient for a band at 470 mm was 880 which is too high to be considered as a ligand field transition. It therefore seems likely that the bands previously assigned to ligand field transitions are in fact charge transfer bands.

A compound of silver(II) with 8 hydroxyquinoline arising from disproportionation of Ag(I) into Ag(o) and Ag(II) in boiling aqueous solutions of silver acetate and ligand molecule has been reported[46]. The compound, however, is diamagnetic[47] and there is no evidence for Ag in the bivalent state[48].

Argentic picolinate[49], prepared by solution of silver nitrate with potassium persulphate in the presence of picolinic acid has been shown to be co-omorphous with the analagous copper compound by X-ray diffraction analysis[50]. Although its X-ray diffraction pattern could not be elucidated, the isomorphism with the corresponding cupric complex whose structure has been studied suggests a square planar structure.



The nicotinate and isonicotinate[51] are also known to be isomorphous[52] with the cupric compound. The stability of Ag(II) complexes of pyridine mono, bis and tricarboxylic acids decreases with increase in the number of carboxyl groups present. The position of these carboxyl groups has a definite influence on stability, with the exception of the mono acids. This variation in stability has been attributed to steric effects hindering the formation of the planar configuration around the metal[52].

CHAPTER I

EXPERIMENTAL

1.1 Chemicals and analysis

Chemicals - Amino-pyridines and 2-bromopyridines were obtained from Koch Light Laboratories Limited; p-cymene was obtained from Hopkin and Williams. The author would like to thank Midland and Yorkshire Tar Distillers for gifts of 2-amino-4-methylpyridine and 2-amino-6-methylpyridine.

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

(1) Analytical Laboratory, Department of Chemistry, Reading;
(2) Dr. F. B. Strauss, 10 Carlton Road, Oxford;
(3) A. Bernhardt, 5251 Elbach über Engelskirchen, West Germany, Fritz-Pregl-Strasse 14-16; and
(4) University of Aston analytical laboratory.

Solvents - Solvents were obtained from commercial sources and were purified by literature methods; nitromethane[70], acetone[71] and ethanol[72].

1.2 Physical Techniques

Conductivity - Molar conductivities were measured with a Mullard conductivity bridge using a standard conductivity cell (constant = 1.36). Measurements were made for 10^{-3}M nitromethane solutions.

Magnetic Susceptibility determinations - Magnetic susceptibilities were measured by the Gouy method at room temperature. The electromagnet was water-cooled and all determinations were carried out using a current of 10 amps. The tube was calibrated using $HgCo(NCS)_4$, ($\chi g = 16.44 \times 10^{-6}$ cgs units at 20°C). $HgCo(NCS)_4$ was also used to determine the height to which the tube should be packed. The pull vs length of tube packing was found to reach a plateau of 9.5 cm. In all subsequent determinations the tube was packed to a height of 10.3 cm. Diamagnetic corrections were made from Pascals constants[73].

Magnetic susceptibilities were calculated using the equation:

$$10^6 \chi = \frac{\alpha + \beta F}{\Delta \omega}$$

where $\alpha = 0.017$, $\beta = 0.2305$, F = force or pull and $\Delta \omega$ = weight of sample.

X-ray powder photographs - X-ray powder photographs were obtained using Cu Kα radiation with nickel filters ($\lambda = 1.54$ A^{-}). Exposure time of 1½ - 3 hours was used.

Infra red spectra - Infra red spectra were recorded for nujol and fluoro-chemical mulls (for solids) and for liquid films (for oils). The instruments used were Perkin Elmer 225, 237, and 457 spectrometer between 4000^{-1} and 250^{-1}.

Diffuse reflectance spectra - Diffuse reflectance spectra were obtained using Unicam S.P. 700 spectrophotometer using S.P. 735 diffuse reflectance attachment. Magnesium oxide was used as a reference and, in some cases, as a diluant. The instrument was calibrated using holmium glass[74] where the following results were obtained:

Band position from SP 700	Expected band position	Difference
kK	kK	kK
27.530	27.850	0.320
23.706	23.964	0.258
21.882	22.085	0.203
21.530	21.239	0.209

The average error is 247 cm^{-1}. The values quoted in this thesis are corrected values.

Electron spin resonance spectra - Electron spin resonance spectra were measured using Hilger Watts microspin spectrometer using DPPH as a reference and Fremy's salt and copper sulphate pentahydrate as calibrants. Spectra were measured at room temperature in all cases and, in several cases, at liquid nitrogen temperature. The spectra were obtained for microcrystalline samples contained in melting point tubes. Solution spectra were obtained in several cases for nitromethane and dimethyl formamide solutions.

Nuclear magnetic resonance spectra - Nuclear magnetic resonance spectra were obtained using Perkin Elmer R.12 spectrometer, the frequency of operation being 100MHz. The spectra were obtained for carbon tetrachloride and deuterochloroform solutions on scale factors 10 and 1. Tetramethyl silane was used as a reference.

^{57}Fe Mössbauer spectra - Mössbauer spectra were measured using an NSEC Model B analyser. A 1 millicurie ^{57}Co was used, embedded in a stainless steel matrix. The absorber was moved at velocities from 0 to 6 mm/sec relative to the stationary source. Spectra were measured at liquid nitrogen temperature and isomer shifts are quoted relative to sodium nitro prusside.

1.3 Preparation of complexes

Preparation of complexes with ferrous perchlorate

All preparations were carried out under oxygen-free dry nitrogen, solvents having been saturated with nitrogen.

Preparation of ferrous perchlorate hexahydrate.

British Standard specification iron metal was mixed with perchloric acid (50/50 v/v). After reacting for five hours, the pale green solution was decanted from the unreacted metal and the solvent volume reduced under low pressure. Pale green crystals of ferrous perchlorate were obtained.

Preparation of bis(4-methyl-2-pyridyldi-2-pyridyl)amine ferrous perchlorate

Freshly prepared ferrous perchlorate hexahydrate (0.2 g) was added to 4-methyl-2-pyridyldi(-2-pyridyl) amine (0.75 g) (See Chapter II for synthesis) in ethanol (15 ml). A red solution was formed which yielded a bright red crystalline solid within half a minute. The solid was filtered and washed with ethanol and ether and dried over phosphorous pentoxide under reduced pressure. Yield 0.45 g.

Preparation of bis[5-methyl-2-pyridyldi-2-pyridylamine] ferrous perchlorate

Freshly prepared ferrous perchlorate hexahydrate (0.25 g) was added to an ethanolic solution (10 ml) of 5-methyl-2-pyridyldi-2-pyridylamine (0.5 g)(See Chapter II for synthesis) forming a bright red solution. A red solid was obtained which was filtered and washed with ethanol and ether. Yield 0.45 g.

Attempted preparation of bis[6-methyl-2-pyridyldi (-2-pyridyl)amine]ferrous perchlorate

Freshly prepared ferrous perchlorate was added to 6-methyl-2-pyridyldi(-2-pyridyl)amine (See Chapter II for synthesis) in ethanol. A yellow solution was formed which did not yield a precipitate even after cooling to 0°C and reducing the solvent volume. This method was attempted several times.

The preparation was then attempted by adding ferrous chloride to an aqueous ethanolic solution of 6-methyl-2-pyridyldi(-2-pyridyl)amine containing an excess of sodium perchlorate. However, precipitation did not occur.

A mixture of ferrous sulphate heptahydrate in water was added to an aqueous ethanolic solution of 6-methyl-2-pyridyldi(-2-pyridyl)amine saturated with sodium perchlorate. A small quantity of a pale yellow precipitate was obtained on cooling on an ice bath. Analytical data suggested that the compound was Fe $(6mpdpa)_2(ClO_4)_2$ but the failure to obtain a Mössbauer spectrum indicated the absence of iron. The appearance of a strong perchlorate band in the infra red spectrum, together with ample evidence of the aromatic nature of the compound, suggested the formation of a ligand perchlorate.

Preparation of diaquo bis/_5-nitro-2-pyridyldi(-2-pyridyl)amine_7ferrous perchlorate

Ferrous chloride (0.9 g) was added to an ethanolic solution (10 ml) of 5-nitro-2-pyridyldi(-2-pyridyl)amine (0.04 g) saturated with sodium perchlorate. A bright yellow solid was formed which was filtered and washed with ethanol and ether. Yield 1.2 g.

Preparation of bis /_4-methyl-2-pyridyldi(-2-pyridyl)amine_7cobalt(II) perchlorate

Cobalt(II) perchlorate hexahydrate (0.36 g) in ethanol (10 ml) was added to 4-methyl-2-pyridyldi(-2-pyridyl)amine in ethanol (10 ml). The solution was warmed for several minutes and then left to stand for two hours. A buff solid was deposited which was recrystallized from acetone/ethanol. Yield 0.32 g.

Preparation of bis[5-methyl-2-pyridyldi(-2-pyridyl)amine]cobalt(II) perchlorate

5-methyl-2-pyridyldi(-2-pyridyl)amine (1.1 g) in ethanol (10 ml) was added to cobaltous perchlorate (0.7 g) and the solution became cloudy on leaving to stand for five minutes. After standing for two hours the solution was filtered and the precipitate recrystallized from acetone/ethanol.Yield 0.8 g.

Preparation of bis[6-methyl-2-pyridyldi(-2-pyridyl)amine]cobalt(II) perchlorate

Cobalt perchlorate (0.7 g) in ethanol (10 ml) was added to 6-methyl-2-pyridyldi(-2-pyridyl)amine (0.95 g) in ethanol (10 ml). After refluxing for five minutes precipitation occurred. The filtered solid was recrystallized from acetone/ethanol. Yield 0.41 g.

Preparation of bis[tri(-4-methyl-2-pyridyl)amine]cobalt(II) perchlorate

Cobaltous perchlorate hexahydrate (0.3 g) in ethanol (10 ml) and tri(-4-methyl-2-pyridyl)amine (0.55 g) were mixed and a pale yellow solid was obtained on standing in an ice bath for one hour. The product was recrystallized from acetone/ethanol. Yield 0.39 g.

Preparation of diaquo bis[5-nitro-2-pyridyldi(-2-pyridyl)amine]cobalt(II) perchlorate

Cobaltous perchlorate hexahydrate (0.56 g) in acetone (10 ml) was added to 5-nitro-2-pyridyldi(-2-pyridyl)amine (0.91 g) in acetone (10 ml). The solution was refluxed for five minutes forming a red oil which, on further heating, formed a pale pink solid. The precipitate was recrystallized from acetone/ethanol. Yield 0.99 g.

Preparation of bis[4-methyl-2-pyridyldi(-2-pyridyl)amine]nickel(II) perchlorate

Nickel perchlorate hexahydrate (0.5 g) in ethanol (10 ml) was added to 4-methyl-2-pyridyldi(-2-pyridyl)amine (0.71 g) in ethanol (10 ml). A pink solid was obtained which was recrystallized from acetone/ethanol. Yield 0.74 g.

Preparation of bis[5-methyl-2-pyridyldi(-2-pyridyl)amine]nickel(II) perchlorate

Nickel perchlorate hexahydrate (1.0 g) in ethanol (10 ml) was added to 5-methyl-2-pyridyldi(-2-pyridyl)amine (1.52 g) in ethanol (10 ml). A dark green solution was obtained which, on warming, yielded a pink solid. The solid was recrystallized from acetone/ethanol. Yield 1.35 g.

Preparation of bis[6-methyl-2-pyridyldi(-2-pyridyl)amine]nickel(II) perchlorate

Nickel perchlorate hexahydrate (0.3 g) in ethanol (5 ml) and 6-methyl-2-pyridyldi(-2-pyridyl)amine (0.5 g) in ethanol (5 ml) were mixed and warmed. The dark green solution afforded a pale pink solid which was recrystallized from acetone/ethanol. Yield 0.4 g.

Preparation of diaquo bis[6-methyl-2-pyridyldi(-2-pyridyl)amine]nickel(II) perchlorate

The pale blue solution remaining after recrystallizing $Ni(6mpdpa)_2(ClO_4)_2$ was left overnight, a pale blue-grey solid being obtained on evaporation of the solvent.

Preparation of bis[tri(-4-methyl-2-pyridyl)amine]nickel(II) perchlorate

Nickel perchlorate hexahydrate (0.3 g) in ethanol (5 ml) was added to tri(-4-methyl-2-pyridyl)amine (0.53 g) in ethanol (10 ml). The solution became dark green on mixing, heating for a couple of minutes affording pale pink crystals. The solid was recrystallized from acetone/ethanol. Yield 0.53 g.

Preparation of diaquo bis[5-nitro-2-pyridyldi(-2-pyridyl)amine]nickel(II) perchlorate

5-nitro-2-pyridyldi(-2-pyridyl)amine (0.96 g) in acetone (10 ml) was added to nickel perchlorate hexahydrate

(0.53 g) in acetone (10 ml). A pale blue solution was formed which, on heating for five minutes, formed a blue oil which finally precipitated. The solid was recrystallized from acetone and dried over phosphorus pentoxide, the colour changing from blue to green. Yield 1.16 g.

Preparation of diperchlorato bis[4-methyl-2-pyridyldi(-2-pyridyl)amine]copper(II)

Ethanolic solutions of copper perchlorate hexahydrate (0.35 g) and 4-methyl-2-pyridyldi(-2-pyridyl) amine were mixed and refluxed for a short time (~ 15 mins). On putting aside, a small quantity of yellow-green crystals were formed. The filtered solid was washed with ether. Yield 0.12 g.

Preparation of bis[4-methyl-2-pyridyldi(-2-pyridyl) amine]copper(II) perchlorate

Copper perchlorate hexahydrate in acetone (10 ml) was added to 4-methyl-2-pyridyldi(-2-pyridyl)amine (0.6 g) in acetone (10 ml) and heated for a minute when a pale blue precipitate of a diaquo complex was formed. This was filtered and the remainder of the solution refluxed for several minutes followed by reduction of the solvent volume. A green-blue complex was formed which, on heating in an oven to 100°C for 30 minutes, formed a mauve complex. Yield 0.25 g.

Preparation of diperchlorato bis[6-methyl-2-pyridyldi(-2-pyridyl)amine]copper(II)

Copper perchlorate hexahydrate (0.33 g) in ethanol (10 ml) was added to 6-methyl-2-pyridyldi(-2-pyridyl) amine (0.5 g) in ethanol (10 ml). A dark green precipitate was formed immediately, which spontaneously changed to a paler yellow-green complex. On filtering the precipitate was washed with ethanol and ether. Yield 0.45 g.

Preparation of bis[6-methyl-2-pyridyldi(-2-pyridyl) amine]copper(II) perchlorate

The yellow-green complex prepared above was dissolved in aqueous ethanol (50/50 v/v) and the solvent volume reduced by evaporation until a pale blue-grey precipitate of diaquo-bis[6-methyl-2-pyridyldi(-2-pyridyl) amine]copper(II) perchlorate was formed. The grey complex was heated in a silicone oil bath forming a yellow-green complex below 100°C. On further heating between 120°C and 180°C a mauve-blue complex was formed. It was noted that heating $[Cu(6mpdpa)_2(ClO_4)_2]$ directly did not cause isomerism to occur prior to explosive decomposition at 260°C.

Preparation of [diaquoibis (5 nitro-2-pyridyldi-2-pyridyl) amine]copper(II) perchlorate

Copper perchlorate hexahydrate (0.82 g) in ethanol (10 ml) was added to 5-nitro-2-pyridyldi(-2-pyridyl) amine (1.2 g) in ethanol (10 ml) forming a pale blue-green complex. The filtered solid immediately absorbed atmospheric moisture to afford a dark green $Cu(5mpdpa)_2(H_2O)_2(ClO_4)_2$. Yield 1.03 g.

[Diperchloratobis (5-nitro-2-pyridyldi-2-pyridyl)amine] copper(II)

Ethanolic solutions (10 ml) of copper perchlorate hexahydrate (0.9 g) and 5npdpa (1.3 g) were mixed and a pale blue precipitate formed. On refluxing the mixture for five minutes a blue-grey precipitate was formed which, on filtering, was not hygroscopic. The solid was washed with ether. Yield 1.6 g.

[Diacetonebis (5-nitro-2-pyridyldi-2-pyridyl)amine]copper (II) perchlorate (Mauve modification)

Hot ethanolic solutions (10 ml) of 5-nitro-2-pyridyldi-(2-pyridyl)amine (0.45 g) and copper perchlorate hexahydrate (0.31 g) were mixed forming a turquoise blue solution, which turned cloudy. A grey complex appeared which on treatment with acetone under reflux formed a blue solution. On cooling a mauve-blue complex was obtained. Yield 0.2 g.

[Diacetonebis (5-nitro-2-pyridyldi-2-pyridyl)amine] copper(II) perchlorate (Grey modification)

Acetone solutions (10 ml) of 5-nitro-2-pyridyldi-(2-pyridyl)amine (0.5 g) and of copper(II) perchlorate hexahydrate (0.32 g) were mixed to afford a dark grey precipitate (0.41 g). Alternatively, the same complex was prepared by heating diaquobis (5-nitro-2-pyridyldi-

(2-pyridyl)amine copper(II) perchlorate in refluxing acetone for fifteen minutes.

Diperchloratobis[tri-(2-pyridyl)amine]copper(II) and bis[tri-(2-pyridyl)amine]copper(II) perchlorate

These were prepared by the method of reference 69. All analytical data are presented in Table 1.1.

TABLE 1.1

Analytical Data for Complexes

Complex	Colour	Recrystallised from	FOUND			REQUIRED		
			C	H	N	C	H	N
$[Fe(5mpdpa)_2](ClO_4)_2$	Red-brown	-	49.2	3.9	14.2	49.3	3.6	14.4
$[Fe(4mpdpa)_2](ClO_4)_2$	Red-brown	-	49.4	3.6	14.6	49.3	3.6	14.4
$[Fe(5npdpa)_2(H_2O)_2](ClO_4)_2$	Yellow	-	41.3	3.1	16.3	41.0	3.0	16.0
$[Co(6mpdpa)_2](ClO_4)_2$	Buff	Acetone/ethanol	48.7	3.6	14.4	49.1	3.6	14.3
$[Co(5mpdpa)_2](ClO_4)_2$	Buff	Acetone/ethanol	48.7	3.5	14.3	49.1	3.6	14.3
$[Co(4mpdpa)_2](ClO_4)_2$	Buff	Acetone/ethanol	48.7	3.6	13.9	49.1	3.6	14.3
$[Co(tri\text{-}4m\text{-}pyam)_2](ClO_4)_2$	Buff	Acetone/ethanol	Analysis figures not satisfactory					
$[Co(5npdpa)_2(H_2O)_2](ClO_4)_2$	Pink	Acetone/ethanol	40.9	2.9	15.6	40.9	2.9	15.9
$[Ni(6mpdpa)_2](ClO_4)_2$	Pink	Acetone/ethanol	49.1	3.6	14.4	49.1	3.6	14.3
$[Ni(6mpdpa)_2(H_2O)_2](ClO_4)_2$	Blue	Acetone/ethanol	46.9	4.5	13.4	47.0	3.9	13.7
$[Ni(5mpdpa)_2](ClO_4)_2$	Pink	Acetone/ethanol	49.1	3.6	14.2	49.1	3.6	14.3
$[Ni(4mpdpa)_2](ClO_4)_2$	Pink	Acetone/ethanol	49.1	3.6	14.3	49.1	3.6	14.3
$[Ni(5npdpa)_2(H_2O)_2](ClO_4)_2$	Blue	Acetone	41.3	2.8	15.8	40.9	3.0	15.9

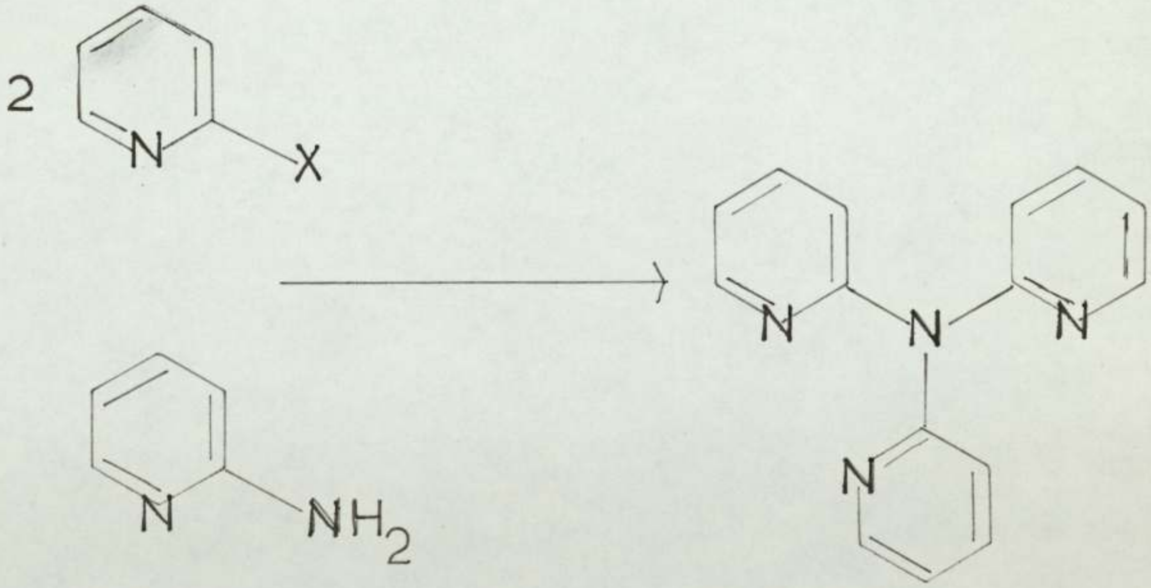
TABLE 1.1 (Cont'd)

Complex	Colour	Recrystallised from	FOUND C	FOUND H	FOUND N	REQUIRED C	REQUIRED H	REQUIRED N
$[Cu(6mpdpa)_2(ClO_4)_2]$	Yellow-grey	-	48.8	3.6	14.1	48.8	3.6	14.2
$[Cu(6mpdpa)_2](ClO_4)_2$	Blue	-	48.9	3.6	14.2	48.8	3.6	14.2
$[Cu(4mpdpa)_2(ClO_4)_2]$	Yellow-green	-	48.8	4.0	13.9	48.8	3.6	14.2
$[Cu(4mpdpa)_2](ClO_4)_2$	Blue	-	48.0	3.5	14.3	48.8	3.6	14.2
$[Cu(6mpdpa)_2(H_2O)_2](ClO_4)_2$	Grey	-	46.2	4.1	13.4	46.6	3.9	13.6
$[Cu(5npdpa)_2(ClO_4)_2]$	Grey	-	42.3	2.6	16.4	42.4	2.6	16.5
$[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$	Mauve	-	44.8	3.3	14.5	44.8	3.5	14.5
$[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$	Grey	-	44.7	3.5	14.8	44.8	3.5	14.5
$[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$	Green	-	41.1	3.0	15.6	40.7	2.9	16.0

CHAPTER II

Synthesis, characterization and spectroscopic properties of substituted Tri(-2-pyridyl)amines[79]

Synthesis of tri-2-pyridylamine(tripyam) was first carried out in 1927 by Wibaut and La Bastide[12] using the method of Goldberg[80]. The same workers[13] reported a modified preparation in 1933 by which increased yields were obtained. The preparation involves the condensation of 2-halopyridines with 2-aminopyridine under reflux conditions, for sixteen hours, in a solvent of high boiling point (mesitylene). Copper bronze was used as a catalyst.



where X = Br or I

Several substituted tri-2-pyridylamines were synthesised using the above method, modifications to the preparation being made where necessary. The bases synthesised were 4-methyl-2-pyridyldi-2-pyridylamine (4mpdpa), 5-methyl-2-pyridyldi-2-pyridylamine (5mpdpa), 6-methyl-2-pyridyldi-2-pyridylamine (6mpdpa), tri-4-methyl-2-pyridylamine (tri-4m-pyam) and 5-nitro-2-pyridyldi-2-pyridylamine (5npdpa). Nitro- and methyl-substituents were chosen because of their opposing electronic effects, a nitro substituent being electron-withdrawing by both inductive and mesomeric effects and a methyl substituent being electron-donating by an inductive effect and also by hyperconjugation. The preparations will now be discussed in detail.

2.1 Preparation of several tri-2-pyridylamines

2.1.1 Preparation of (5-nitro-2-pyridyldi-2-pyridyl)amine

The preparation was attempted several times under different reaction conditions before an adequate yield of 5npdpa was obtained. A brief discussion of the attempted preparations and possible explanation for failure will be included.

2-amino-5-nitropyridine (7.1 g) and 2-bromopyridine (15.0 g) were refluxed in mesitylene (100 ml) for sixteen hours in the presence of copper bronze as a catalyst. A yellow solid was extracted from the reaction mixture which was subsequently recrystallized from petroleum-ether (100/120^{o}). Infra red data indicated the presence of N-H (band at 3,300 cm^{-1}) and microanalytical data were unsatisfactory. The preparation was repeated, reaction time being increased to 22 hours. Microanalytical data for the product were consistent with data expected for (5-nitro-2-pyridyl-2-pyridyl) amine. This would not be in agreement with previous observations by Wibaut and La Bastide, who noted that the condensation of 2-aminopyridine (1 mole) with 2-iodopyridine (1 mole) resulted in the formation of tri-2-pyridylamine only; di-2-pyridylamine could not be detected. This suggested that replacement of the first amino hydrogen to form di-2-pyridylamine is the slow step in the reaction now under consideration.

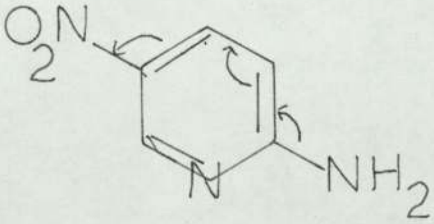
It was evident that more forcing conditions were necessary. Mesitylene (b.p. 162°C) was replaced by p-cymene (b.p. 177°C), enabling a higher reaction temperature to be employed. Condensation of 2-amino-5-nitropyridine (7.5 g) and 2-bromopyridine (17 g) in p-cymene as solvent under reflux conditions (16 hours) yielded 0.13 g 5npdpa, a yellow crystalline solid. The yield was, however, insufficient to allow a study of the coordination properties of the base. In an attempt to increase the yield 2-bromopyridine (b.p. 192°C) was employed as solvent, the reflux temperature being raised by a further 15°. The condensation was attempted in 2-bromopyridine as solvent for twenty hours when 0.4 g 5npdpa was obtained. The reaction resulted in excessive carbonation, suggesting that the temperature might be too high. 2-bromopyridine was then replaced by 2-iodopyridine, p-cymene being used as solvent. After refluxing for 16 hours 1 g 5npdpa was obtained. The reaction time was then increased to 24 hours when a workable yield was obtained.

5-nitro-2-pyridylamine (10 g), freshly prepared 2-iodopyridine (20 ml) and copper bronze (5.4 g) were refluxed in p-cymene (150 ml) for 24 hours in the presence of potassium carbonate (12.1 g) and a trace of potassium iodide as initiator. The reaction mixture was filtered and the solvent volume reduced under low pressure. A yellow-orange solid precipitated, which, on recrystallization from petroleum ether (100/120°), yielded 10.1 g 5npdpa.

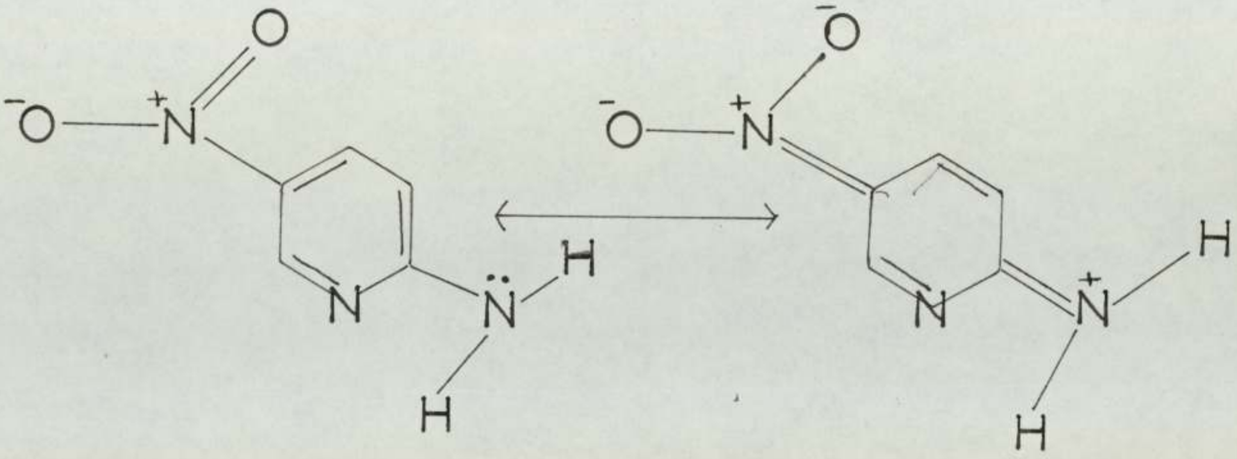
Obtained : C 61.4; H 4.0; N 23.5

Calculated for $C_{15}H_{11}N_5O_2$: C 61.4; H 3.8; N 24.0

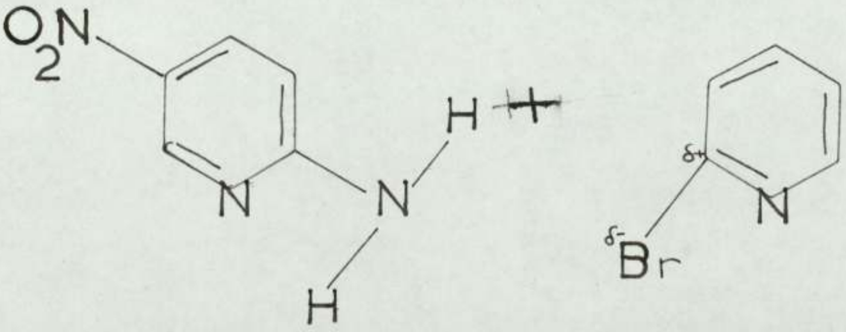
The difficulties experienced in the synthesis of 5npdpa are probably a direct result of the presence of the strongly electron-withdrawing nitro-substituent. Wibaut and La Bastide attempted to condense 2-halopyridines with 2-amino-5-nitro-pyridine without success.



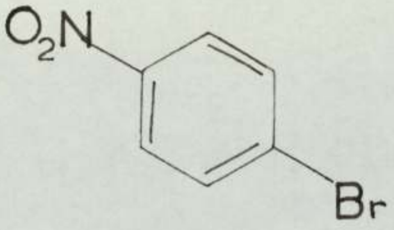
Both inductive and mesomeric effects result in a withdrawal of electrons from the ring. The position of the amino group relative to the nitro group (para) suggests that the mesomeric effect of the nitro group will be strongly felt by the amino group, thus causing a reduction in the electron density on the amino nitrogen.

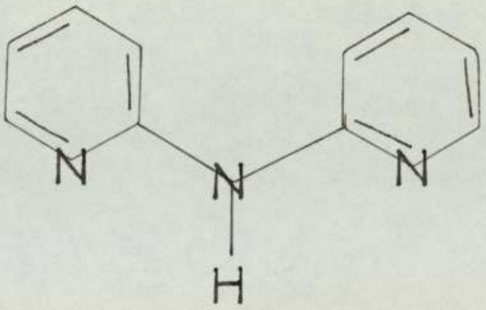


As the rate of the reaction probably depends on the nucleophilicity of the amino nitrogen, the attack of the 5-nitro-2-aminopyridine on the relatively electropositive carbon of 2-halopyridine occurs more slowly as a result of the presence of a nitro substituent para to the amino group.



One possible answer to the problem would be to utilize the electronic effect of the nitro substituent to enhance the reaction rate rather than to retard it. This could be achieved by condensing 2-bromo-5-nitropyridine with di-2-pyridylamine.

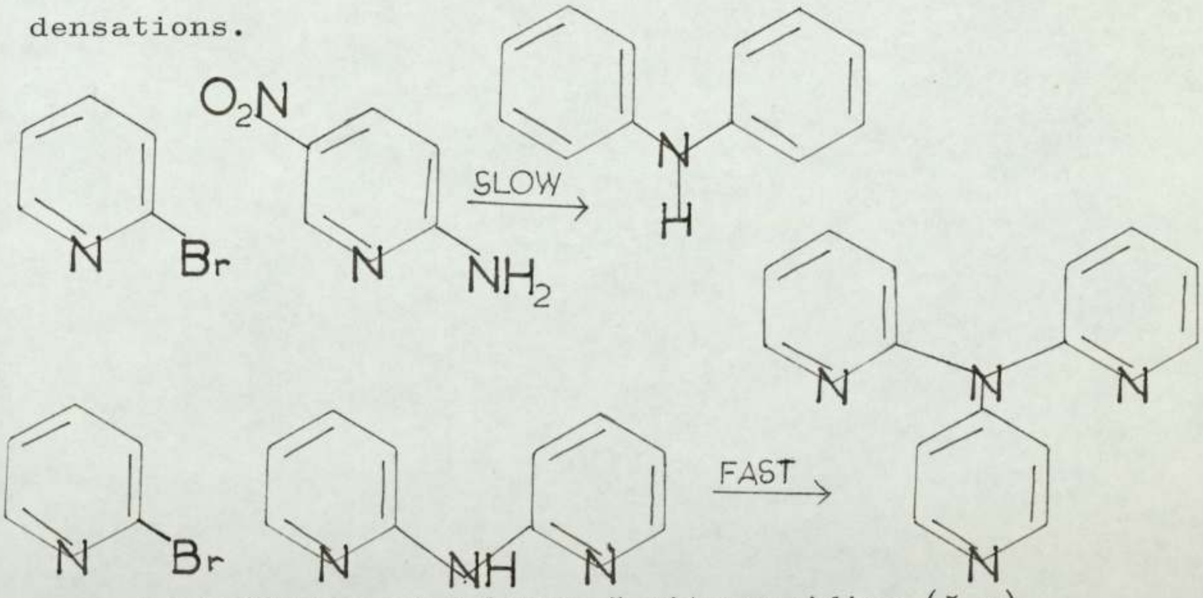




This method should have a dual advantage because:-

(i) the electronic effect of the nitro substituent will render the carbon adjacent to the bromo group more electropositive, thus enhancing the electrophilicity of the carbon atom;

(ii) the use of di-2-pyridylamine avoids the rate determining step in the reaction in the earlier condensations.



Availability of 2-bromo-5-nitropyridine (5 g) allowed the synthesis to be attempted only once when a yield of 0.95 g was obtained. However, the stirring was inadequate throughout the reaction due to a fault in the stirrer and it was therefore not possible to discuss the merits of the synthesis, and, as 5npdpa was obtained in workable yields prior to the planned synthesis of 2-bromo-5-nitropyridine, it was not necessary to carry out this reaction again.

2.1.2 Preparation of 6-methyl-2-pyridyldi-2-pyridylamine

2-amino-6-methylpyridine (10.4 g), potassium carbonate (20 g) and 2-bromopyridine were refluxed with stirring for 20 hours in 100 ml p-cymene as solvent, in the presence of copper bronze (10.4 g) and a trace of potassium iodide as initiator. The solvent was removed by steam distillation and the reaction mixture was filtered. Any product remaining in the solid was removed by extracting in boiling water. The volume of water was reduced, under reduced pressure, depositing a green solid and a dark brown oily substance. The brown oil was extracted into petroleum-ether ($100/120^o$) from which a yellow oil was obtained. The oil was then purified from petroleum-ether ($100/120^o$). Infra red data indicated the absence of N-H and a test for bipyridyl, with ferrous sulphate, proved to be negative. On standing for several weeks the oil formed an oily pseudo-crystalline product.

This preparation was carried out several times, using a variety of conditions. It was evident that the yield was not appreciably increased by the use of large amounts of catalyst. Similarly, the yield was not noticeably affected by increasing the reaction time to 20 hours. It was also found that extraction of the product could be effected by filtering the p-cymene mixture without first removing the solvent by steam distillation. The volume of p-cymene was reduced under reduced pressure. Yield 15.1 g.

Found: C 72.9; H 5.6; N 21.4

Calculated for $C_{16}H_{14}N_4$: C 73.3; H 5.4; N 21.4

Use of p-cymene as solvent produced up to 50% greater yield than when mesitylene was used.

2.1.3 Preparation of 5-methyl-2-pyridyldi-2-pyridylamine

2-amino-5-methylpyridine (10.1 g), 2-bromopyridine (25 ml) and copper bronze (5.1 g) were refluxed with continuous stirring for sixteen hours in p-cymene as solvent in the presence of potassium carbonate (20 g) and a trace of potassium iodide. The mixture was filtered and the solvent removed under reduced pressure leaving a yellow-brown oil. The oil was extracted in petroleum-ether (100/120°) and subsequently purified from petroleum-ether (100/120°). The solvent was removed by heating in an oven for 1 to 2 hours. On cooling an oily pseudocrystalline product was obtained. Yield 10.3 g.

Obtained : C 73.3; H 5.4; N 21.4

Calculated for $C_{16}H_{14}N_4$: C 73.3; H 5.4; N 21.4

2.1.4 Preparation of 4-methyl-2-pyridyldi-2-pyridylamine

2-amino-4-methylpyridine (9.3 g), 2-bromopyridine (15 ml) and copper bronze (4 g) were refluxed for 16 hours in p-cymene as solvent (150 ml) and in the presence of potassium carbonate (20 g) and potassium iodide (trace).

The mixture was stirred continuously. After refluxing the boiling solution was immediately filtered and the solvent volume reduced allowing a brown oil to settle out of solution. The oil was extracted and subsequently purified from petroleum-ether (100/120°). On standing an oily pseudocrystalline solid was formed. Yield 6.3 g.

The low yield is not necessarily a function of the reaction, but possibly due to the fact that the preparation was not carried out a sufficient number of times for a statistical value to be obtained. It was necessary for the preparation to be carried out only once.

Obtained : C 73.2; H 5.4; N 21.4

Calculated for $C_{16}H_{14}N_4$: C 73.3; H 5.4; N 21.4

2.1.5 Preparation of tri(-4-methyl-2-pyridyl)amine

2-amino-4-methylpyridine (7.2 g), potassium carbonate (12 g) and freshly prepared 2-bromo-4-methylpyridine (30 g) were refluxed with continuous stirring for 16 hours in the presence of copper bronze (4.3 g) as a catalyst and p-cymene (150 ml) as solvent. The reaction micture was filtered and the solvent removed under reduced pressure. A brown-yellow crystalline solid was obtained, which, on recrystallization from petroleum-ether (100/120°) and water, yielded a colourless crystalline solid. Yield 3.9 g.

Obtained : C 74.4; H 6.3; N 19.2

Calculated for $C_{18}H_{18}N_4$: C 74.5; H 6.1; N 19.3

2.1.6 Preparation of tri(-2-pyridyl)amine

Di-2-pyridylamine (8.3 g), potassium carbonate (8.0 g), 2-bromopyridine (7.9 g) and a trace of potassium iodide were refluxed with continuous stirring for 16 hours in the presence of copper bronze (3.0 g) as catalyst and p-cymene as solvent. The reaction mixture was filtered and p-cymene removed under reduced pressure. The off-white crystals obtained afforded white needle-like crystals on recrystallization from petroleum-ether ($100/120^{\circ}$) and water. Yield 6.1 g.

Obtained: C 72.1; H 4.8; N 22.3

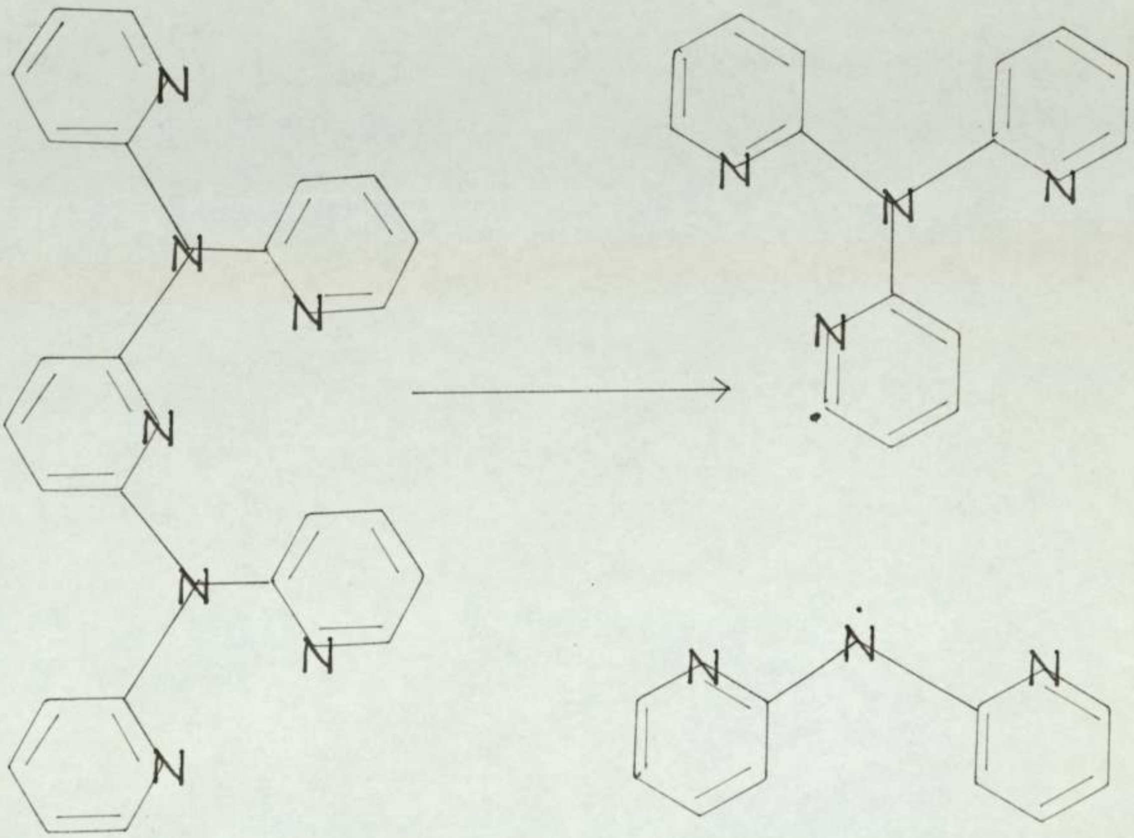
$C_{15}H_{12}N_4$ requires: C 72.5; H 4.9; N 22.6

2.1.7 Attempted synthesis of 2,6-di(di-2-pyridyl amino) pyridine (ddpap)

Synthesis of ddpap involves the condensation of 2-halopyridine (4 moles) with 2,6-diaminopyridine (1 mole). Freshly recrystallized 2,6-diaminopyridine was refluxed with 2-bromopyridine for 24 hours in p-cymene as solvent. The product was extracted and recrystallized from petroleum-ether ($100/120^{\circ}$). A yellow oil was obtained, infra red data indicating the presence of N-H. This suggested that the reaction had not gone to completion so the preparation was repeated, 2-bromopyridine being replaced by freshly prepared 2-iodopyridine. The product was extracted and purified from petroleum-ether. A yellow oil was obtained at first but on further standing a white crystalline solid came out of solution (0.13 g). Infra red data on the oil indicated the presence of N-H, whereas no evidence for N-H was found in the infra red spectrum of the white solid. The preparation was repeated with increased reaction time (30 hours) when 1.05 g of the white crystalline solid was obtained. Nuclear magnetic resonance and mass spectra were obtained. The parent ion peak appeared at 248 amu, with another large peak at 170 amu. At first it was considered feasible that the peaks were due to the breakdown products of ddpap. However, on careful analysis of nmr and infra red spectra, it was discovered that tri-2-pyridylamine had been formed. Two possible explanations are considered:

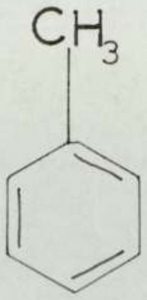
(i) Impurities of 2-aminopyridine in the 2,6-diaminopyridine used. However, tri-2-pyridylamine was not formed when 2-bromopyridine was used initially so this is not the likely source of tripyridylamine.

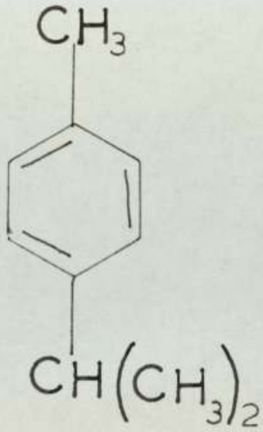
(ii) Formation of ddpap followed by scission of N-C bond. The presence of a suitable donor would enable the radicals formed to abstract hydrogen atoms forming tri-2-pyridylamine and di-2-pyridylamine.



Attempts to isolate di-2-pyridylamine were fruitless but in the light of previous work it is likely that any di-2-pyridylamine formed would rapidly be converted to tri-2-pyridylamine, providing an excess of 2-halopyridine was used initially.

There are two possible sites at which hydrogen abstraction can take place. Reaction of 2-halopyridine with 2-aminopyridine results in the formation of HX. However, the concentration of HX is likely to be very small due to the presence of potassium carbonate. A more likely source of hydrogen atoms is p-cymene. Toluene is known to be an efficient radical scavenger and is not too dissimilar to para-cymene.





P-cymene

As tertiary aliphatic hydrogen atoms are abstracted more easily than primary hydrogen atoms, p-cymene should be capable of acting as an efficient radical scavenger.

Thermodynamic data for the scission of ddpap followed by hydrogen abstraction indicates an exothermic overall process. The process involves scission of two C-H bonds and a C-N bond and formation of C-H, N-H and C-C bonds for which $\Delta H = -7.4$ Kcal/mole. Unfortunately it is not possible to estimate ΔS.

Preparation of 2-iodopyridine

The method[81] employed was that of Tschitschibabin and Rjasarzew. Potassium iodide (388 g), glacial acetic acid (80 g) and water (75 g) were boiled under reflux. To the boiling solution a mixture of 2-aminopyridine (93 g) and sodium nitrite (75 g) in water (180 ml) was added slowly. When evolution of nitrogen had ceased, the contents of the flask were cooled and basified with sodium hydroxide. The 2-iodopyridine was obtained by extraction with ether and subsequent distillation. Final distillate collected 221°-223°C.

Preparation of 2-bromo-4-methylpyridine[82]

2-amino-4-methylpyridine (48 g) was added slowly to 47% hydrobromic acid (280 ml). Bromine (68 ml) was added slowly during which time a solid orange perbromide was formed. A solution of sodium nitrite (85 g) in water (120 ml) was added slowly, the temperature being kept below 0°C by an acetone/dry ice bath. Sodium hydroxide (180 g) in water (460 ml) was added, keeping the temperature below 25°C. The resulting liquid was extracted into ether and distilled, the sample being collected between 220° and 226°C. Yield 63 g.

2.2 Preparation of tricarbonyl molybdenum derivatives of substituted tri-2-pyridylamines

The method used was that of Kulasingam and McWhinnie[15]. The reaction involved refluxing hexacarbonyl molybdenum (1μ mole) with substituted tri-2-pyridylamine (1μ mole) in toluene as solvent under a nitrogen atmosphere for 1½ hours. The orange-red precipitate was filtered and washed with toluene (10 ml) and petroleum-ether (10 ml).

	C	H	N	C	H	N
Mo(4mpdpa)(CO)$_3$	51.3	3.5	12.7	51.6	3.2	12.7
Mo(5mpdpa)(CO)$_3$	51.7	3.2	12.3	51.6	3.2	12.7
Mo(6mpdpa)(CO)$_3$	52.0	3.1	12.9	51.6	3.2	12.7

The preparation was attempted with 5npdpa but an ill-defined product was obtained. Infra red evidence suggested that a carbonyl complex had been prepared in low yield. The above complexes were synthesised as an aid to characterization of the bases. The formation of the tricarbonyl derivatives obtained is only possible if the ligands are terdentate and similar to tri-2-pyridylamine.

On careful analysis of the infra red spectra of the above complexes, in particular ν (C-O)A and ν (C-O)E (Table 2.1), it is noted that a shift in carbonyl stretching frequencies takes place to lower wave number with respect to corresponding absorptions in Mo(tripyam)(CO)$_3$. This indicates a reduction in bond order of C-O bond due to π donation from the metal to antibonding orbitals on the carbonyl group. This increase in π donation from metal to carbonyl group suggests a greater availability of π electrons on the metal and hence a reduction in π acceptor abilities of the methyl-substituted tri-2-pyridylamines.

Infra red spectra were also examined closely to detect any possibility of splitting of the degenerate E mode due to asymmetry in the ligand. However, no splitting was observed in the solid state spectra, decomposition preventing examination of solution spectra. Mo(6mpdpa)(CO)$_3$ was of particular interest in this respect in view of the anticipated steric interaction of the 6-methyl group hanging close to the metal. However, on careful examination of the solid state infra-red spectrum in the region of absorption for ν (C-O)E over an expanded scale, no evidence of splitting was noted. Attempts to obtain solutions for the purpose of obtaining the infra red spectrum in solution failed except with dichloromethane as solvent. However,

TABLE 2.1

Infra red spectra of tricarbonyl molybdenum complexes of tri-2-pyridylamine and methyl-substituted tri-2-pyridylamines in the region of ν(CO)

Complex	ν (CO) cm^{-1}	
	A_1	E
$\mathrm{Mo(6mpdpa)(CO)_3}$	1894	1774
$\mathrm{Mo(5mpdpa)(CO)_3}$	1895	1778
$\mathrm{Mo(4mpdpa)(CO)_3}$	1898	1776
$\mathrm{Mo(tripyam)(CO)_3}$[69]	1908	1790

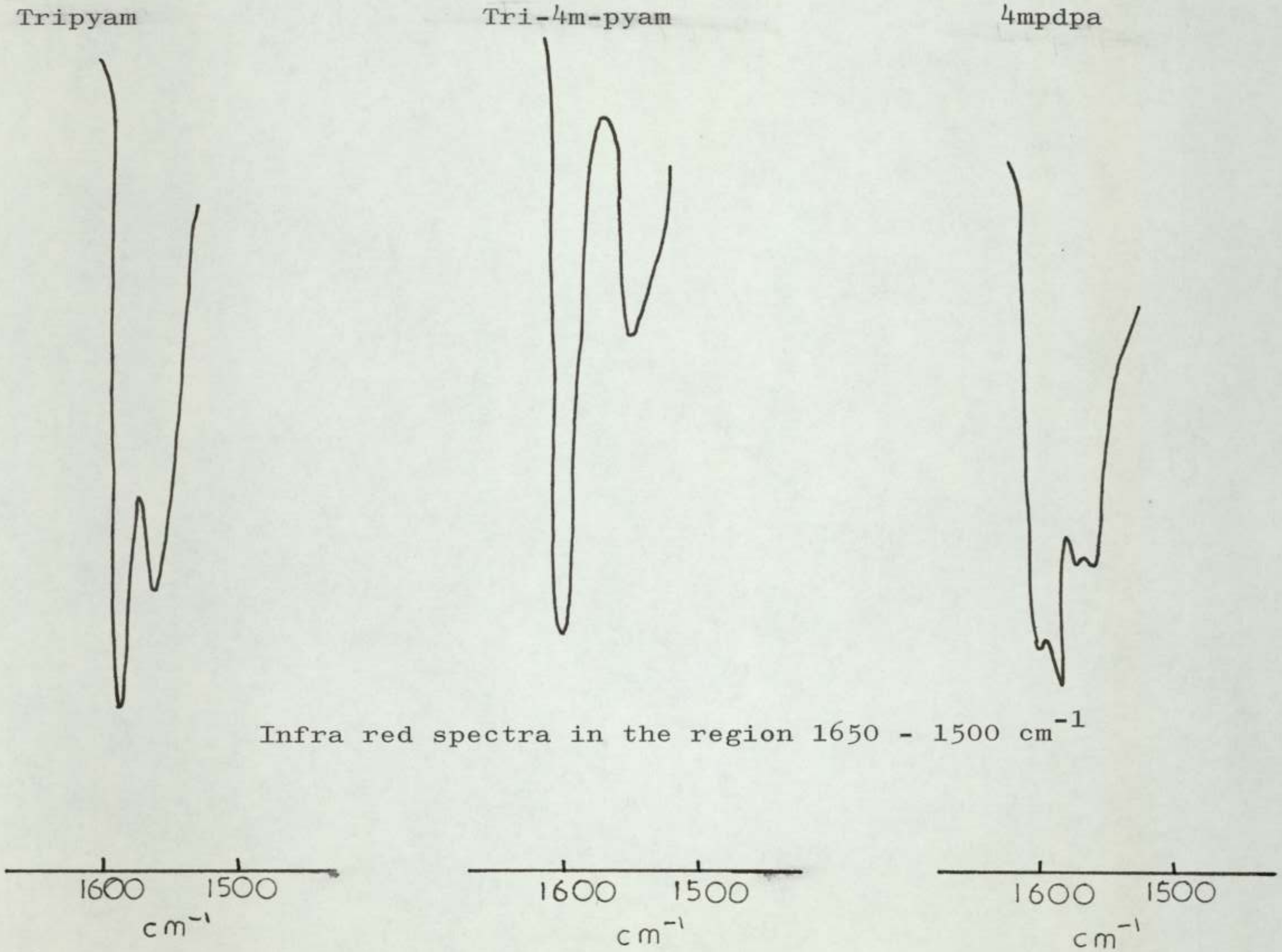
the spectrum changed within minutes, due to the instability of the complex in chlorinated solvents and therefore it was not possible to look for splitting of the E mode.

2.3 Infra red spectra of substituted tri-2-pyridylamines

The infra red spectra of the ligands were obtained for liquid films for 4mpdpa, 5mpdpa, 6mpdpa for nujol and fluorochemical mulls for tri-4m-pyam, 5npdpa and tripyam and are tabulated in table 2.2 for the region below 2000 cm^{-1}.

The spectra indicated the absence of N-H, indicating the absence of unreacted or partially reacted amino pyridines. The spectra of the ligands containing a substituent in position 5 were more complex than those of the other substituted ligands. Careful analysis of the ligand absorption bands in the region of 1600 cm^{-1} (assigned to $C \overset{\cdots}{=} N$ stretching in the pyridine ring) showed that the spectra of the methyl substituted tri-2-pyridylamines contain well-defined bands at 1605 cm^{-1} (4mpdpa), 1606 cm^{-1} (5mpdpa) and 1603 cm^{-1}(tri-4m-pyam) with an intense shoulder at 1603 cm^{-1} in the spectrum of 6mpdpa.

The infra red spectrum of tri-2-pyridylamine, however, does not possess a strong band above 1600 cm^{-1}. Comparison of the spectra of 4mpdpa, tri-4m-pyam and tri-2-pyridylamine illustrates the point (Fig. 2.1). The spectrum of tri-2-pyridylamine contains a single band at 1588 cm^{-1}, whereas the spectrum of tri-4m-pyam contains a sharp band at 1603 cm^{-1}. The spectrum of 4mpdpa contains two strong bands in this region, at 1605 cm^{-1}



Infra red spectra in the region 1650 - 1500 cm^{-1}

Fig. 2.1

and 1588 cm^{-1}, the latter being the more intense band. The presence of a methyl substituent is likely to increase the electron density in the ring and an increase in the bond order of $C \overset{-}{\cdots} N$ is considered likely, enhanced by the electron attracting ability of the ring nitrogen atom. The bands at about 1605 cm^{-1} have therefore been assigned to $C \overset{-}{\cdots} N$ stretching in the substituted pyridine ring, the greater frequency being due to the greater bond order.

TABLE 2.2

The infra red spectra of several tri-2-pyridylamines (frequency in cm^{-1})

6mpdpa	5mpdpa	4mpdpa	tri-4m-pyam	5npdpa	tripyam	Assignments
1624 sh	1622 sh	1625 sh				
		1620 sh				
1618 sh			1618 sh			
					1610 sh	
1603 sh	1606 s	1605 s	1603 s			
					1599 sh	
1587 s	1590 s	1588 s		1590 s	1588 s	
			1576 sh			
1570 s	1570 s			1570 sh		
		1568 sh		1568 sh		
1559 sh	1560 sh	1560 s	1560 sh	1560 sh	1560 s	In plane C-N and C-C
	1554 sh		1555 sh	1555 sh		
			1550 m	1550 sh		
			1545 sh			
	1536 sh		1539 sh	1538 sh	1539 sh	
	1530 sh	1530 w		1532 sh		
1525 w	1523 sh					
	1520 w					
1505 w	1508 w	1506 sh				
	1494 sh			1494 s		
				1494 sh		
	1483 sh					
		1480 sh	1479 m			

6mpdpa	5mpdpa	4mpdpa	tri-4m-pyam	5npdpa	tripyam	Assignments
1475 sh	1475 sh	1475 sh		1476 sh		
			1472 sh	1474 sh	1472 sh	
1468 s	1470 s	1476 s		1461 s	1469 s	
		1460 sh				
	1459 sh			1457 sh	1457 sh	
	1454 sh					
1448 s						
	1439 sh					
	1437 sh					
	1432 s			1432 sh		
1429 s	1430 s	1430 s		1428 s	1429 s	
			1425 sh			
			1420 sh	1420 sh	1420 sh	In plane C-N and C-C
			1415 sh			
		1404 s				
			1400 s	1400 m		
1371 w	1372 s					
	1330 s	1335 s		1330 s	1331 s	
1327 s		1323 s	1320 s			
	1313 sh					
				1310 s		
	1303 sh					
		1280 m	1283 s	1289 s	1282 s	
1279 s	1278 s			1278 s		β C-H in plane
				1264 sh		
					1259 w	X sensitive in plane
				1255 sh	1253 w	
1240 w		1240 w				

6mpdpa	5mpdpa	4mpdpa	tri-4m-pyam	5npdpa	tripyam	Assignments
				1238 s		
	1230 w					X sensitive in plane
1220 w	1220 w			1220 m		
			1181 s			
		1169 w		1165 w		
					1162 s	
			1156 sh			
1150 m	1151 m	1150 m		1151 m	1150 m	β C—H in plane
				1125 m		
		1114 w	1110 w		1110 w	
1090 w	1098 w	1096 w	1102 w	1100 w	1101 w	
1050 m	1050 w	1050 w			1051 m	
	1048 w					β C—N in plane
1033 w	1028 m		1032 w			
				1014 w		
				1002 w		
993 m	993 m	992 m	991 m	993 m	995 m	in plane ring breathing
					984 m	
		974 w	970 w			
958 w					958 w	
945 w	950 w	946 w		948 w		γ C—H out of plane
				940 w		
	912 w					
			892 w			
871 w		871 w	866 w		878 w	

6mpdpa	5mpdpa	4mpdpa	tri-4m-pyam	5npdpa	tripyam	Assignments
				857 w		
		841 w		841 m		
			830 sh			γ C—H out of plane
834 w						
	827 m		821 m			
		818 w	818 sh			
			808 m			
				787 m	780 s	
775 s	776 s	775 s		777 s		possibly X sensitive
				767 s		
				749 s	747 s	
			749 w			
				744 s		
		741 m	742 w			
740 s	740 s			736 s		γ C—H
					734 sh	
				724 s		
	720 w		722 w			
662 w	663 w	665 sh	665 sh			
		659 m	660 m	661 m	660 m	
647 m	646 w					
				630 w		α C—C—C
				626 w		
620 m	621 w	619 m		618 m	620 s	

6mpdpa	5mpdpa	4mpdpa	tri-4m-pyam	5npdpa	tripyam	Assignments
			594 w			
	585 m	580 w				
			569 w			Out of plane ϕ C-C
				551 m		
546 w				545 sh		
	540 w			540 m		
528 w	525 w			528 m	529 sh	
	515 w	518 sh	519 w			
508 m		508 m			514 s	
	505 w					
			478 w	492 w		Out of plane ϕ C-C
460 w		465 sh				
		446 sh	451 m	450 w		
			442 m	441 w		
	419 sh			418 sh	415 m	
410 m	412 w	411 w		411 m		
				364 w		
348 w		348 w			353 m	In plane X sensitive
				325 w		

2.4 Discussion of Nuclear Magnetic Resonance Spectra

The pyridylamines synthesised were characterized using infra-red and nuclear magnetic resonance spectroscopy, by microanalysis and by synthesis of tricarbonyl molybdenum derivatives (where possible) followed by their subsequent characterization. The tricarbonyl molybdenum derivatives will be discussed in more detail in a later chapter.

Careful analysis of the nmr spectra yielded information which we consider to be significant. The position of absorption of aromatic protons is dependent upon at least three factors. The first is a diamagnetic shielding which is dependent upon the electron density of the carbon atom to which the aromatic proton is attached. This effect arises due to inducement of electronic circulations around the proton by the applied magnetic field; the diamagnetic shielding always reduces the apparent magnetic field at the proton. The second is paramagnetic shielding due to the ring current within the π cloud of the ring.

The magnitude of the ring current effect is greater for aromatic rings containing electron-releasing substituents than for rings containing electron-withdrawing substituents. The presence of an electron-donating substituent increases the electron density in the π cloud and therefore the induced field is greater. There is also a third possible contributory factor in substituted aromatic rings; that is the diamagnetic anisotropy effect. This effect is greatest at positions ortho to the substituent.

The presence of a hetero atom in an aromatic ring influences the ring densities of the ring carbon atoms (ortho > para > meta). Hence for pyridine, where the ring nitrogen reduces the electron density of the carbon atoms, the diamagnetic shielding is reduced and absorptions of the ring protons occur to lower field. In particular, the ortho protons absorb to lower field than the para proton, the meta proton absorption being least affected by the inclusion of the hetero atom.

The nuclear magnetic resonance spectra of the tri-2-pyridylamine bases were obtained for carbon tetrachloride solutions and recorded on scale factors 10 and 1. The concentration dependence of the spectra was studied but dilution did not affect the chemical shifts noticeably. The chemical shifts and coupling constants are tabulated in Tables 2.3 and 2.4.

TABLE 2.3

Chemical shifts obtained from ^{1}H nuclear magnetic resonance spectra of several tri-2-pyridylamines

Protons	Chemical shift (ppm vs T.M.S.)					
	6mpdpa	5mpdpa	4mpdpa	tri-4m-pyam	5npdpa	tripyam
6	1.72	1.71	1.72		1.58	1.68
4	2.45	2.42	2.44		2.30	2.38
6'		1.82	1.84	1.84	0.95	
4'					1.69	
33'55'	3.05	3.03	3.06	3.17	2.85	2.96
methyl	7.60	7.68	7.76	7.72		

where the primed numbers refer to the ring carrying the substituent.

TABLE 2.4

Coupling constants obtained from the 'H nuclear magnetic resonance spectra of several tri-2-pyridylamines

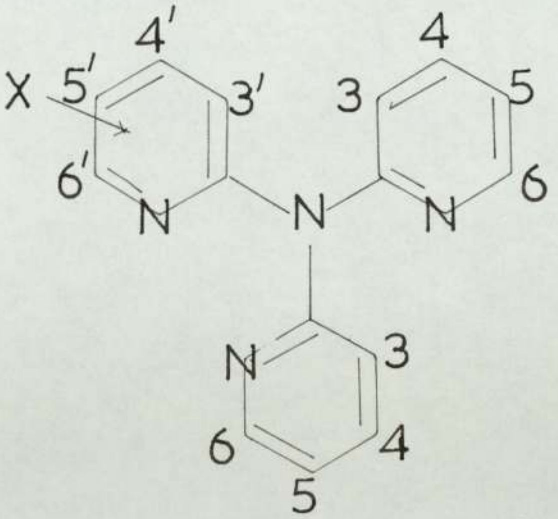
	Spin-spin Coupling Constants (Hz)				
$J_{5,6}$	5.09	5.07	-	4.80	4.94
$J_{4,6}$	1.98	2.12	-	2.82	2.11
$J_{3,6}$	1.13	0.85	-	0.98	0.98
$J_{3,4}$	8.06	8.16	8.45	8.00	8.15
$J_{4,5}$	7.09	7.04	7.32	7.75	7.18
$J_{5',6'}$	-	-	4.80	-	-
$J_{4',6'}$	-	2.12	-	2.82	-
$J_{3',6'}$	-	-	-	-	-
$J_{3',4'}$	-	-	-	9.30	-

The primed numbers refer to the ring carrying the substituent.

2.4.1 (5-nitro-2-pyridyldi-2-pyridyl)amine

Nitro substituents are strongly electron-withdrawing via both inductive and mesomeric effects. The effect of introducing a nitro-group into one of the pyridine rings would be (a) to reduce the electron density at the neighbouring carbon atoms, thus reducing the diamagnetic shielding of protons attached to these carbon atoms and (b) to reduce the electron density within the ring, which would result in a reduction in paramagnetic shielding.

Examination of the spectrum of 5npdpa (Figs. 2.2, 2.3 and 2.4) indicates two distinct absorption positions for both ortho and para protons corresponding to protons on the substituted and unsubstituted rings. Absorptions due to protons in the substituted ring occur downfield to those due to protons in the unsubstituted rings.



The chemical shift observed for proton 6' (0.95τ) is well separated from that of proton 6 (1.58τ) representing considerable downfield shift due to substituent.

100 MH$_z$ 'H nmr spectrum of 5 nitro-2-pyridyldi-(2-pyridyl)amine

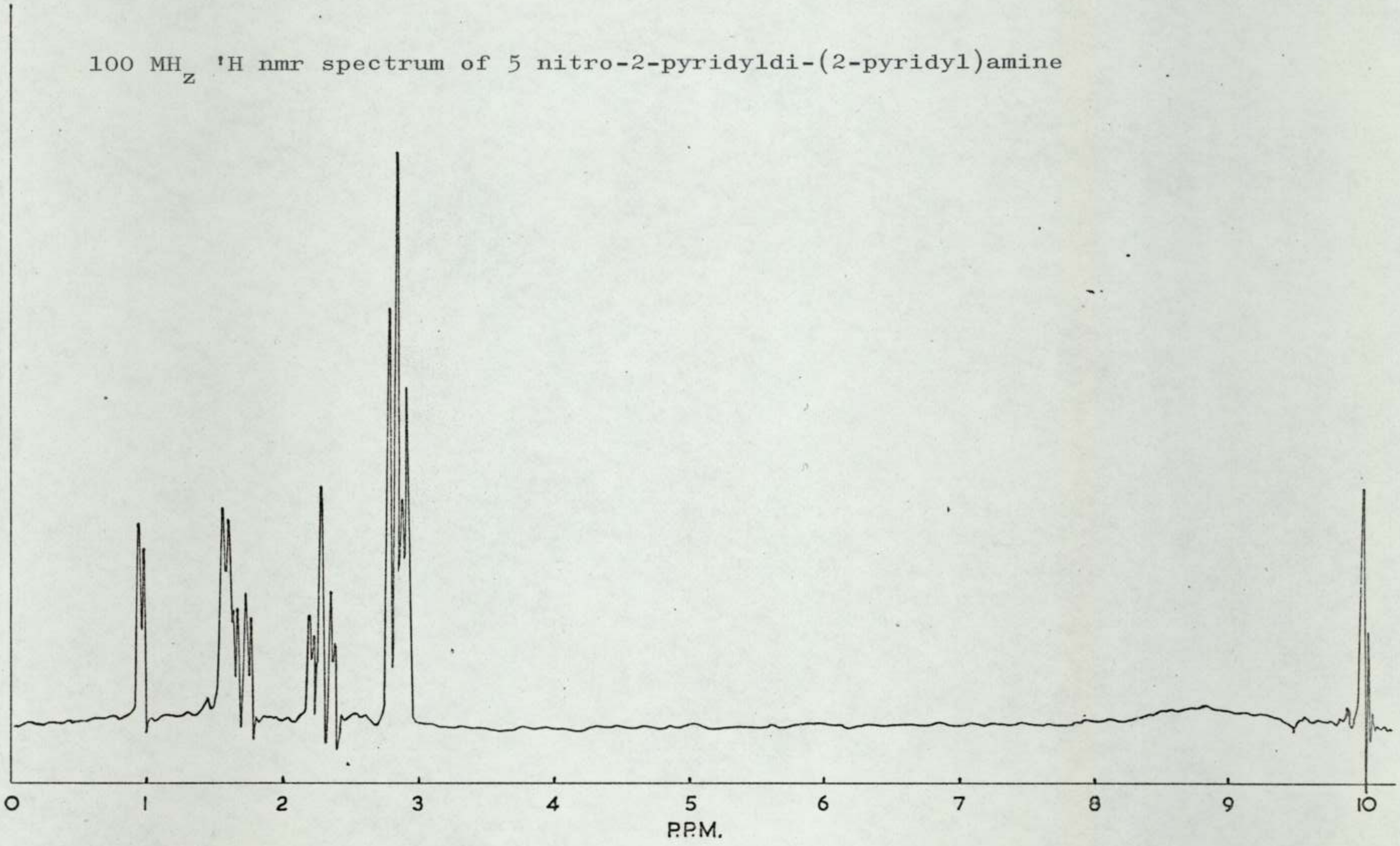


Fig. 2.2

Expanded nmr spectrum of 5npdpa for protons 6 and 6'

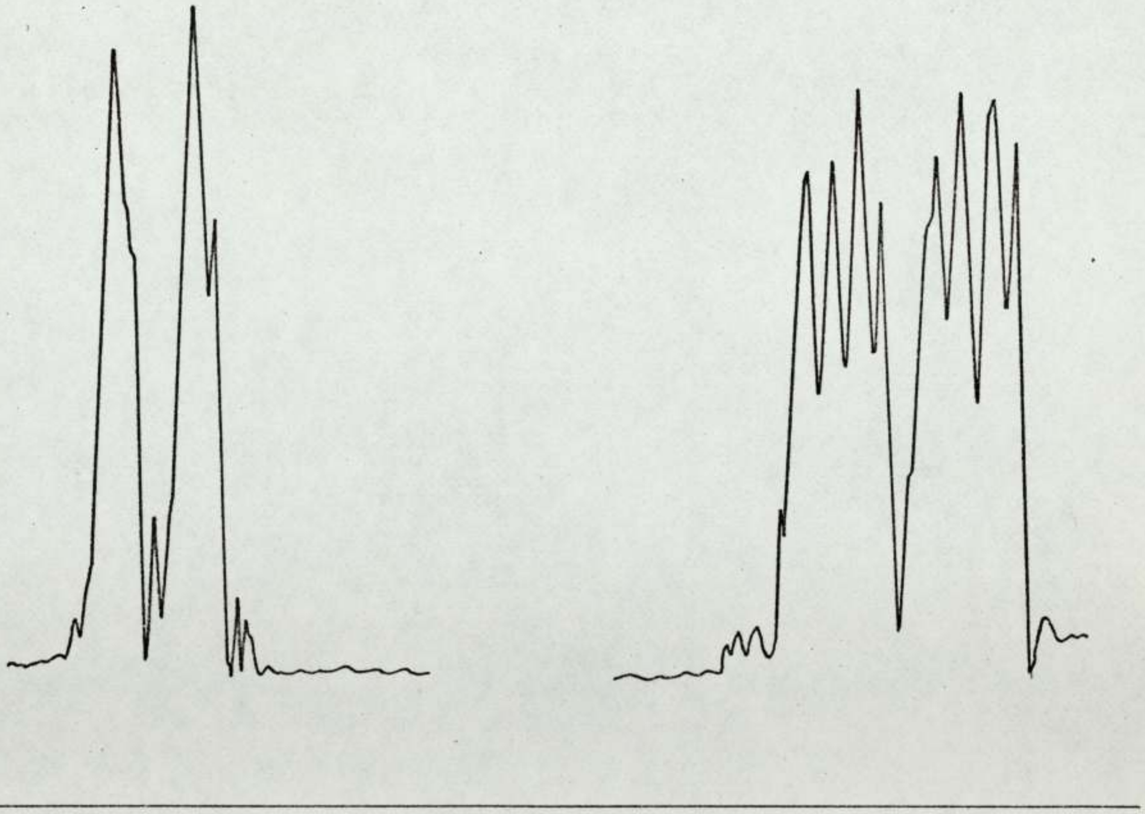


Fig. 2.3

Expanded ¹H nmr spectrum of 5npdpa for protons 4 and 4'

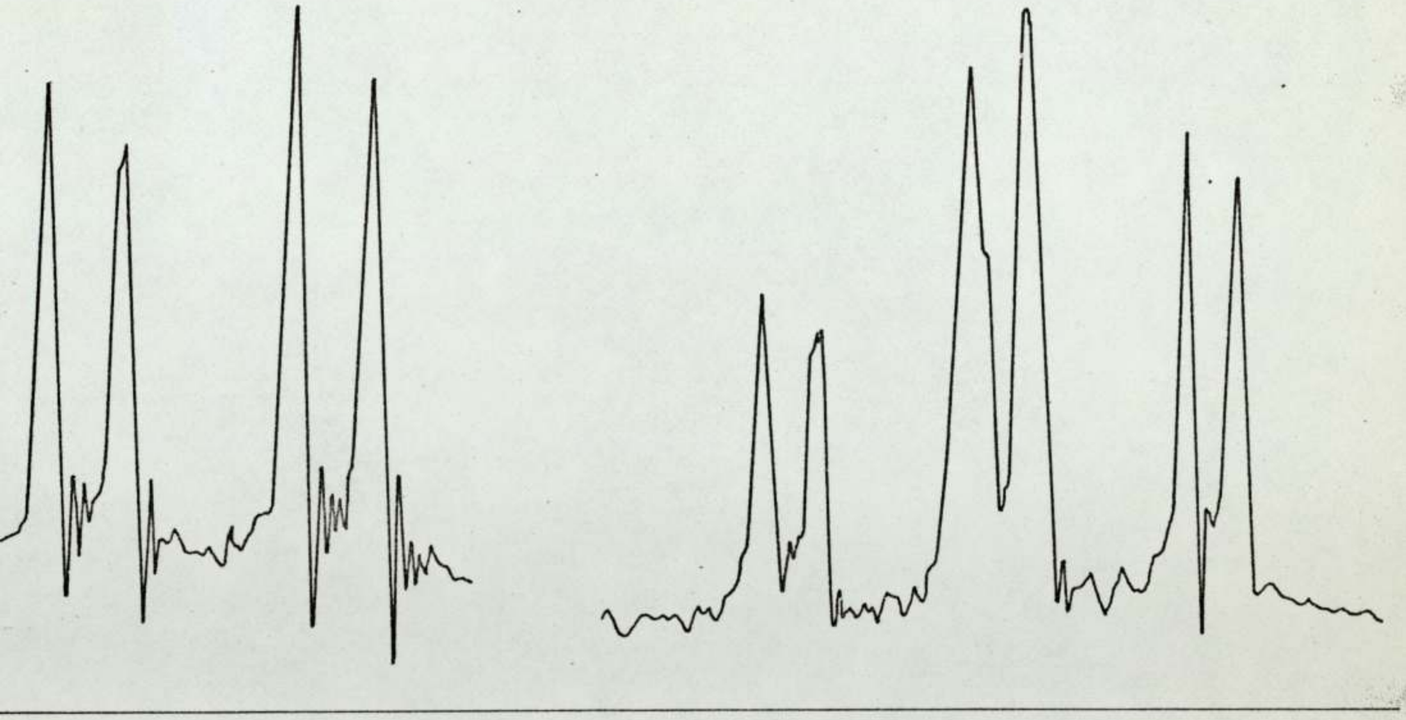
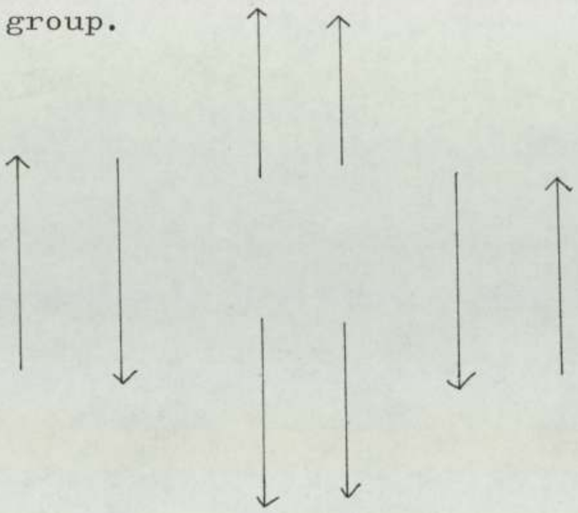


Fig. 2.4

Similarly, absorption of proton 4' (1.69τ) is well separated downfield to that for proton 4 (2.30τ). It was not possible on simple analysis to separate absorptions due to protons 3, 3', 5 and 5'. Partial deuteration of the rings and computer analysis were both beyond the scope of this work. For this reason, absorption of meta protons is quoted as an average value and further discussion would be meaningless.

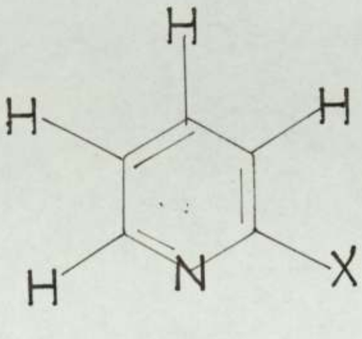
It is evident that the strong electronic effect of the nitro group is causing a downfield shift for substituted ring protons. The lower electron density resulting from the influence of the nitro substituent causes the de-shielding of the proton and absorption to higher field is expected. However, the reduced electron density in the π cloud of the ring will result in a lowering of the ring current and a shift to higher field would be expected from this effect. The overall downfield shifts of absorptions for protons 6' and 4' relative to protons 6 and 4 indicate the importance of the diamagnetic shielding. It is feasible that a small part of $\Delta\tau$ for protons 4 and 4' (also 6 and 6') results from a diamagnetic anisotropy effect. However, the contribution from this effect is likely to be very small and will be discussed more fully later.

The magnetic field experienced by protons of one group is influenced by the spin arrangements of protons on adjacent groups. The protons of the methylene group of ethanol can align in three possible spin orientations that affect the resonance frequencies of the protons of the methyl group.

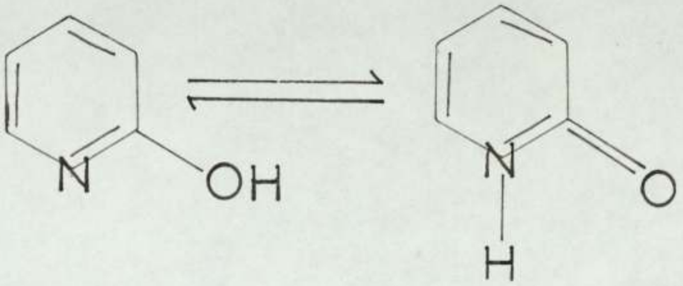


As the effect of these instantaneous spin arrangements is transmitted to the neighbouring group protons, the neighbouring group proton absorption is split into a triplet with relative intensities 1 : 2 : 1.

Similar interactions are observed for the ring protons, absorption lines being split into doublets. It was possible to evaluate many of the coupling constants from the expanded spectra of the ligands and they are tabulated in Table 2.4. The values obtained were in good agreement with previous values for pyridine systems. However, for 5npdpa J_{34} was of interest because it was considerably higher than observed for pyridine. Cox and Bothner-By[21] studied the effect of substituents on the nmr spectra of compounds of the form:

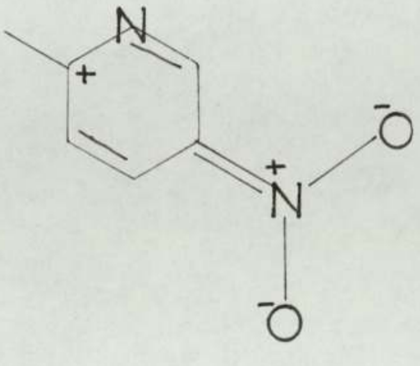


In general, they noted that chemical shifts of substituted pyridines appeared to lower field as the electronegativity of the substituent was increased. More particularly, they noted that for normal 2-substituted pyridines (X = NH_2, Cl, OMe), J_{34} is 7.98 - 8.38 H_z and increases to 9.21 in 2-pyridones. Similar observations were made for J_{56}.



This has been attributed to an increase in double bond character of the C-C bond compared to normal 2-substituted pyridines.

The coupling constant observed for $J_{3'4'}$ in 5npdpa was found to be 9.30 cps, suggesting that the double bond character between positions 3 and 4 is increased due to the electronic effect of the substituent.



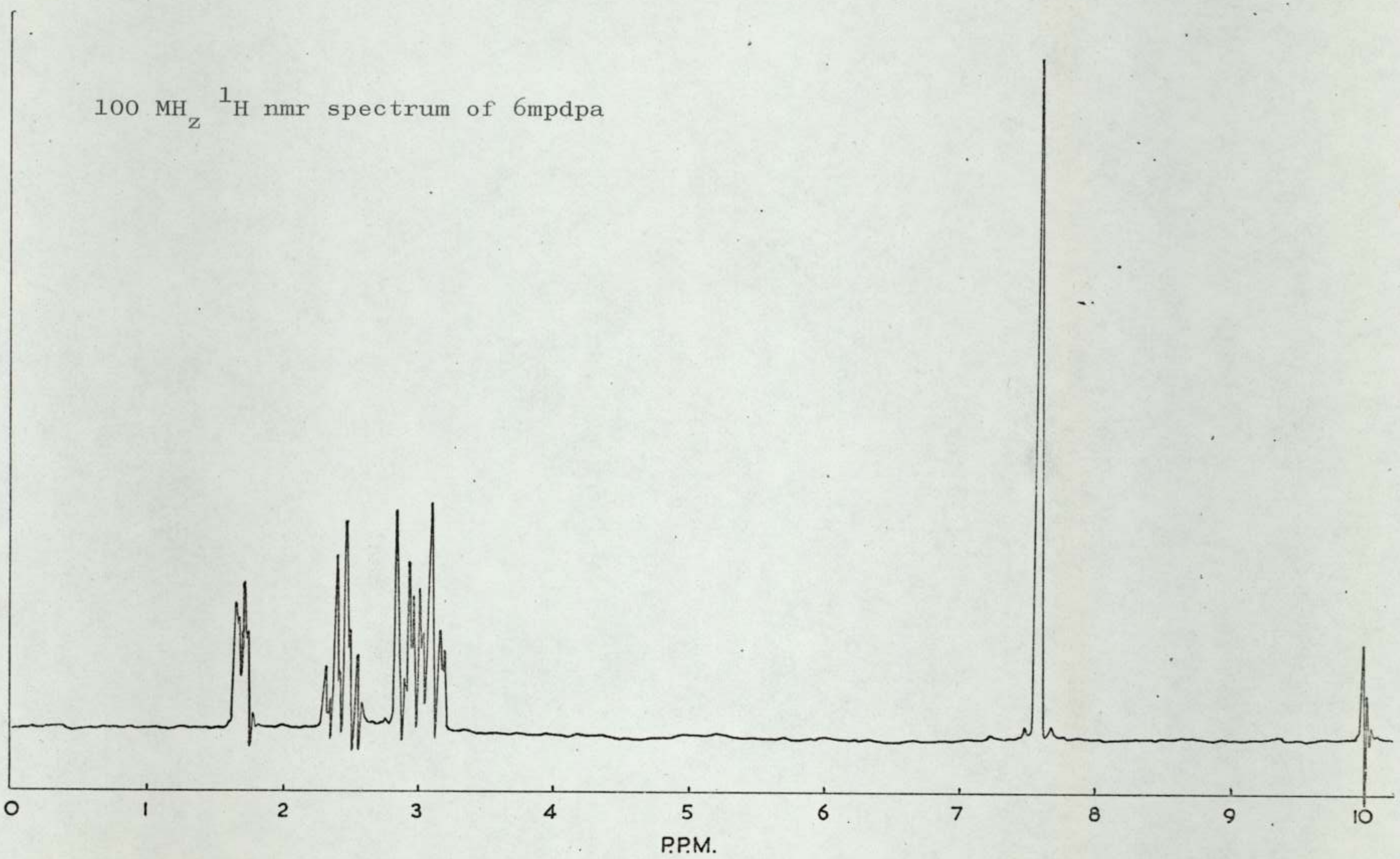
The results therefore suggest that contributions of the form indicated above are important.

2.4.2 ⌈6,-(5- and 4-)-methyl-2-pyridyldi-2-pyridyl⌋ amine

Methyl substituents in a pyridine ring increase the electron density in the ring due to both their inductive and hyperconjugative effects. Therefore, absorption positions for ring protons in the substituted ring are expected to be shifted upfield relative to absorptions in the unsubstituted rings, provided diamagnetic shielding is the most sensitive to changes in electron concentration. Upfield shifts were observed although the magnitude of the shifts is small compared to the downfield shifts observed on introducing a nitro substituent. The small shifts probably reflect the weaker electronic effect of methyl substituents compared to nitro substituents.

The spectrum of 6mpdpa (Fig. 2.5) was simplified by the absence of proton 6' and it was therefore possible to calculate J_{56}, J_{46} and J_{36}. It was not possible to locate the centre of absorption for proton 4' due to overlap of the absorptions for protons 4 and 4'.

Analysis of the spectrum of 5mpdpa enabled absorption positions of protons 6, 6' and 4 to be noted, although it was not possible to locate the centre of the absorption for proton 4.


100 MH_z ^1H nmr spectrum of 6mpdpa

<u>Fig. 2.5</u>

2.4.3 Tri-2-pyridylamine and tri(-4-methyl-2-pyridyl)amine

The nuclear magnetic resonance spectrum of tri-2-pyridylamine (Fig. 2.6) was greatly simplified compared with spectra discussed above. It was possible to obtain chemical shifts for protons 4 and 6 (absorptions due to protons 3 and 5 still overlapped) and resolution was such that coupling constants could be evaluated with reasonable precision.

The spectrum of tri(-4-methyl-2-pyridyl)amine was obtained to confirm the absence of any protons in position 4.

It is of interest to note that the chemical shift for proton 4' in both 4-methyl-2-pyridyldi-2-pyridylamine and tri(-4-methyl-2-pyridyl)amine is 1.84τ. A more significant observation, however, is the variation of chemical shifts for protons 4 and 6 (in the unsubstituted rings) in 4mpdpa, 5mpdpa, 6mpdpa and 5npdpa with respect to τ values observed for 4 and 6 protons in tripyam. Reference to Table 2.3 shows that proton 6 in the methyl-substituted bases absorbs at about 1.72 τ, in the nitro-substituted base absorbs at 1.58τ and in tri-2-pyridylamine absorbs at 1.68τ which is in between. Similar observations apply to the shifts obtained for the 4 (para) protons. It was noted that the difference between the absorption position for proton 6 in the substituted tri-2-pyridylamines and the absorption position of proton 6 in tri-2-pyridylamine is 4×10^{-2}ppm for 6mpdpa and 4mpdpa, 3×10^{-2}ppm for 5mpdpa and -10 x

Expanded nmr spectrum of tri-2-pyridylamine for protons 4 and 6

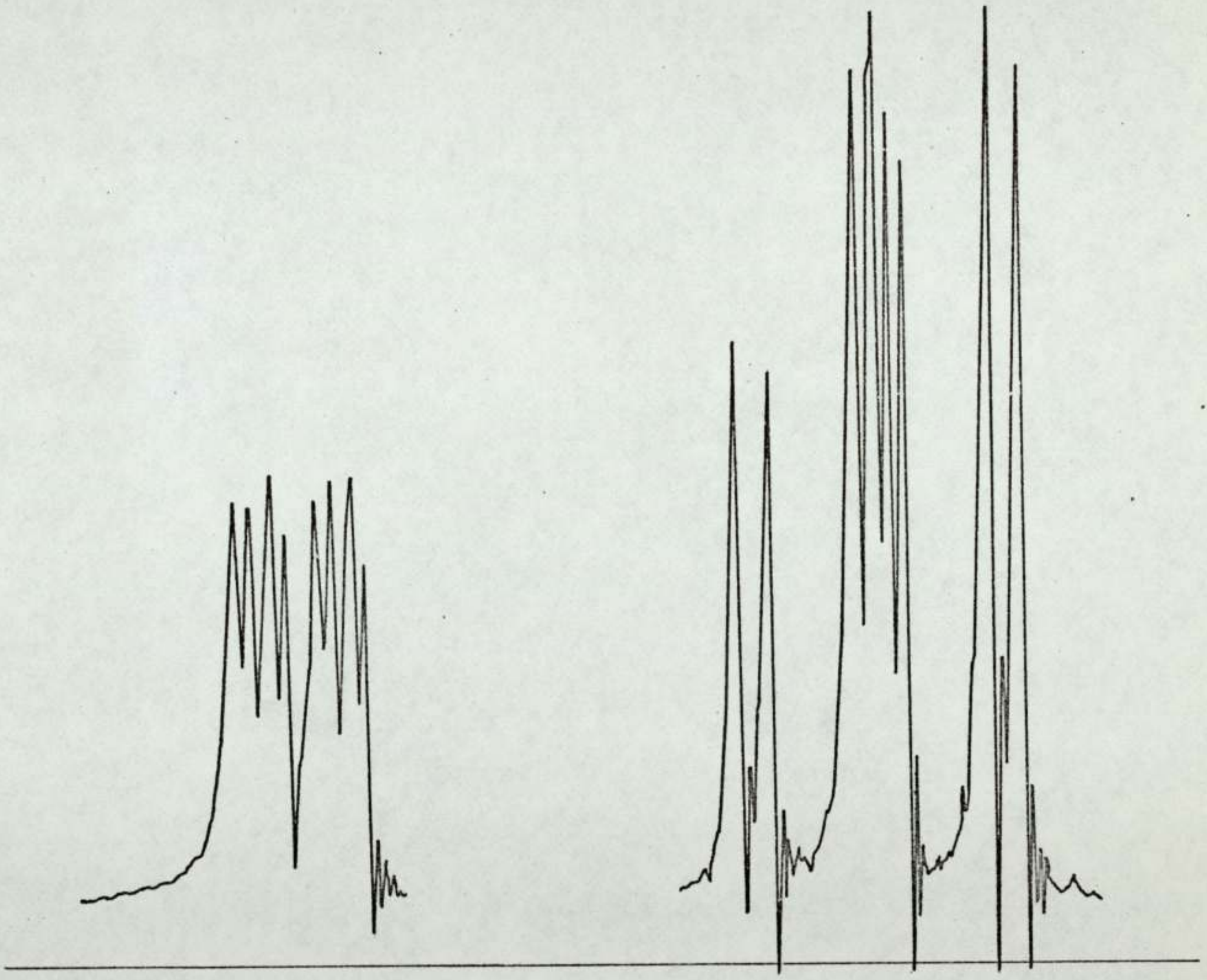
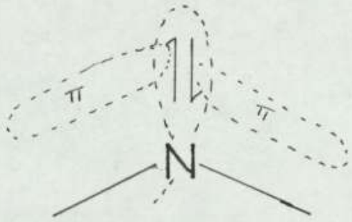


Fig. 2.6

10^{-2}ppm for 5npdpa. Similarly, for proton 4 absorptions the differences are 7 x 10^{-2}ppm for 6mpdpa, 4 x 10^{-2}ppm for 5mpdpa, 6 x 10^{-2}ppm for 4mpdpa and -8 x 10^{-2}ppm for 5npdpa. It also seems significant that the change in shift relative to that observed for tripyam protons is (a) downfield for nitro-substituted bases and (b) upfield for methyl-substituted bases. The observations suggest the possibility of the electronic effect of the substituent being transmitted, to a small extent, to the unsubstituted rings. This could be due to overlap between the π clouds of the pyridine rings and the lone pair of electrons on the amino nitrogen.



This postulation is consistent with and offers an explanation for earlier observations by several workers. Watson and Mann noted that on protonation (or methylation) of tripyam, they were only able to protonate (or methylate) two of the three pyridine rings. This was difficult to explain in terms of a system containing three equivalent pyridine rings. However, in the light of present work it seems possible that the third ring is deactivated to a certain extent due to an electronic effect resulting from protonation of the two other rings.

Kulasingam and McWhinnie studied extensively the complexing ability of tripyam with transition metal ions and noted that bidentate co-ordination was preferred to terdentate co-ordination in many cases. This was difficult to understand in terms of the far greater ligand field strength of tripyam when co-ordinated terdentate (12,800 cm^{-1}) than bidentate (11,000 cm^{-1}). Deactivation of the third ring (on co-ordination of the other two rings) via a reduction of electron density in the ring is once more a possible explanation.

It is possible, however, that the small shifts observed, which are the basis for the above discussion, are due to effects other than electronic. The spectra were run several times to eliminate error due to instrumental fluctuations and concentration dependence was examined. It was found that τ did not vary with concentration within the limits of the instrument. The occurrence of a diamagnetic anisotropy effect due to anisotropy in the magnetic susceptibility tensor of the bond between the substituent and the ring (Fig. 2.7) was considered to be more likely and for this reason attempts were made to assess the possible extent of this effect. Homer and Callagan[83] derived an equation which enabled the diamagnetic anisotropy (σd) to be calculated for methyl-substituted aromatic systems:

$$\sigma_d = \frac{\Delta\chi(1-3\cos^2\theta)}{3R^3}$$

Illustration of the diamagnetic anisotropy effect for 6mpdpa

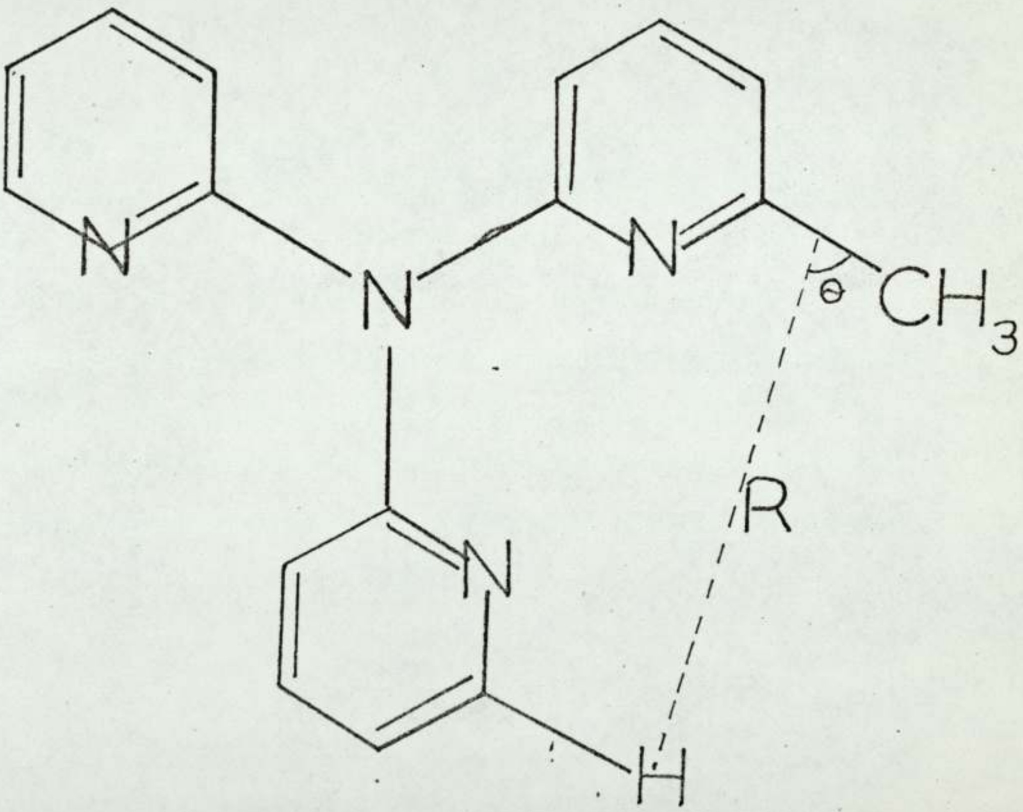
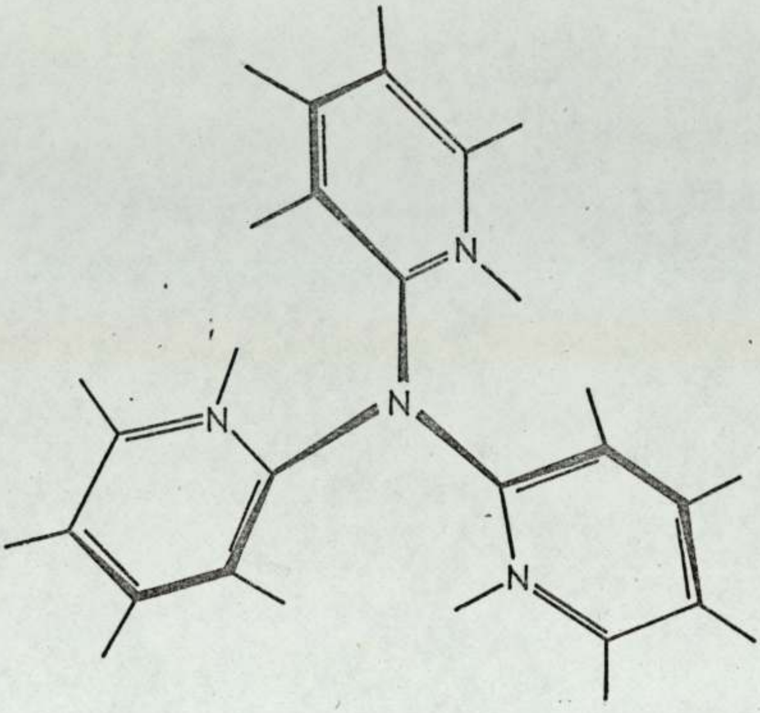
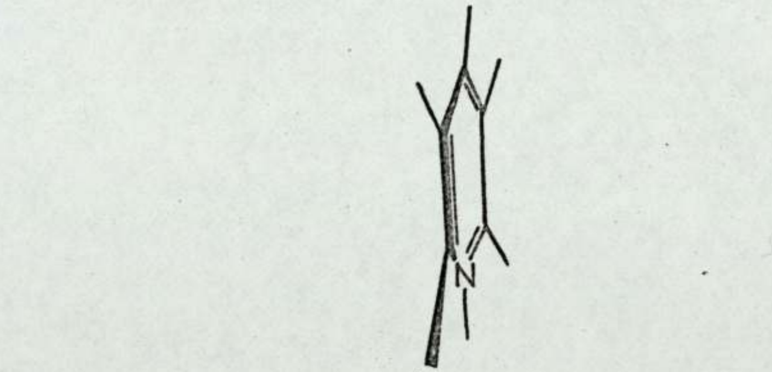


Fig. 2.7

Pyramidal conformations of tri-2-pyridylamines



(b)



(c)

Fig. 2.8

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where R = distance between proton and C-C bond, and θ is the angle between C-C bond at its mid point and the proton.

Unfortunately, the exact conformation of tripyam (and substituted tripyams) is not known but the presence of C_3 axis in tripyam has been verified. The conformation could be planar or any one of an infinity of pyramidal arrangements. For this reason three random conformations were chosen [one planar (a) and two pyramidal (b) and (c)] (Fig. 2.8) and σ d calculated (Table 2.5) . For 6mpdpa, a planar conformation would result in a σd value of the same order as the shift observed for protons 4 and 6. Similarly for conformation (b) interaction with proton 4 is of the same order as the $\Delta\tau$ observed, as is the interaction with proton 6 in conformation (c). For 5mpdpa, the value of σ d is not of the same order as $\Delta\tau$ for any of the conformations. For 4mpdpa the interaction of the methyl group with proton 6 in conformations (a) and (b) is large enough to explain the $\Delta\tau$ value as resulting from a diamagnetic anisotropy effect. However, the interaction of protons 4 with a methyl substituent in position 4 is small.

Therefore, in the case of 4mpdpa and 5mpdpa σ_d for proton 4 in the unsubstituted rings is always of lower order than the $\Delta\tau$ observed. In these cases, $\Delta\tau$ observed can only be explained in terms of an electronic effect transmitted between the rings, provided one of the conformations chosen is representative of the actual conformation. It is considered that a propellor-like

T A B L E 2.5

Values of σ_d for three random conformations of the pyridyl rings

Conformation	Substituent Position	Proton Position		R A^o	σd p.p.m.
Planar (a)	6	6	95	2.08	3.30×10^{-1}
	6	4	26	5.28	1.2×10^{-2}
	5	6	109	3.32	1.03×10^{-2}
	5	4	97	7.00	7.0×10^{-3}
	4	6	180	7.68	-2.1×10^{-2}
	4	4	125	8.68	negligible
Pyramidal (b)	6	6	72	7.88	3.51×10^{-3}
	6	4	95	4.88	2.08×10^{-2}
	5	6	11	8.88	-6.53×10^{-3}
	5	4	41	6.48	-6.31×10^{-3}
	4	6	96	4.6	2.40×10^{-2}
	4	4	69	7.32	-3.8×10^{-3}

Conformation	Substituent Position	Proton Position		R_o A^o	σ d p.p.m.
Pyramidal (c)	6	6	75	5.6	1.10×10^{-2}
	6	4	50	7.6	-1.32×10^{-3}
	5	6	30	8.72	-4.53×10^{-3}
	5	4	36	7.2	-6.23×10^{-3}
	4	6	25	7.6	-8.05×10^{-3}
	4	4	51	7.8	-9.18×10^{-4}

conformation similar to (b) is the most likely conformation, in which case σd is only significant in two cases. Insufficient data prevents similar calculations being carried out on the nitro-substituted bases.

As a result of the calculations carried out, the postulation of an electronic interaction between the pyridine rings is still considered to have basis but indisputable evidence is not available.

It is, however, considered probable that interaction between rings via the amino nitrogen will be cut down considerably or eliminated completely, on terdentate co-ordination to transition metal ions. Co-ordination causes a reduction of the overlap between π cloud of the ring and the lone pair on the nitrogen due to the configuration of the rings.

CHAPTER III

Spectroscopic study of the bonding of tri-2-pyridylamine ligands to transition metal ions

/Fe(II), Ni(II) and Mo(o)/ [87]

3.1 Introduction

The co-ordination behaviour of tri-2-pyridylamine with transition metal ions has been studied[11,15,16,17] and the ability to function both as a bi-and terdentate ligand is well known. It is evident from previous work that bidentate co-ordination is preferred in many cases despite the considerably more favourable ligand field strength for the terdentate base (Δ = 12.800 kK) compared with 11.000 kK for the bidentate ligand. It is not possible to explain preference for bidentate co-ordination as resulting from a steric effect. Construction of models of the complexes with the ligand molecules co-ordinated terdentate to the metal suggests that the complex molecule is free or nearly free of strain. However, as suggested in the previous chapter, it is possible that the preference for bidentate co-ordination results from an electronic effect transmitted between the three rings via the amino nitrogen, causing a lowering of basicity of the third ring on co-ordination of the first two rings.

The nature of tri-2-pyridylamine ligands enforces a rigid stereochemistry on the complexes when the ligand molecules are co-ordinated terdentate, to such an extent that the microsymmetry around the metal ion is considered to be truly O_h. It is also evident that bonding of the ligand to the metal can involve both σ and π bonding. However, little is known about the relative contributions of σ and π bonding to the high ligand field strength that the ligand possesses. For this reason, several mono-substituted tri-2-pyridylamines were synthesised, the role of the substituent being to alter the relative contributions of the σ and π bonding of the ring carrying the substituent. Complexes were prepared in which the ligands are co-ordinated terdentate to the metal ion (where possible) in the hope that the electronic effect of the substituent would affect the bonding of the substituted ring sufficiently for spectroscopic techniques to detect the change.

Metal perchlorates were used to facilitate terdentate co-ordination, the perchlorate ion being a weakly co-ordinating anion.

3.2 Discussion of complexes with Nickel(II) perchlorate

All the methyl-substituted tri-2-pyridylamines were found to co-ordinate as terdentate ligands to both nickel (II) and iron(II) [except 6mpdpa in the case of iron(II)]. Infra red data indicated the ionic nature of the perchlorate anion and the absence of co-ordinated solvent molecules. The electronic spectra (diffuse reflectance spectra) were found to contain two bands of equal intensity, the third band being concealed by the ultra-violet spectra of the ligands. In the case of 6mpdpa there was a tendency to form a diaquo complex in which the ligand

TABLE 3.1

Physical data for nickel(II) complexes with substituted tri-2-pyridylamines

Complex	Electronic spectrum kK				10Dg cm^{-1}	B' cm^{-1}	μ eff. B.M.
	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{2g}$	$^3A_{2g} \rightarrow {}^1E_g$			
$Ni(6mpdpa)_2(ClO_4)_2$	-	18.65 16.8 (sh)	12.25	11.8	12,000	748	3.18
$Ni(5mpdpa)(ClO_4)_2$	-	19.55	12.95	11.35sh	12,950	744	3.14
$Ni(4mpdpa)_2(ClO_4)_2$	-	19.7	13.05	11.55sh	13,050	754	3.15
$Ni(tri\text{-}4m\text{-}pyam)_2(ClO_4)_2$	-	-	12.90	-	12,900	780	3.18
$Ni(5npdpa)_2(H_2O)_2(ClO_4)_2$	-	17.5	10.45	-	11,200	-	3.19
$Ni(tripyam)_2(ClO_4)_2$	26.80	19.05	12.80	10.70sh	12,800	754	3.28

is co-ordinated bidentate. Dissolution of $[Ni(6mpdpa)_2](ClO_4)_2$ in hot aqueous acetone for recrystallization followed by cooling resulted in isolation and crystallization of a pure sample of $[Ni(6mpdpa)_2](ClO_4)_2$. The remainder of the solution was left to stand and a pale blue complex was obtained, $[Ni(6mpdpa)_2(H_2O)_2](ClO_4)_2$. This tendency to form the diaquo complex is not shown by the other methyl-substituted tri-2-pyridylamine complexes or $[Ni(tripyam)_2](ClO_4)_2$. It is therefore attributed to the steric interference of the 6-methyl group with the metal ion causing the substituted ring to free itself. This results in a removal of the hindrance, the substituted ring being out of range of the metal ion.

The infra red data of the copper complexes (discussed later) suggest that the ring carrying the substituent is unco-ordinated when the 6mpdpa is co-ordinated bidentate.

It was not possible to prepare any complexes in which 5npdpa co-ordinates as a terdentate ligand. Several attempts were made to prepare both the iron(II) and nickel(II) complexes but the diaquo complex was formed in all cases. This is attrubited to the electronic nature of the nitro-substituent which is a strong electron-withdrawing substituent both inductively and mesomerically. It seems that the basicity of the substituted ring nitrogen is lowered to such an extent that co-ordination of the ring is no longer possible.

The infra red spectra of all the complexes indicated the perchlorate groups to be ionic, a single band being observed at about 1100 cm^{-1} (ν_3) with a low intensity for ν_1 at 930 cm^{-1}. The magnetic moments of the complexes were in agreement with values expected for spin-free nickel(II) (μ eff = 3.1 - 3.2 B.M.). The diffuse reflectance spectra (Figs. 3.1, 3.2) were consistent with an octahedral environment around the metal ion, although the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ absorption is concealed by the ligand absorptions in the region of 26,000 kK However, it was possible to determine the field strength (Δ) of the ligands, the longest wavelength allowed band being a direct measure of Δ.

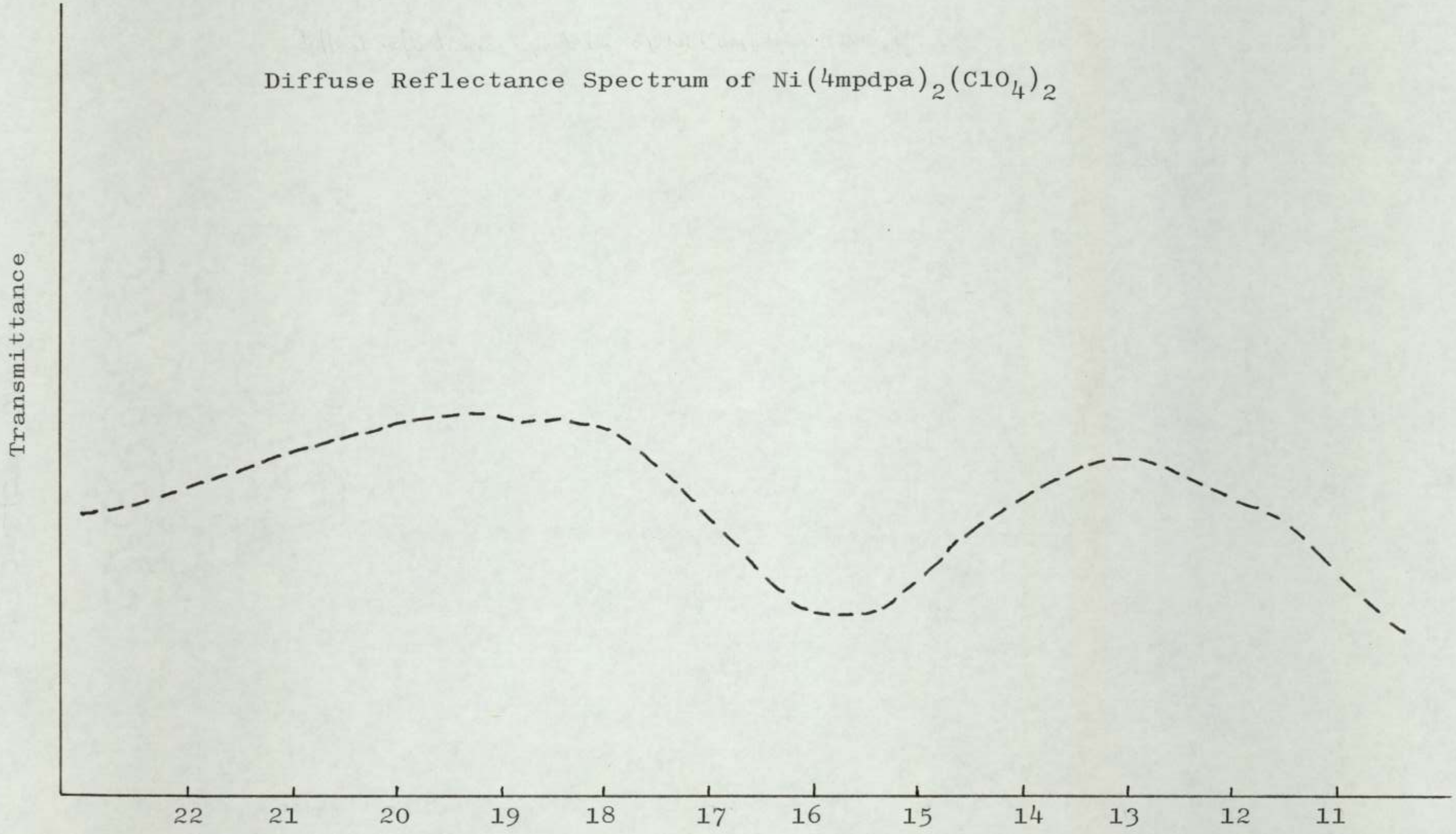
In octahedral stereochemistry, there are three spin allowed transitions:

(1) ${}^3A_{2g} \rightarrow {}^3T_{2g}$

(2) ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$

(3) ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$

Bands (1) and (2) are clearly visible in the spectra, band (3) being concealed by the ultra-violet absorptions of the ligands. However, the spectra all contain a shoulder on the Δ band which has previously been assigned to the occurrence of a spin-forbidden transition (${}^3A_{2g} \rightarrow {}^1E_g$)[84]. Busch and co-workers studied the electronic spectra of octahedral nickel(II) complexes with a variety of α di-imine ligands and found that the occurrence of the spin-forbidden transition complicated the assignment of the Δ band. By using a variety of



Diffuse Reflectance Spectrum of $Ni(4mpdpa)_2(ClO_4)_2$

Fig. 3.1

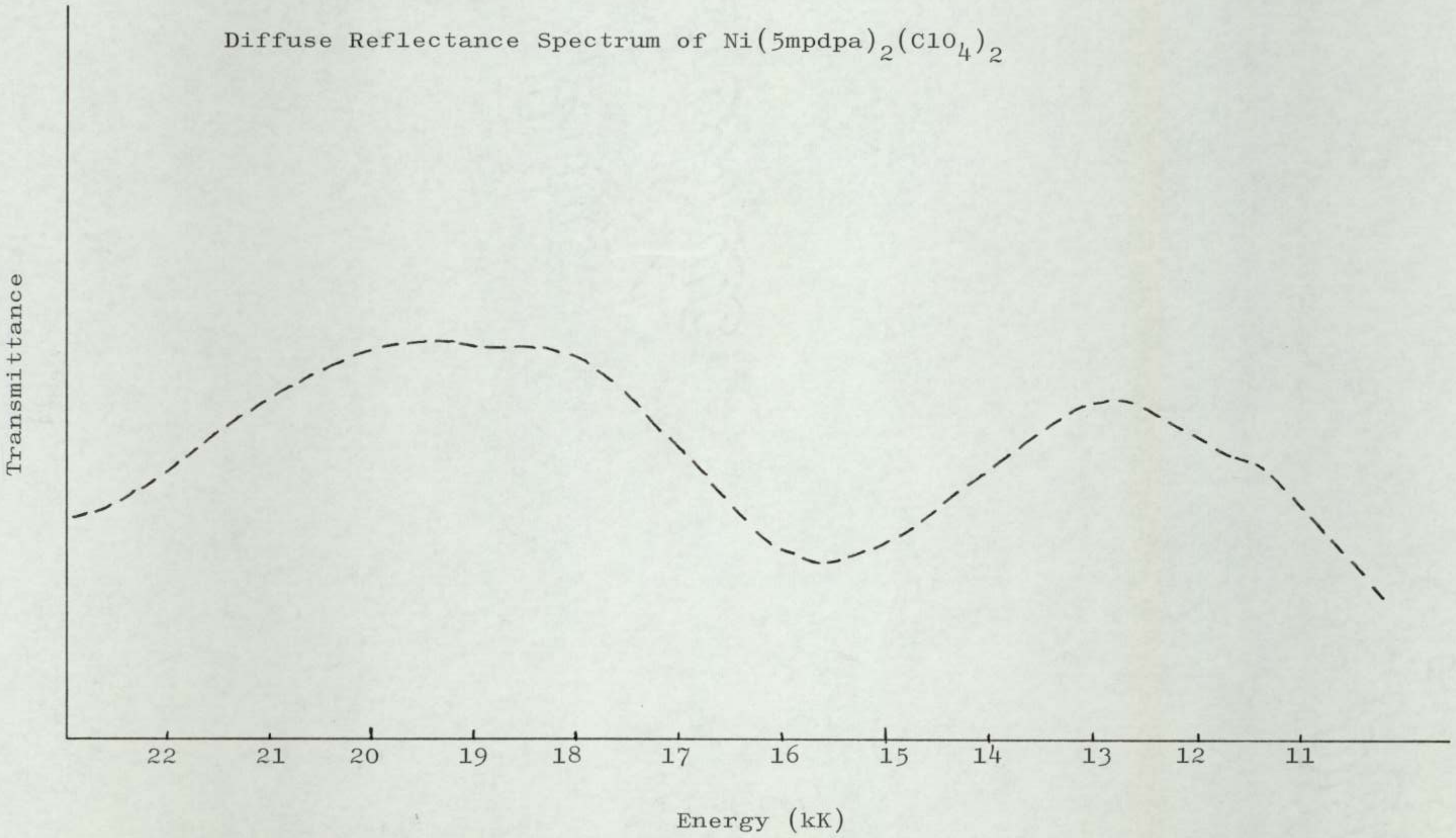

Diffuse Reflectance Spectrum of $Ni(5mpdpa)_2(ClO_4)_2$

Fig. 3.2

ligands with varying ligand field strengths it was found that the shift of the Δ band to higher wave numbers resulted in a similar shift of the $^3A_{2g} \rightarrow {}^1E_g$ band to lower wave numbers. It was also noted that the spin-forbidden band was lower in intensity than the Δ band.

More recently, Palmer and Piper[85] studied the polarised crystal spectra of $Ni(bipy)_3Br_2$ and discussed the complex in terms of D_3 symmetry (the true symmetry) rather than O_h symmetry suggested by Bush. Palmer and Piper suggested that the spin-forbidden band assigned by Busch could be due to a trigonal splitting of the $^3T_2$ level, but considered it unlikely. In the nickel(II) complexes with tri-2-pyridylamines, where the ligands are co-ordinated terdentate to the metal ion, the symmetry of the complexes is known to be very close to octahedral, especially in the cases of tri-2-pyridylamine and tri(-4-methyl-2-pyridyl)amine. The presence of the shoulder on the Δ band in the spectra of all the nickel(II) complexes cannot be explained in terms of a trigonal splitting of the $^3T_2$ energy state and therefore supports Busch's earlier assignment.

The ligand field strengths of the ligands are listed in Table 3.1. The value of Δ for 6mpdpa is 12,000 kK which is considerably lower than that observed for tri-2-pyridylamine. In fact there is some uncertainty about the exact position of the absorption maximum of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition. It is not possible to separate the above absorption from that due to the spin-forbidden transition. It is, therefore, possible that the Δ band occurs as low as 11,600 kK.

Despite the uncertainty about the exact value of Δ, it is evident that there is a considerable lowering of Δ relative to that observed for tri-2-pyridylamine. This is difficult to understand in terms of the increased basicity of the ring nitrogen of the substituted ring. However, as indicated earlier, construction of molecular models of the complex illustrates that there is a considerable steric interaction between the methyl group and the metal ion when the ligand is co-ordinated terdentate. It is suggested that partial relief of the interaction is achieved at the expense of weakening the co-ordination links between the metal ion and ligands and that this weakening of the bonds is directly responsible for the considerable reduction of Δ for 6mpdpa relative to that of tri-2-pyridylamine.

Both 5mpdpa and 4mpdpa afford ligand field strengths slightly greater than that observed for tri-2-pyridylamine. There is little likelihood of a steric interaction between the metal ion and the methyl substituents in the complexes of these ligands. The increase in the Δ value is thought to be a direct consequence of the electron-donating effect of the methyl substituents, causing an increase in the basicity of the ring nitrogens of the substituted rings.

The ligand field strength of 5npdpa is 11,200 kK, considerably lower than that observed for the other ligands. Comparison with the Δ values for the other tri-2-pyridylamines is not possible as 5npdpa co-ordinates as a bidentate ligand only. It is, however, of the same order as Δ for di(-2-pyridyl)phenylamine, di-2-pyridylamine and tri-2-pyridylamine when co-ordinating as a bidentate ligand.

It was not possible to calculate accurately the nephelauxetic parameters B' by using the Tanabe Sugano diagrams because only two of the three absorption maxima are known. The values of B' were, therefore, obtained by the graphical method of Lever.[90] The values were found to be in the range of 744 cm^{-1} to 754 cm^{-1} compared to a free ion value of 1040 cm^{-1}, similar to the value obtained for tri-2-pyridylamine. The nephelauxetic parameter reflects the extent of the d electron cloud expansion when the metal ion d orbitals overlap with the ligand atom orbitals. The relative abilities of ligands to accommodate the d electron cloud can be assessed and a spectrochemical series set up for the ligands. It may be argued that for the complexes of the methyl-substituted tri-2-pyridylamines and tri-2-pyridylamine itself, the covalency is similar in all cases as the ligands are sufficiently alike to discount factors other than symmetry restricted covalency to contribute to the nephelauxetic effect.

The increases in the Δ values for 4mpdpa and 5mpdpa compared to that of tri-2-pyridylamine suggest that the co-ordinating ability of the ligand depends largely on the basicity (i.e. σ donor power) of the ring nitrogen atom. The effect of the methyl substituents is likely to increase the electron density in the aromatic ring and therefore the ease of back π bonding from the d orbitals of the metal to the π orbitals of the ligand is likely to be decreased. The overall inference from the increased Δ values is that σ bonding is more important than π bonding. A nitro substituent is known to have an electron-withdrawing effect on the aromatic ring which will (a) reduce the electron density on the ring nitrogen atom, thus reducing the basicity of the nitrogen and (b) reduce the π electron density delocalized over the ring as a whole. This will reduce the σ donor power of the ring but should increase its π acceptor capacity. The inability of 5npdpa to yield a complex in which the ligand is co-ordinated terdentate to the transition metal ion suggests that the decrease in σ donor power of the ring carrying the nitro substituent is sufficient to prevent the ring from co-ordinating. If, however, π bonding is of major importance in the strength of co-ordination, the reduction of π electron density in the ring would effectively render the ring more able to take part in the back π bonding involving d electrons from the metal ion. This again suggests that σ bonding is of more importance than π bonding.

However, the similarity of the nephelauxetic parameters is not consistent with the complete absence of π bonding. In order for the degree of covalency to remain the same, any increase in σ donor ability of the ligand must be countered by a reduction in π bonding. There is further evidence in the data of Chapter II for the fact that π bonding is not completely absent. The infra red spectra of the tricarbonyl molybdenum derivatives of the methyl-substituted tri-2-pyridylamines (Table 2.1) were examined and it was noted that a shift for ν(CO) of 20 cm^{-1} to lower energy was experienced relative to ν(CO) for Mo(tripyam)$(CO)_3$. As mentioned earlier, this is indicative of an increase in d electron density available on the metal ion for occupying the carbonyl antibonding orbitals for the complexes with the methyl-substituted ligands, relative to that with tri-2-pyridylamine. The greater electron availability on the metal ion in the complexes with 6mpdpa, 5mpdpa and 4mpdpa is considered to be a direct result of a reduction in π bonding between the ligand and the metal ion.

The ligand field strength of tri(-4-methyl-2-pyridyl)amine was found to be 12,900 cm^{-1} which is lower than for 4mpdpa. It is difficult, therefore, to explain this in terms of a substituent effect. The B' value was calculated and found to be 780 cm^{-1},, This suggests that there is a reduction in the electron cloud expansion due to a reduction in the amount of back π bonding from the metal to the ligand.

In complexes with mono-substituted tri-2-pyridylamines, there is little electronic interaction between the rings when the ligand is co-ordinated terdentate to the metal. Therefore, the presence of one ring containing a methyl substituent is not likely to affect the cloud expansion greatly because there are still two rings capable of accommodating the d electron density from the metal ion. However, when all three rings contain methyl substituents, there is a reduction in the bonding to all three rings and hence the reduction in the nephelauxetic parameter.

Finally, it is worth while to place the ligands discussed in the ligand spectrochemical series:

$$\text{Py} \sim \text{NH}_3 < \text{en} < \text{bipy} < \text{phen} < \text{tripyam} < \text{5mpdpa} \sim \text{tri-4m-pyam} < \text{4mpdpa} \ll \text{CN}^-$$

The high ligand field strength of the tri-2-pyridylamine ligands is enhanced by the large degree of flexibility within the bases, the strain involved on co-ordination to transition metal ions being minimal.

3.3 Discussion of the complexes with ferrous perchlorate

Tri-2-pyridylamine and ferrous perchlorate were found to complex forming $[\text{Fe(tripyam)}_2](\text{ClO}_4)_2$ in which tri-2-pyridylamine functions as a terdentate ligand. Magnetic measurements indicated a low but noticeable magnetic moment suggesting that the iron was in the low spin state. The low magnetic moment was attributed to temperature independent paramagnetism as the Mössbauer spectrum did not indicate the presence of iron(III) or high spin iron(II). The Mössbauer spectrum consisted of a single sharp peak which was attributed to the presence of a regular octahedral environment around the metal ion.

Synthesis of iron(II) complexes with mono-substituted tri-2-pyridylamines was carried out for several reasons. Firstly, it was hoped that the presence of the substituent in one of the rings would alter the bonding capabilities of that ring so that the mode of bonding of the ligand could be studied. Mössbauer spectroscopy, being a very sensitive technique, provides a means of assessing whether the asymmetry of the ligand is being transmitted to the metal ion. Secondly, differences in σ donor and π acceptor abilities of the ligands should be reflected in the isomer shift δ which is sensitive to changes in both. Variations in the isomer shifts arise because the spacings of the nuclear energy levels depend minutely on the chemical environment of the nucleus. The chemical shift may be written:

$$\delta = \text{constant} \cdot \frac{\Delta r}{r} \cdot \Delta [\Psi_s(0)]^2$$

where Δr is the difference between the radius of the excited state and the radius of the ground state ($r_{ex} - r_{gr}$) and $\Delta [\Psi_s(0)]^2$ is the difference in s electron density at the nucleus in going from the source to the absorber. For positive values of dr/r, an increase in s electron density at the nucleus is reflected by a positive isomer shift; for negative values of dr/r, an increase in s electron density at the nucleus is reflected by a negative isomer shift. For Fe(II), $\Delta r/r$ is negative and so a positive isomer shift represents a decrease in s electron density at the iron nucleus. The s electron density at the nucleus can be changed in two ways:

(i) the σ donor power of the ligand is likely to affect the density directly;

TABLE 3.2

Physical data for iron(II) complexes with substituted tri-2-pyridylamines

Complex	Electronic Spectrum kK		μ eff B.M.	δ mm sec^{-1}	P.C.S. mm sec^{-1}	Eq	Λ_M
$Fe(5mpdpa)_2(ClO_4)_2$	22,85	19.65sh	1.19	0.68	0.08	0.17	165
$Fe(4mpdpa)_2(ClO_4)_2$	22.2	19.5 sh	1.00	0.64	0.077	0.11	171
$Fe(5npdpa)_2(H_2O)_2(ClO_4)_2$	10.85	8.95 sh	5.74	1.47	-	1.54	175
$Fe(tripyam)_2(ClO_4)_2$	23.0	19.6 sh	0.90	0.63	0.76	0.00	-

where δ is relative to sodium nitroprusside

P.C.S. = partial centre shift quoted for $\frac{1}{3}$ ligand relative to 302 ss stainless steel

and Λ_M determined for 10^{-3}m solutions in pure nitromethane.

(ii) the π acceptor capacity of the ligand will affect the s electron density indirectly.

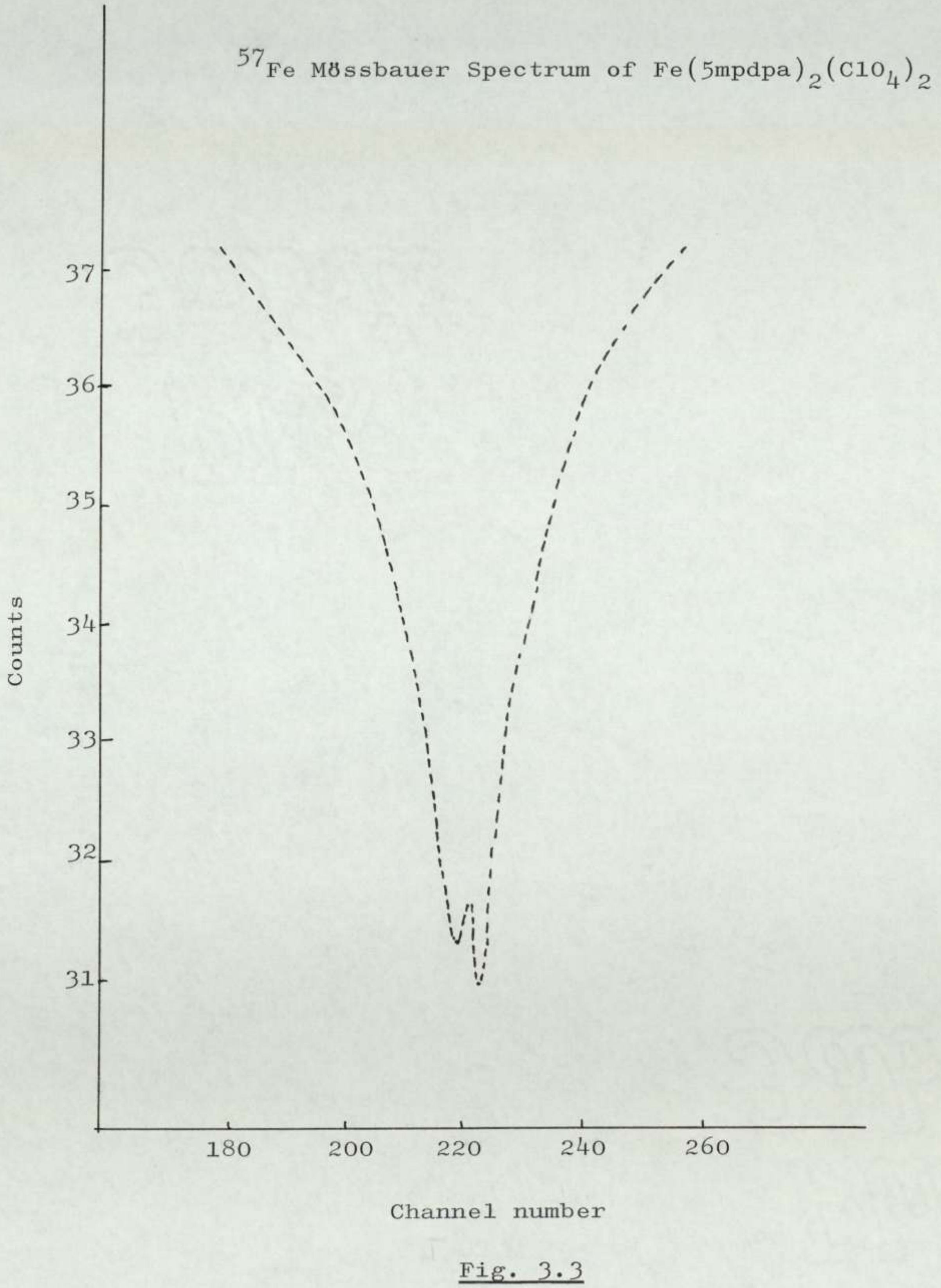
Back π bonding from the metal ion to the ligand reduces the d electron density around the metal ion. This results in less efficient shielding of the outer s electrons and will consequently allow an increase in s electron density at the nucleus.

Ferrous perchlorate complexes were obtained for all the substituted tri-2-pyridylamines except 6mpdpa. Several attempts were made to isolate a complex with this ligand without success. The steric interaction of the methyl group in position 6 when the substituted ring is co-ordinated to the metal has already been discussed and it is likely that this contributes to the inability to obtain complex formation. However, it is difficult to understand why it is not possible to isolate a complex containing 6mpdpa co-ordinated bidentate to the ferrous ion.

Complexes with 4mpdpa, 5mpdpa and tri-4m-pyam all contain ligands co-ordinated terdentate to the ferrous ion, with the iron in the low spin state. The magnetic moments are of the same order as that observed for $[Fe(tripyam)_2](ClO_4)_2$ and the small moment is attributed to temperature-independent paramagnetism. It was not possible to prepare a complex with 5npdpa in which the ligands were co-ordinated terdentate, the diaquo complex $[Fe(5npdpa)_2(H_2O)_2](ClO_4)_2$ being formed in all cases. The magnetic moment (μeff = 5.7 B.M.) is consistent with the iron(II) in the high spin state.

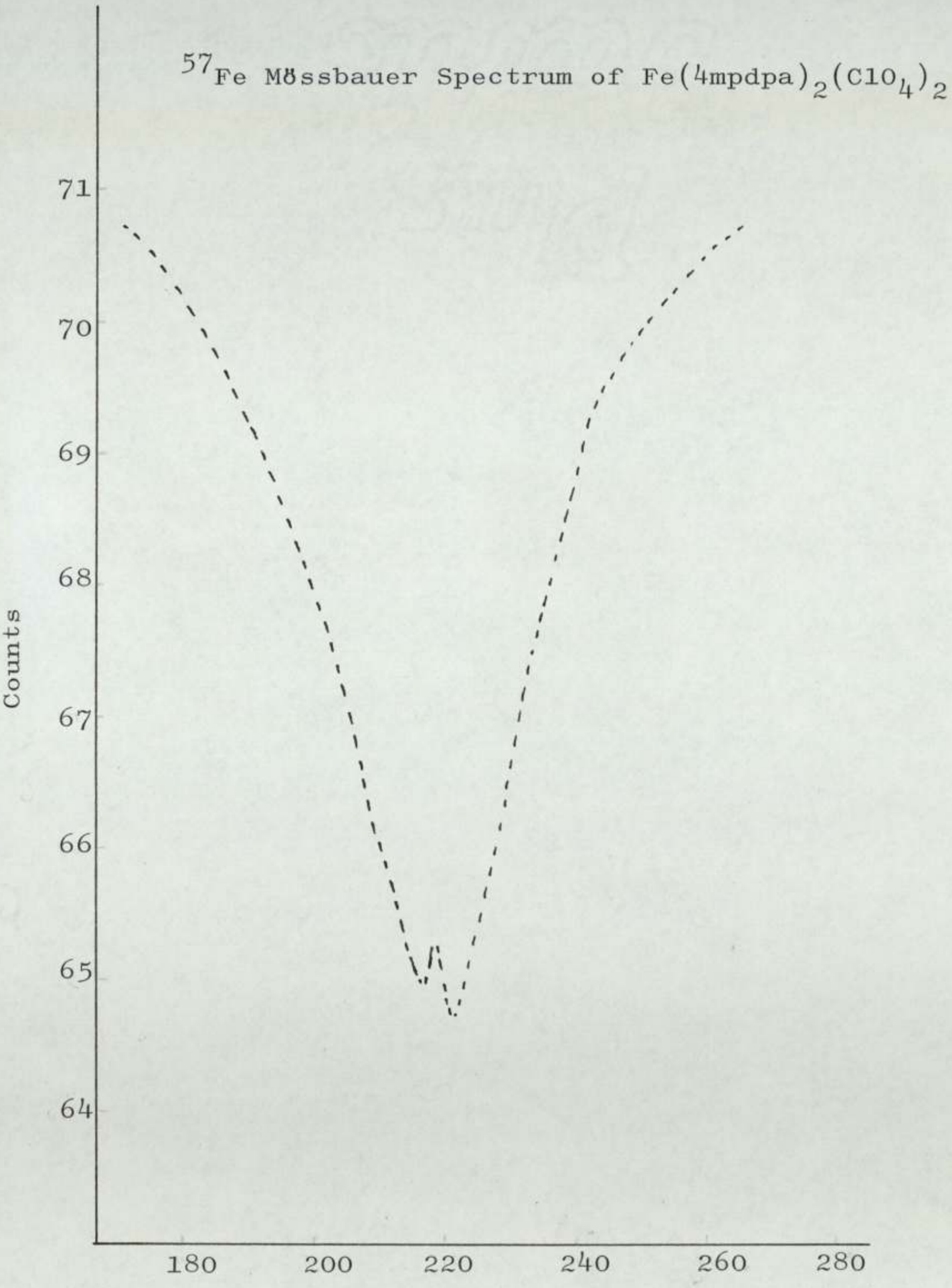
The infra red spectra of the complexes indicated that the perchlorate is ionic in all cases, and in the case of the complex with 5npdpa the presence of water is indicated. It has been suggested that the preference for formation of high spin or low spin complexes is a direct function of the ligand field strengths of the ligands co-ordinated to the metal, the critical value being 11.63 - 11.70 kK [86]. Ligands with Δ lower than the critical value form high spin complexes. Above this value it is more favourable for the electrons to pair up, leaving the e_g orbitals vacant in octahedral complexes. As the Δ values for 4mpdpa, 5mpdpa and tri-4m-pyam are all in excess of the critical value, it would be expected that complexes with these ligands contain iron in the low spin state. This was found to be the case. Similarly, the Δ band for $[Ni(5npdpa)_2(H_2O)_2](ClO_4)_2$ is consistent with the formation of a high spin complex, $[Fe(5npdpa)_2(H_2O)_2](ClO_4)_2$.

The Mössbauer spectra of the complexes were obtained and the results are tabulated in Table 3.2. $[Fe(5mpdpa)_2](ClO_4)_2$ and $[Fe(4mpdpa)_2](ClO_4)_2$ (Figs. 3.3 and 3.4) both yielded spectra ($\Gamma \frac{1}{2}$ = 0.55 mm/sec and 0.58 mm/sec respectively) containing a peak slightly broader than that observed for $[Fe(tripyam)_2](ClO_4)_2$ ($\Gamma \frac{1}{2}$ = 0.50 mm/sec). There was definite evidence of splitting in the band. The data were computed, the results obtained confirming the presence of a small quadrupole splitting. The nature of the ligands is such that an asymmetry is present around the metal ion and when the ligands are co-ordinated



^{57}Fe Mössbauer Spectrum of Fe(5mpdpa)$_2$(ClO$_4$)$_2$

Fig. 3.3



^{57}Fe Mössbauer Spectrum of Fe(4mpdpa)$_2$(ClO$_4$)$_2$
71
70
69
68
67
66
65
64
Counts
180
200
220
240
260
280
Channel number

Fig. 3.4

terdentate, it is not possible for the effect of substituent to be transmitted from one ring to another. The occurrence of the small quadrupole splitting suggests that the electronic effect of the substituent is being transmitted to the metal ion and it may therefore be considered likely that the bond between the substituted ring and the metal ion is affected by the substituent. The spectrum of $[\mathrm{Fe(5npdpa)_2(H_2O)_2}](\mathrm{ClO_4})_2$ showed a large quadrupole splitting, as expected for a tetragonal complex.

The isomer shift of $[\mathrm{Fe(tripyam)_2}](\mathrm{ClO_4})_2$ was found to be 0.63 mm/sec which is in the region for low spin iron(II) complexes. The isomer shifts obtained for the complexes with 4mpdpa and 5mpdpa are 0.64 and 0.68 mm/sec respectively. However, the slight increases in isomer shift are within experimental error and it is not possible to postulate a decrease in s electron density at the nucleus. It is evident that there is little, if any, variation in the s electron density at the nucleus. This observation is of interest because previous data (ligand field parameters and basicity) suggest that the σ donor ability of the methyl-substituted ligands is greater than for tri-2-pyridylamine. The observation of the quadrupole splitting in the Mössbauer spectra of $[\mathrm{Fe(5mpdpa)_2}](\mathrm{ClO_4})_2$ and $[\mathrm{Fe(4mpdpa)_2}](\mathrm{ClO_4})_2$ is evidence for the effect of the methyl substituent being transmitted to the metal. Therefore, in the absence of any variations in π bonding, a shift of δ to < 0.63 mm/sec would be expected. However, it is known that the bonding of the tri-2-pyridylamines to transition metal ions is not purely σ in nature, bonding via the $d\pi$ - $p\pi$ network contributing to the strength of the co-ordination link. It was noted that the carbonyl stretching frequency in the infra-red spectra of the $Mo(L)(CO)_3$ complexes decreased when methyl substituents are present, suggesting a reduction in the amount of π bonding involved on co-ordination of the methyl-substituted ligands. A reduction in the amount of back π bonding from the metal to the ligand would reduce the cloud expansion of the d orbitals, i.e. the d electrons would be held closer to the metal ion. This would result in more efficient shielding of the 4s electron cloud from the metal, thus reducing the s electron density at the nucleus.

Hence the reduction in π bonding capacity of 4mpdpa and 5mpdpa relative to tri-2-pyridylamine would tend to increase δ above 0.63 mm/sec observed for $[Fe(tripyam)_2](ClO_4)_2$. It seems that the increased σ donor capacity and decreased π acceptor capacity of the methyl-substituted ligands have nearly equal but opposite effects on the s electron density at the iron(II) nucleus in $[Fe(5mpdpa)_2](ClO_4)_2$ and $[Fe(4mpdpa)_2](ClO_4)_2$.

The isomer shift observed for $[Fe(5npdpa)_2(H_2O)_2](ClO_4)_2$ (δ = 1.47 mm/sec) is consistent with values expected for spin free iron(II) complexes (Fig. 3.5). The magnetic susceptibility (μ eff = 5.7 B.M.) confirms the high spin nature of the iron.

The diffuse reflectance spectrum indicated the pres-

^{57}Fe Mössbauer Spectrum of Fe(5npdpa)$_2$(H$_2$O)$_2$(ClO$_4$)$_2$

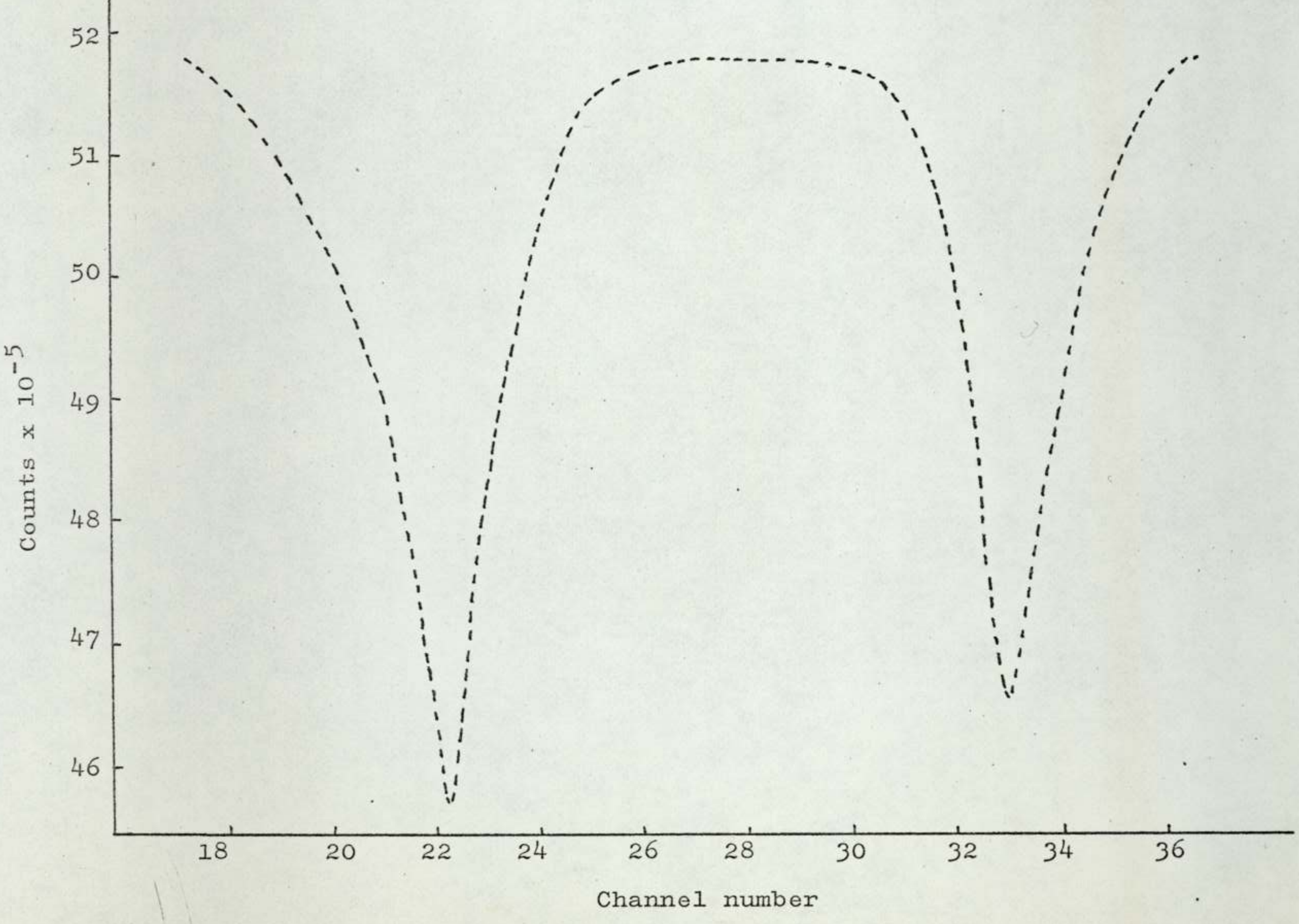


Fig. 3.5

ence of a tetragonal environment around the metal ion, the water molecules probably occupying the axial co-ordination sites. It is worth noting that, for complexes of 5npdpa with iron(II) and nickel(II) it was not possible to prepare the diperchlorato complex, the diaquo complex being preferentially formed.

In conclusion, the results discussed in this chapter illustrate the importance of both σ and π bonding in the co-ordination of pyridylamine ligands to transition metal ions. It is evident that increasing the σ donor capacity of the ring nitrogen results in an increase in the σ network contribution to bonding, while an increased electron density in the π network of the pyridine ring reduces the back π bonding contributions.

Similarly, reduction of the electron density in the pyridine and at the ring nitrogen lowers the σ bonding capabilities of the ligand but the ring is more able to accommodate d electrons from the metal ion. The inability to isolate complexes in which 5npdpa is co-ordinated terdentate to the metal ion illustrates the greater importance of σ bonding in the co-ordination of these ligands to transition metal ions.

CHAPTER IV

A study of copper(II) complexes with several -2-pyridylamine ligands

4.1 Complexes with methyl-2-pyridyldi-2-pyridylamines

Earlier workers[69] found that the reaction of copper perchlorate with tri-2-pyridylamine resulted in the formation of two isomeric complexes, a blue complex in which the ligand is co-ordinated terdentate to the copper(II) ion and a yellow-green complex where the ligand is co-ordinated bidentate. The two remaining co-ordination sites in the yellow-green complex are occupied by partially co-ordinated perchlorate anions. It was found that isomerization is achieved by heating the yellow-green complex to 260°C.

$$\underset{\text{yellow-green}}{[\mathrm{Cu(tripyam)_2(ClO_4)_2}]} \underset{\substack{\text{on standing}\\ \text{for several}\\ \text{months}}}{\overset{260^{\circ}\mathrm{C}}{\rightleftharpoons}} \underset{\text{blue}}{\mathrm{Cu(tripyam)_2(ClO_4)_2}}$$

Partial isomerization from the blue isomer to the yellow-green isomer took place on standing for several months.

The reaction of copper perchlorate hexahydrate with 6mpdpa affords a yellow-green complex in which the ligand is co-ordinated bidentate to the metal ion. The infra red spectrum indicates partial co-ordination of the perchlorate anions. Synthesis of the complex in which the ligand is co-ordinated terdentate to the copper ion is not possible directly. Similarly, heating $[\mathrm{Cu(6mpdpa)_2(ClO_4)_2}]$ on an oil bath up to 260°C did not result in isomerization but, in several cases, explosion occurred. However, it was possible to prepare the complex with terdentate 6mpdpa via the diaquo complex $[Cu(6mpdpa)_2(H_2O)_2](ClO_4)_2$. Heating this complex to $180^{\circ}C$ resulted in the formation of a mauve-blue complex in which 6mpdpa functions as a terdentate ligand. The steric hindrance caused by the methyl group in position 6 when the ring containing the substituent is co-ordinated to the metal ion has been discussed in Chapter 3. There is a considerable reduction in the ligand field strength for terdentate 6mpdpa (12.000 kK) compared to terdentate tri-2-pyridylamine (12.800 kK) and also a tendency to form the diaquo complex $[Ni(6mpdpa)_2(H_2O)_2](ClO_4)_2$ which is not shown by tri-2-pyridylamine. A possible explanation for the inability to form $Cu(6mpdpa)_2(ClO_4)_2$ directly from $[Cu(6mpdpa)_2(ClO_4)_2]$ is that co-ordination of the ring carrying the methyl substituent is only possible via a major disruption of the lattice. On heating the diaquo complex, the water molecules become unco-ordinated, vacating two of the co-ordination sites around the metal. The unco-ordinated ring of the ligand then competes with the perchlorate anion for the vacant site.

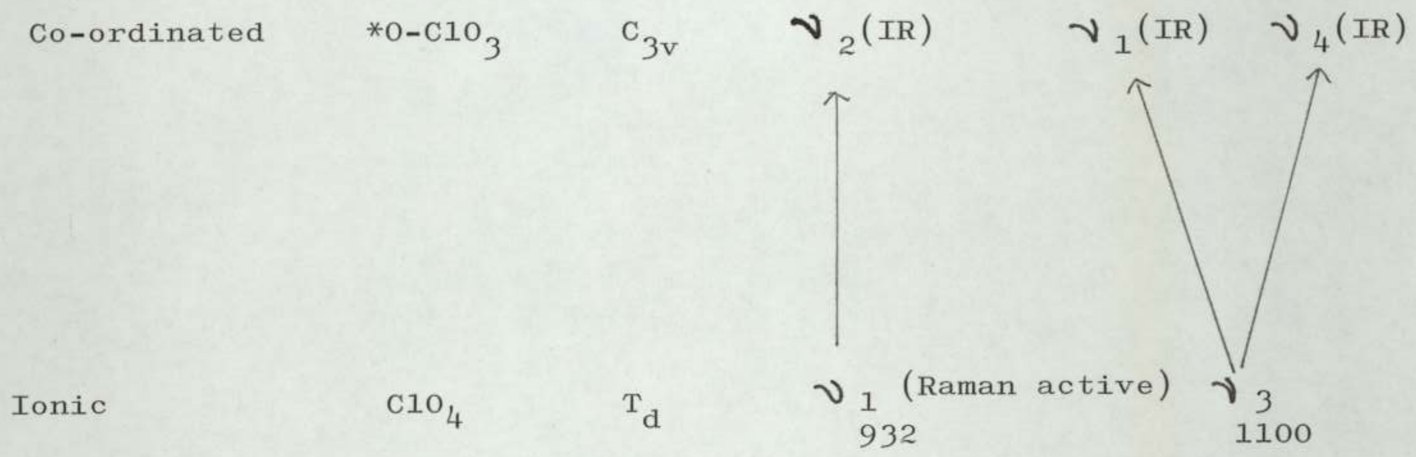
It was not possible to isolate complexes with 5mpdpa similar to those obtained with tri-2-pyridylamine and 6mpdpa. However, complex formation with 4mpdpa followed a similar pattern to tri-2-pyridylamine where isolation of both isomers was possible. Allowing the reaction mixture to stand resulted in precipitation of $[Cu$

$(4mpdpa)_2(ClO_4)_2$_7 in poor yield whereas reduction of solvent volume resulted in precipitation of a complex intermediate in colour between the yellow-green and mauve-blue isomers. On heating to 100°C for 30 minutes complete isomerization to $Cu(4mpdpa)_2(ClO_4)_2$ was achieved. The infra red spectrum of the intermediate compound was complex and a broad band in the 1100 cm^{-1} region for ν_3 perchlorate absorption suggested that the material is, in fact, intermediate between the yellow-green and mauve forms.

4.1.1 Infra red spectra

The infra red spectra of the complexes provide valuable information on the role of the anions in the complexes, i.e. whether they are ionic or co-ordinated. In the ionic state, the perchlorate ion has a regular tetrahedral structure and belongs to the point group T_d. In general the triply degenerate ν_3 mode observed in the infra red spectrum of ionic perchlorates appears as a broad strong band in the region of 1100 cm^{-1}. The non degenerate band ν_1 which is theoretically forbidden in the infra red, usually occurs at a very weak absorption at 930 cm^{-1}. This absorption becomes weakly allowed owing to distortion of the anion in a crystal field of lower symmetry than itself.

If the perchlorate group becomes involved in partial covalent bonding between one of its oxygen atoms and a cation, this oxygen atom is no longer equivalent to the other three and the overall symmetry of the anion is lowered to C_{3v}. (Fig. 4.1)



*refers to co-ordinated oxygen.

Fig. 4.1

In C_{3v} symmetry the triply degenerate ν_3 mode is split into two and the non-degenerate ν_1 mode becomes infra red active. Therefore, increase in intensity of ν_1 mode together with splitting of the ν_3 mode provides a useful guide to the occurrence of partially co-ordinated perchlorate anions.

The spectrum of $[Cu(6mpdpa)_2(ClO_4)_2]$ indicated that the perchlorate is co-ordinated, the ν_3 band in the region of 1100 cm^{-1} being clearly split into two bands (1108 cm^{-1}, 1066 cm^{-1}). This was found to be the case for $[Cu(4mpdpa)_2(ClO_4)_2]$ ($\nu_3$1102 cm^{-1}, 1063 cm^{-1}) and $[Cu(5npdpa)_2(ClO_4)_2]$ (ν_3 1102 cm^{-1}, 1068 cm^{-1}). The splitting in the case of $[Cu(5npdpa)_2(ClO_4)_2]$ is smaller than for the other two complexes possibly reflecting a smaller interaction with the metal ion in this case. However, in C_{3v} symmetry (which is the symmetry of the perchlorate anion when co-ordinated as a monodentate ligand), the ν_1 vibration at about 930 cm^{-1} is infra red active. In the spectra of all three complexes the intensity of the ν_1 band is low and does not indicate complete co-ordination. Therefore, it is considered that all three complexes contain partially co-ordinated anions. The spectra of $Cu(6mpdpa)_2(ClO_4)_2$ and $Cu(4mpdpa)_2(ClO_4)_2$ indicate the presence of ionic perchlorate anions.

Kulasingam noted that infra red spectroscopy provides a useful guide to differentiating between tri-2-pyridylamine when co-ordinated (a) bidentate to the metal ion and (b) terdentate to the metal ion. He found

T A B L E 4.1

Infra red and visible data for Copper(II) complexes with tri-2-pyridylamine ligands

Complex	Colour	$\nu_3(ClO_4^-)cm^{-1}$	$\nu_1(ClO_4^-)cm^{-1}$	Electronic spectrum $(kK)^c$
$[Cu(6mpdpa)_2(ClO_4)_2]$	Yellow-green	1108s,1066s	932m	19.95, 15.8 sh*
$[Cu(6mpdpa)_2](ClO_4)_2$	Mauve to blue	1075s		17.35, 12.1 sh
$[Cu(4mpdpa)_2(ClO_4)_2]$	Yellow-green	1102s,1063s	930w-m	18.9 (assym. to low*cm^{-1})
$[Cu(4mpdpa)_2](ClO_4)_2$	Mauve to blue	1090s		17.30, 12.0 sh
$[Cu(6mpdpa)_2(H_2O)_2](ClO_4)_2$	Grey	1104s		16.15, 14.4 sh
$[Cu(5npdpa)_2(ClO_4)_2]$	Grey	1102s,1068s		17.9 (sym. to low cm^{-1})
$[Cu(5npdpa)_2(Acetone)_2](ClO_4)_2$	Mauve	1090s		17.65
$[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$	Grey	1091s		17.7
$[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$	Green	1085s		16.8, 15.8sh, 10.3 sh
$[Cu(tripyam)_2(ClO_4)_2]$	Yellow-green	1119s,1060s	938m-s	k *
$[Cu(tripyam)_2](ClO_4)_2$	Mauve to blue	1096s		17.54, 11.90

c - diffuse reflectance spectra vz. MgO

* - we were unable to identify any definite maximum below 10.0 kK for these complexes.

k - virtually impossible to detect maximum that the complexity of the spectrum is increased when the ligand is co-ordinated bidentate to the metal ions. This is understandable because on bidentate co-ordination, (a) the symmetry of the complex is lower (C_s compared to C_{3v} when the ligand is co-ordinated terdentate), and (b) the pyridine rings are present in two different environments, co-ordinated and unco-ordinated.

However, it was not possible to extend these observations to complexes with substituted tripyridylamines as the symmetry of the complexes is only C_s irrespective of whether the ligands are co-ordinated bidentate or terdentate.

In the tri-2-pyridylamine complexes with copper(II) perchlorate the three pyridine rings are equivalent before co-ordination and therefore any of the three pyridine rings may remain unco-ordinated in the bidentate complexes. With the mono-substituted tri-2-pyridylamines the equivalence of the three rings is no longer present and the problem of determining which ring is unco-ordinated in the bidentate complexes arises. In the ligands containing methyl substituents, the basicity of the substituted ring nitrogen is increased and therefore the co-ordinating ability of the ring is greater. Alternatively, in 5npdpa, the basicity of the ring carrying the nitro substituent is decreased and therefore the co-ordinating ability of the ring is less. The inability to prepare a complex in which 5npdpa is co-ordinated terdentate to the metal ion suggests that the substituent effect is appreciable and the basicity of the ring nitrogen is lowered sufficiently to prevent co-ordination of the substituted ring. However, the problem is more difficult to resolve in the case of the ligands with methyl substituents. Nitro substituents are known to be *strongly* electron withdrawing, whereas the electron donating ability of the methyl substituent is relatively weak. The question arises as to whether the substituent effect increases the electron density at the ring nitrogen sufficiently for the substituted ring to always co-ordinate in preference to one of the unsubstituted rings. The Mössbauer spectra of the iron(II) complexes suggest that the electronic effect is strong enough to be appreciated by the metal ion, a definite electric field gradient being detected when the ligands are co-ordinated terdentate. With 4mpdpa and 5mpdpa it is only necessary to consider the electronic effects of the methyl substituents, whereas in complexes with 6mpdpa it is necessary to consider the considerable steric interaction of the substituent with the metal ion. The infra red spectra of the complexes of copper(II) perchlorate with 4mpdpa, 5mpdpa and 6mpdpa were examined closely in an attempt to determine which rings are unco-ordinated in $[\mathrm{Cu(6mpdpa)_2(ClO_4)_2}]$ and $[\mathrm{Cu(4mpdpa)_2(ClO_4)_2}]$.

An analysis of the infra red spectra of the metal complexes with tri-2-pyridylamine[69] indicated that a shift of ligand absorption bands (relative to the free ligand) in the infra red spectrum to higher wave number takes place on co-ordination of the ligand to the metal ion. The free ligand contains two bands assigned to C-N stretching at 1599 cm^{-1} (shoulder) and 1588 cm^{-1} (strong) which are shifted to 1612 and 1596 cm^{-1} respectively in the infra red spectrum of $Cu(tripyam)_2(ClO_4)_2$. In the infra red spectrum of $[Cu(tripyam)_2(ClO_4)_2]$ the greater complexity of the infra red spectrum in the region of 1600 cm^{-1} can be attributed to the presence of both co-ordinated and unco-ordinated rings. The infra red spectra of the methyl substituted tri-2-pyridylamines have been discussed earlier (Chapter 2) and it has been suggested that bands between 1600 and 1610 cm^{-1} are due to C-N stretching in the substituted ring. It is noted that in the complexes with copper perchlorate in which the ligands are co-ordinated terdentate, these bands are shifted to 1620 - 1625 cm^{-1}. The spectrum of $Cu(4mpdpa)_2(ClO_4)_2$ contains bands at 1625 cm^{-1} and 1621 cm^{-1} which do not appear in the spectrum of the $Cu(tripyam)_2(ClO_4)_2$. These bands are assignedto C-N stretching in the substituted ring, and the shift to higher wave number reflects the co-ordinated nature of the substituted rings.

In the infra red spectrum of $[Cu(4mpdpa)_2(ClO_4)_2]$ in which the ligand is co-ordinated bidentate, the corresponding bands appear at 1624 cm^{-1} and 1620 cm^{-1}. If the ring carrying the methyl substituent were to become unco-ordinated, a shift to lower wave number would be expected. The fact that there is no shift suggests that it is one of the unsubstituted rings which become unco-ordinated on formation of $[Cu(4mpdpa)_2(ClO_4)_2]$.

Similarly, in the complex with 5mpdpa where the ligands are co-ordinated bidentate, bands at 1623 cm^{-1} and 1619 cm^{-1} suggest that the substituted ring is co-ordinated in this complex.

It is not possible to extend these arguments to the complexes with 6mpdpa because there is not a clear separation of ν(C-N) for the substituted ring from ν(C-N) for the unsubstituted rings in the spectra of $\mathrm{Cu(6mpdpa)_2(ClO_4)_2}$, $[\mathrm{Cu(6mpdpa)_2(ClO_4)_2}]$ or $[\mathrm{Cu(6mpdpa)_2(H_2O)_2}]\mathrm{(ClO_4)_2}$. In particular, the ν(C-N) bands for the substituted ring in $\mathrm{Cu(6mpdpa)_2(ClO_4)_2}$ (terdentate ligands) appear to lower wave number than in the complexes with 5mpdpa and 4mpdpa. However, in $\mathrm{Cu(6mpdpa)_2(ClO_4)_2}$ it is anticipated that there will be strong non-bonded repulsion between the methyl group and the metal ion causing a weakening of the interaction of the metal ion with the ring nitrogen (thus reducing the steric hindrance). This results in a decrease in the shift to higher wave number for ν(C-N) expected on co-ordination and therefore it is not possible to resolve the individual bands for the complexes with 6mpdpa. Earlier evidence, however, suggests that it is the ring carrying the methyl substituent that is unco-ordinated in the bidentate complexes with 6mpdpa.

4.1.2 Electronic and Electron Spin Resonance Spectra

The visible spectrum for $[\mathrm{Cu(tripyam)_2}]\mathrm{(ClO_4)_2}$ has been shown previously to consist of a strong band at 17.54 kK with a shoulder at 11.90 kK suggesting a tetragonal environment around the copper(II) ion. For

$[Cu(tripyam)_2(ClO_4)_2]$ a more distorted spectrum was obtained in which it was virtually impossible to detect a definite maximum. The visible spectra of $[Cu(6mpdpa)_2](ClO_4)_2$ and $[Cu(4mpdpa)_2](ClO_4)_2$ are almost identical as shown in Fig. 4.2 and resemble closely that obtained for the corresponding complex with tri-2-pyridylamine as ligand. Similarly the spectra of $[Cu(6mpdpa)_2(ClO_4)_2]$, $[Cu(4mpdpa)_2(ClO_4)_2]$ (Fig. 4.3) and $[Cu(tripyam)_2(ClO_4)_2]$ are almost superimposable.

The spectra of the complexes with terdentate ligands are consistent with those expected for a tetragonally distorted octahedral stereochemistry. It was noted that the spectrum of $[Cu(6mpdpa)_2](ClO_4)_2$ showed greater asymmetry in the major absorption band, probably due to the additional distortion resulting from the steric hindrance of the methyl substituent in the 6 position. However, it was evident that the technique was insufficiently sensitive to detect the electronic effect of the methyl substituent in the substituted rings.

The esr spectra for $[Cu(4mpdpa)_2](ClO_4)_2$ and $[Cu(6mpdpa)_2](ClO_4)_2$ were not consistent with the asymmetry suggested by the electronic data. Isotropic spectra were obtained in both cases, there being no evidence for two g factors. It is likely, however, that the isotropic nature of the esr spectra can be attributed to one of the following:

(a) a dynamic Jahn Teller distortion where three equivalent (or near equivalent) axes are randomly distorting, Diffuse Reflectance Spectra of Cu(4mpdpa)$_2$(ClO$_4$)$_2$ and Cu(6mpdpa)$_2$(ClO$_4$)$_2$

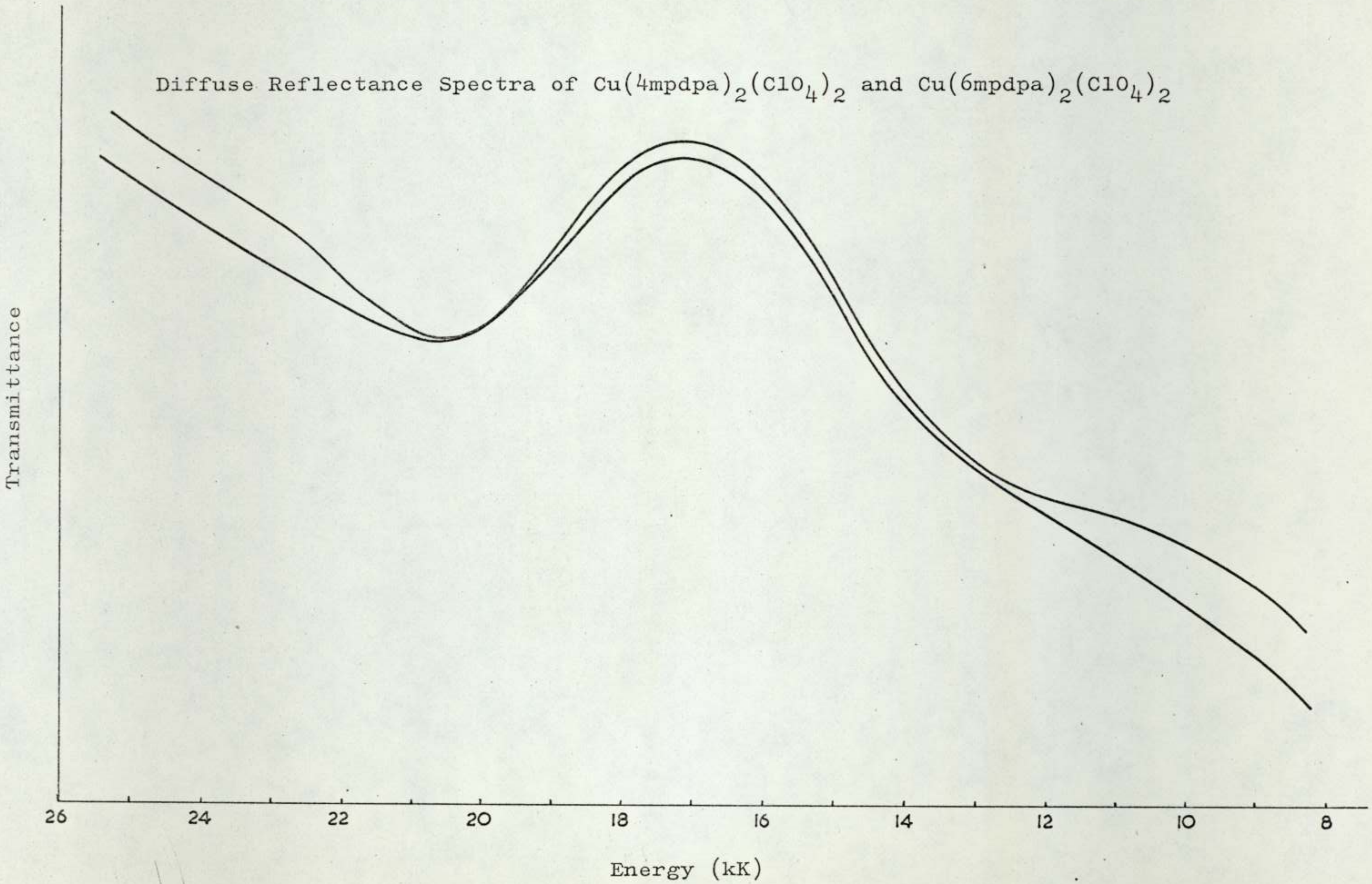
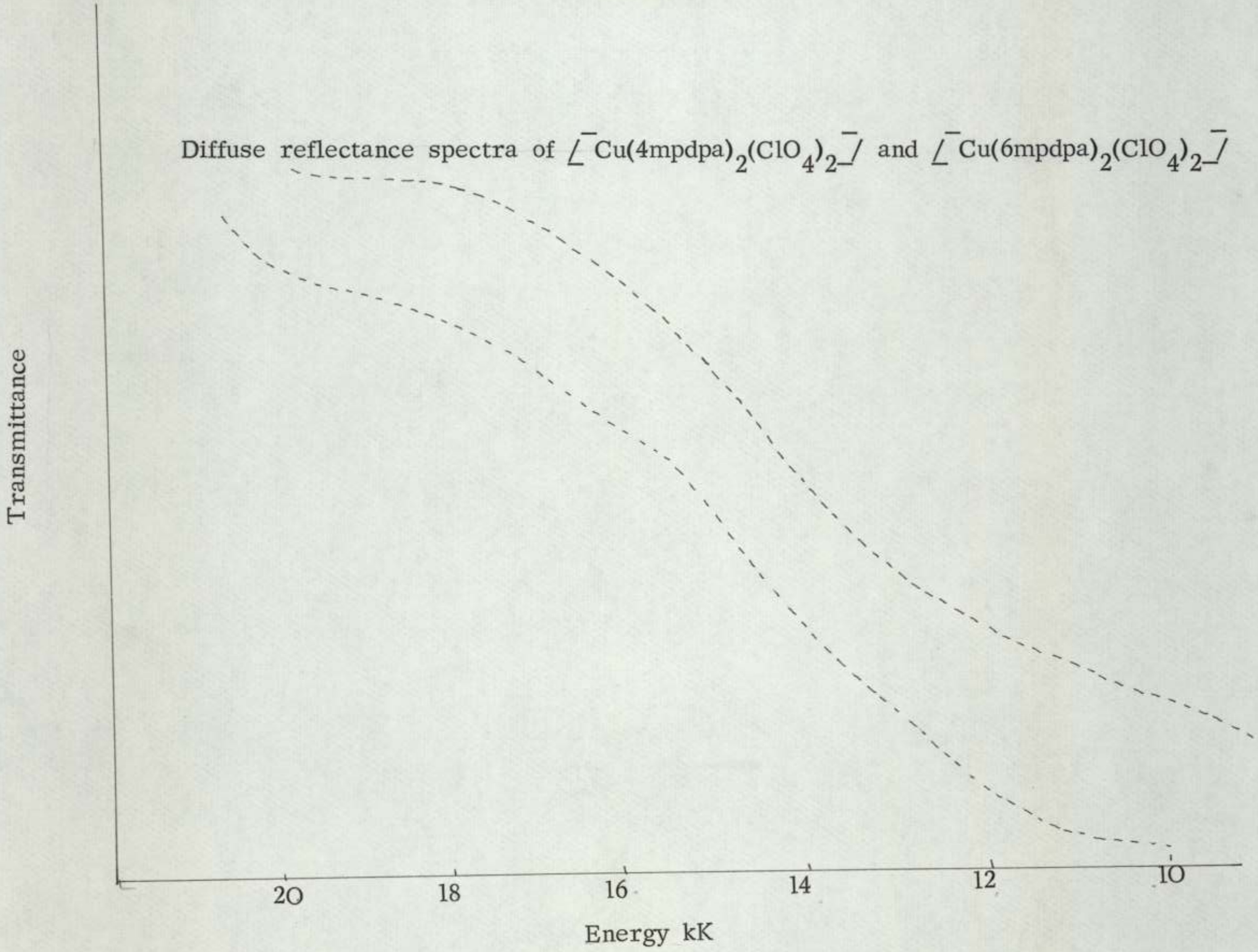


Fig. 4.2



Diffuse reflectance spectra of $[\text{Cu(4mpdpa)}_2(\text{ClO}_4)_2]$ and $[\text{Cu(6mpdpa)}_2(\text{ClO}_4)_2]$

Fig. 4.3

TABLE 4.2

Electron spin resonance data for Copper(II) complexes with tri-2-pyridylamine ligands

Complex	$g_{\perp}$ [a]	$g_{\parallel}$	g_{av} [b]
$[Cu(6mpdpa)_2(ClO_4)_2]$	2.03 (o)	2.21[d]	
$[Cu(6mpdpa)_2](ClO_4)_2$			2.06 (2)
$[Cu(4mpdpa)_2(ClO_4)_2]$			2.05 (3)
$[Cu(4mpdpa)_2](ClO_4)_2$			2.06 (4)
$[Cu(6mpdpa)_2(H_2O)_2](ClO_4)_2$			2.05 (5)
$[Cu(6mpdpa)_2(H_2O)_2](ClO_4)_2($	2.02 (5)	2.22[e]	
$[Cu(5npdpa)_2(ClO_4)_2]$			2.06 (2)
$[Cu(5npdpa)_2(Acetone)_2](ClO_4)_2$			2.06 (2)
$[Cu(5npdpa)_2(Acetone)_2](ClO_4)_2$	2.05 (1)		
$[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$			2.06 (0)
$[Cu(tripyam)_2(ClO_4)_2]$			2.07 (3)
$[Cu(tripyam)_2](ClO_4)_2$			

a - corrected for Gaussian line shape after ref.8

b - estimated from broad isotropic spectra

e - $A_{\parallel}$ = 176 Hz

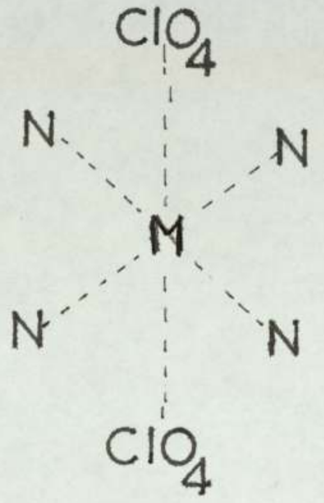
d - $A_{\parallel}$ = 171 Hz

(b) a random orientation of the tetragonal axes within the crystals, or

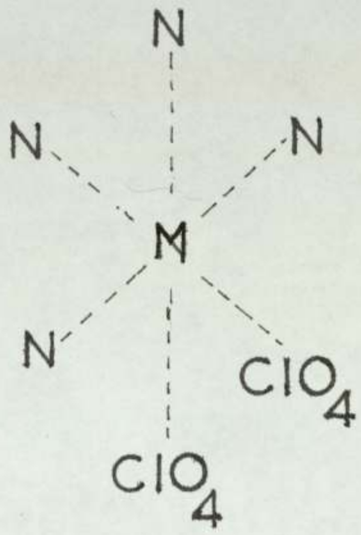
(c) exchange interaction between adjacent copper nuclei.

When the esr spectra were run at liquid nitrogen temperature, there was no indication that the spectra were changing to indicate two g factors. This is not consistent with a dynamic Jahn Teller distortion, where one would expect cooling of the sample to result in the complex being frozen into one of its potential minima. Alternatively, when molecular models are examined, the overall molecule is almost spherical. This would favour a random orientation of the molecular axes as there would not be any preferential way of lining up the spheres. It seems likely, therefore, that the isotropic nature of the esr spectrum is due to a random orientation of the molecular axes. In the case of $[Cu(tripyam)_2](ClO_4)_2$, where x, y and z axes are equivalent, an explanation in terms of a dynamic Jahn Teller[68] effect is more likely than for the complexes with asymmetric ligands. However, cooling the sample to liquid nitrogen temperature did not increase the complexity of the spectrum and therefore misalignment of the molecular axes with the crystals is probably present in this complex also.

The diperchlorate complexes $[Cu(6mpdpa)_2(ClO_4)_2]$ and $[Cu(4mpdpa)_2(ClO_4)_2]$ show similar visible spectra to that obtained for the tripyam analogue. It is difficult to locate the positions of maxima but it is obvious that the spectra contain several absorptions. Two modes of co-ordination are possible for those complexes, one involving trans ligands and trans perchlorate groups, the other involving cis ligands and cis perchlorate anions.



Trans



Cis

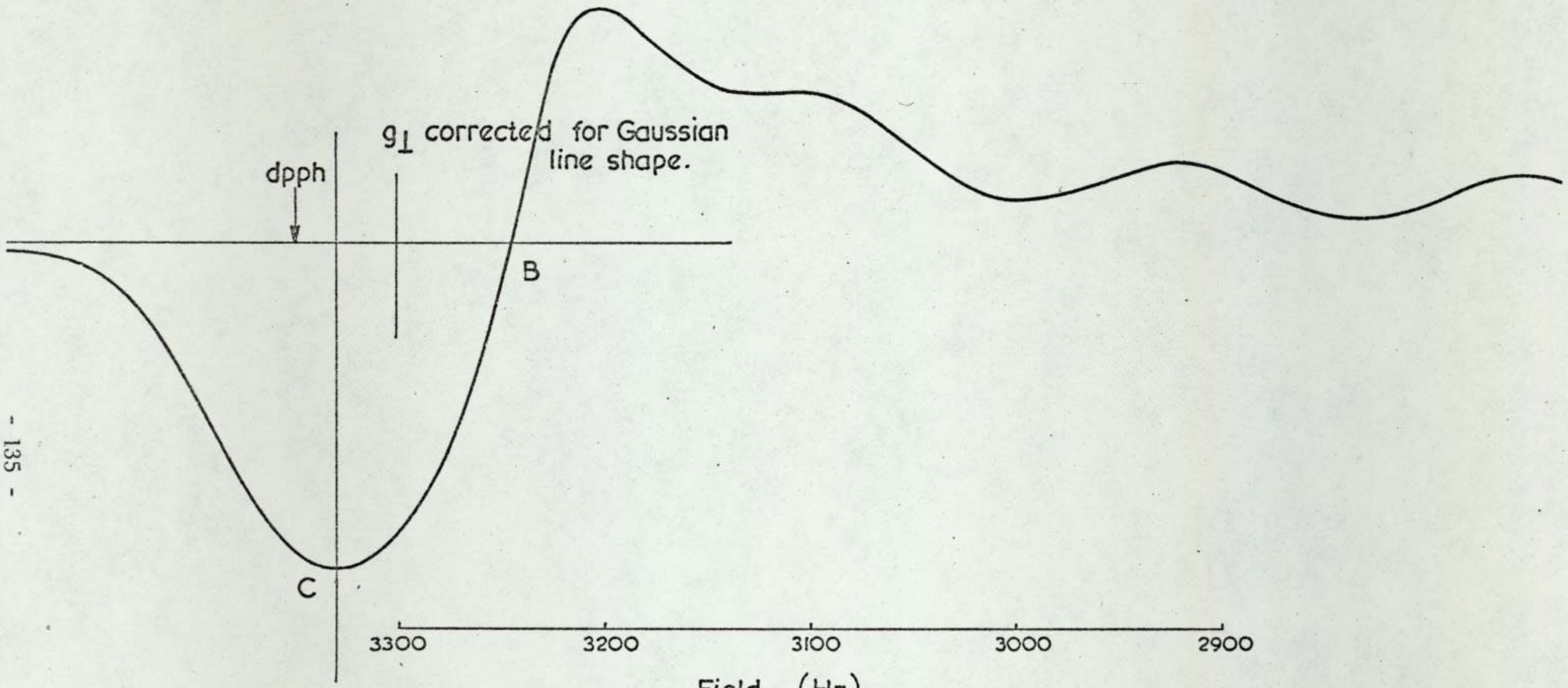
M=Cu

The cis configuration involves a lowering in the symmetry around the metal ion and hence a more complex and intense electronic spectrum would be expected. Evidence for the occurrence of a cis distorted octahedral stereochemistry has been found by Stephens[88] from single crystal X-ray diffraction work on $[Cu(bipy)_2(ONO)]NO_3$. The electronic spectrum obtained contains two bands of equal intensity at 14.6 and 9.5 kK.

A cis octahedral stereochemistry has also been assigned to $[Cu(bipy)_2(OH_2)_2]^{2+}$ [89], $[Cu(bipy)_2(ONO)]$ (NO_2), and $[Cu(bipy)_2(ONO)](ClO_4)$ due to the occurrence of two bands of equal intensity in the ranges 9.2 - 10.8kK and 14.3 - 15.6 kK. On this evidence it seems unlikely that the diperchlorato complexes considered here could have a cis octahedral stereochemistry.

McKenzie[58] studied the correlation of electronic spectra with structural characteristics for many CuN_5^{++} and CuN_6^{++} chromophores. He found that, though electronic data was useful in determining structural differences within a closely related series of complexes, it was not possible to correlate electronic data of one series of compounds with electronic and structural data of another series of complexes. Of particular interest to the present work, McKenzie found that spectra characteristic of a cis octahedral stereochemistry from Hathaway's data were shown by several of the CuN_5^{++} chromophores that he was studying. As it is not possible to form an octahedral structure for a five co-ordinate complex, the limitations of Hathaway's work are evident.

Ideally it is possible to differentiate between a cis distorted octahedral stereochemisty and a tetragonally distorted octahedral stereochemistry by examination of the esr spectrum, the former requiring three g factors and the latter requiring two. Unfortunately, both $[Cu(tripyam)_2(ClO_4)_2]$ and $[Cu(4mpdpa)_2(ClO_4)_2]$ give pseudo isotropic spectra which are therefore of little use for structural determinations. However, $[Cu(6mpdpa)_2(ClO_4)_2]$ (Fig. 4.4) gave a spectrum characteristic of two g factors[62]. This is inconsistent with a cis distorted octahedral stereochemistry and therefore the tetragonally distorted octahedral stereochemistry seems more



e.s.r. spectrum of microcrystalline $[Cu(6\,mpdpa)_2(ClO_4)_2]$

likely. The X-ray powder photographs of the diperchlorato complexes $[\mathrm{Cu(tripyam)_2(ClO_4)_2}]$, $[\mathrm{Cu(6mpdpa)_2(ClO_4)_2}]$ and $[\mathrm{Cu(4mpdpa)_2(ClO_4)_2}]$ are all similar, particularly with reference to the stronger reflections. This suggests that the stereochemistries are similar in all three cases; in particular the heavier atoms (i.e. Cu and Cl) occupy similar lattice sites in all three complexes. It is suggested, therefore, that the three complexes have a trans stereochemistry.

Hathaway has suggested that the esr spectra of copper(II) complexes are also of interest because the value of the lowest g factor indicates the ground state of the copper(II) ion in the complex. Values of $g < 2.05$ indicate a dz^2 ground state whereas $g > 2.05$ are indicative of a $dx^2 - y^2$ ground. For $[\mathrm{Cu(6mpdpa)_2(ClO_4)_2}]$ the value of g was found to be 2.02 which should therefore indicate a dz^2 ground state for the copper ion. However, it is considered that the pyridine rings are almost certainly not in the plane of the copper(II) ion. The flexibility of the ligand together with the knowledge that the perchlorate ions are only weakly co-ordinated to the metal (and therefore distant from it) suggests that a degree of interaction with the $dx^2 - y^2$ orbitals is likely. It is possible that a pure $dx^2 - y^2$ ground state is more favourable than a pure dz^2 ground state. Hickman suggested recently that a degree of hybridization is involved in obtaining the ground state wave function, all five orbitals making a contribution in some cases. It seems, therefore, that interpretation of the lowest g factor

The relationship between the complexes of copper(II) perchlorate and 5-nitro-2-pyridyldi(-2-pyridyl)amine

Scheme

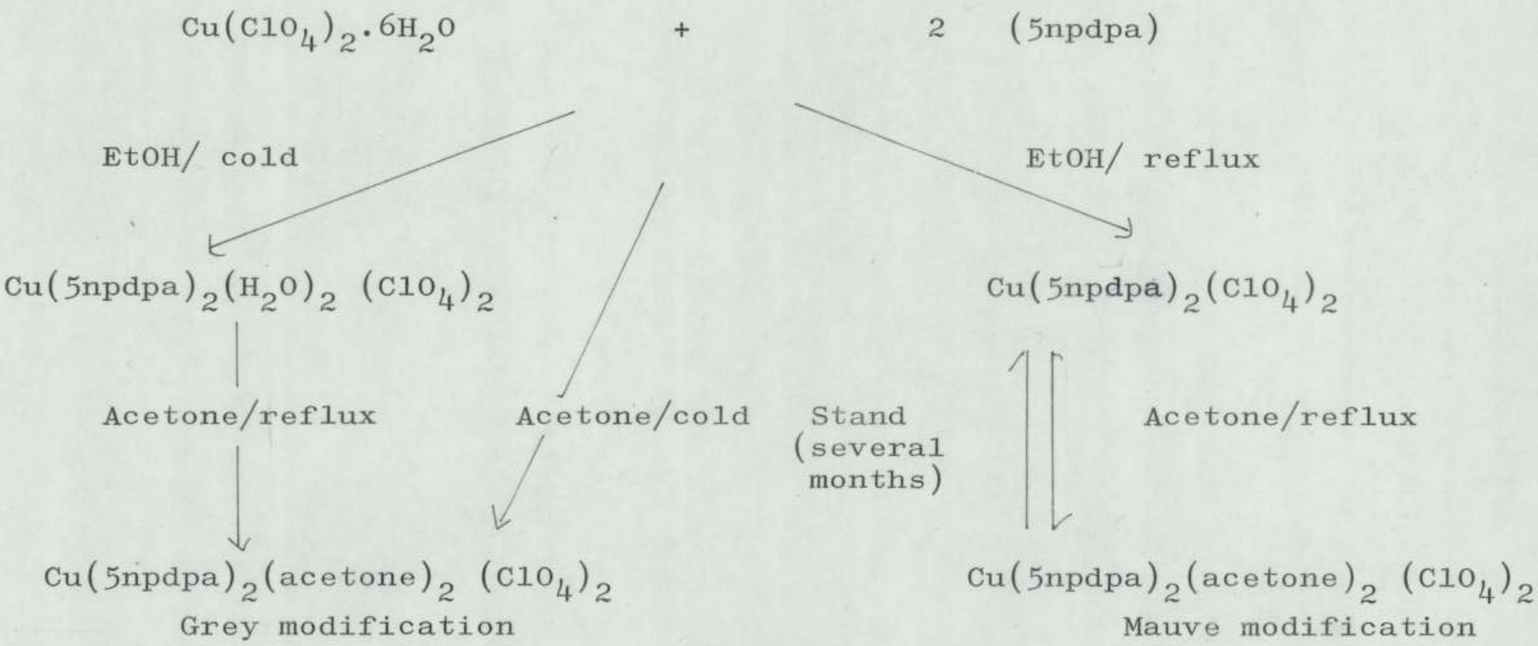
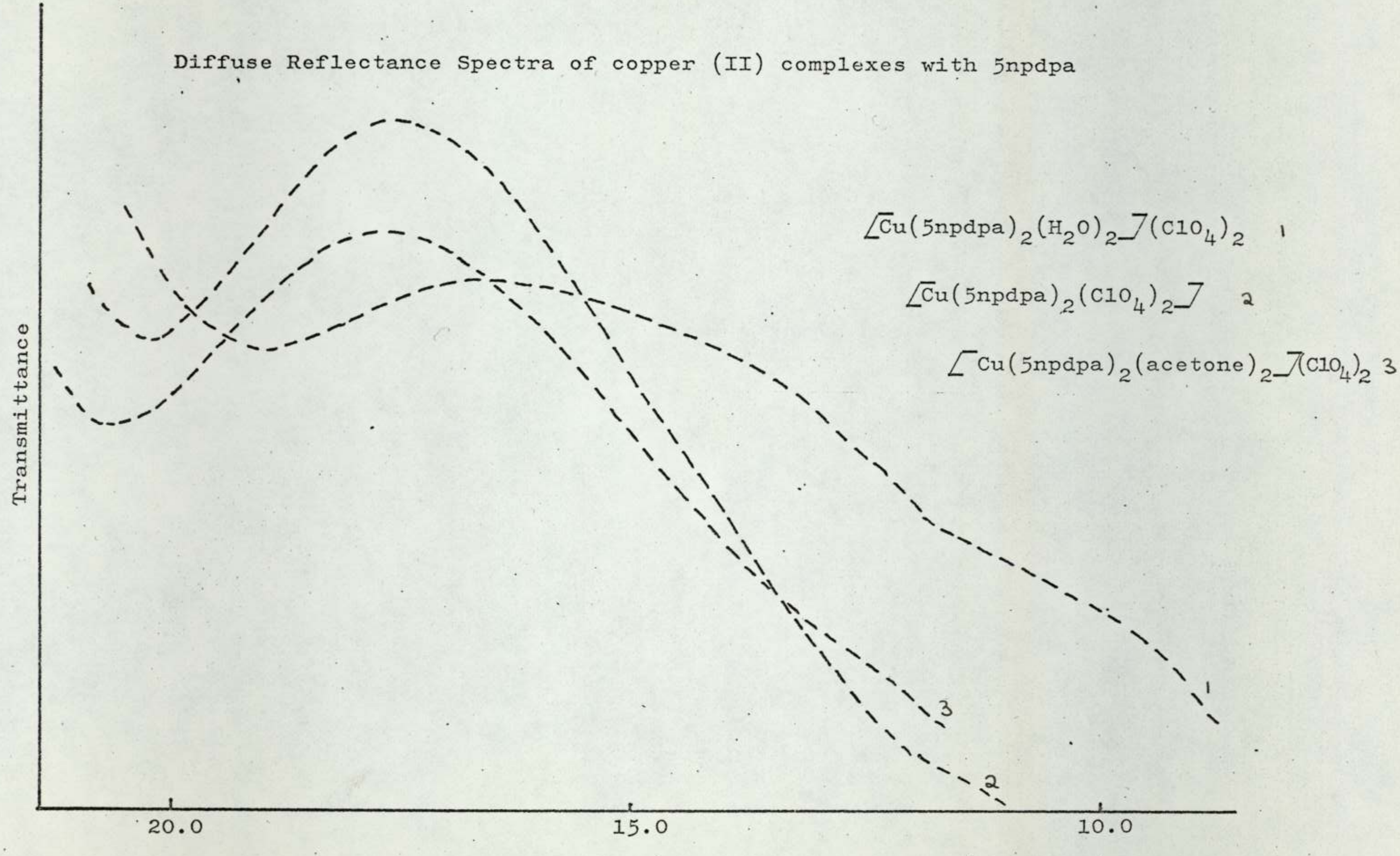


Fig. 4.5

$<$ 2.05 in terms of a pure dz^2 ground state is not valid. This has been supported recently by some of Hathaway's work[55].

4.2 Complexes with 5nitro-2-pyridyldi-2-pyridylamine

The potential of 5npdpa as a ligand with the iron(II) and nickel(II) has been discussed in Chapter 3, where it was noted that bidentate co-ordination occurred in all cases with this ligand. Complex formation with copper perchlorate was found to be consistent with these observations, there being no evidence for terdentate co-ordination in any of the complexes formed. Complex formation of 5npdpa with copper perchlorate is shown schematically in Fig. 4.5. It is evident that conditions (e.g. solvent and reaction temperature) are important in determining the complex formed, five distinct complexes having been observed. Cold ethanolic solutions of ligand and copper perchlorate resulted in the formation of a pale blue-green complex which took up atmospheric moisture within a few seconds. It was not possible to obtain any physical data for this complex due to its inherent instability. Infra red data and microanalytical data indicated the formation of the diaquo complex $[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$ on uptake of atmospheric moisture. This suggests the formation of a disolvato complex initially, the two solvent molecules being loosely held and easily lost when the complex is filtered. Atmospheric moisture then occupies the two vacant co-ordination sites. The visible spectrum of this complex is similar to that observed for $[Cu(tripyam)_2(ClO_4)_2]$



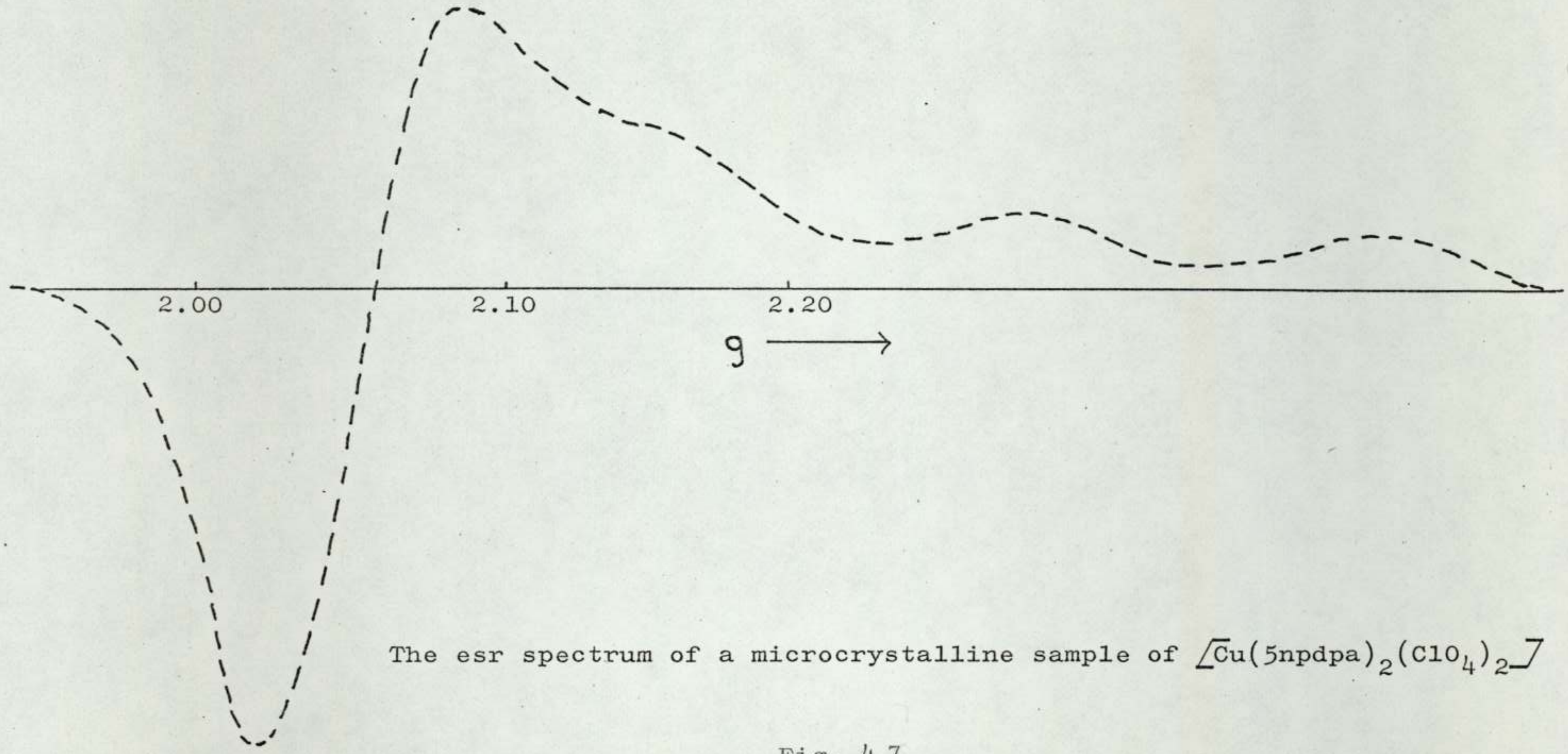
Diffuse Reflectance Spectra of copper (II) complexes with 5npdpa

Fig. 4.6

although positions of maximum absorption are more clearly defined for $[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$. It is, therefore, considered likely that similar stereochemical environments are present around the metal in both cases. Infra red spectroscopy confirms the presence of water and also the ionic nature of the perchlorate anion.

Refluxing ethanolic solutions of the ligand and copper perchlorate resulted in the formation of the diperchlorato complex $[Cu(5npdpa)_2(ClO_4)_2]$. The co-ordinated nature of the perchlorate anion was indicated by the splitting of ν_3 band at 1100 cm^{-1} (1102 cm^{-1}, 1068 cm^{-1}) in the infra red spectrum. The visible spectrum (Fig. 4.6) however, differed noticeably from those of $[Cu(tripyam)_2(ClO_4)_2]$, $[Cu(6mpdpa)_2(ClO_4)_2]$ and $[Cu(4mpdpa)_2(ClO_4)_2]$. In fact, the spectrum was similar to those observed for the terdentate complexes with the above ligands. This will be discussed more fully later.

The complexes obtained from acetone solutions presented a problem which could not be solved with the data available. As indicated in the experimental section and in Fig. 4.5 both mauve and grey modifications of the complex $[Cu(5npdpa)(acetone)_2](ClO_4)_2$ were obtained. The colour difference was still evident even after grinding for ten minutes. However, all the physical data available for those complexes (infra red, visible and esr spectra and X-ray powder photography) suggested that the complexes are in fact identical. It was noted that, after standing for several months, the mauve complex was



The esr spectrum of a microcrystalline sample of $[Cu(5npdpa)_2(ClO_4)_2]$

Fig. 4.7

turning grey. On running the infra red spectrum of the grey complex (derived from the mauve complex) it was found that it was not the grey modification of $[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$ but $[Cu(5npdpa)_2(ClO_4)_2]$, the splitting of ν_3 and the absence of the acetone bands being evident. When the infra red spectrum of the grey modification of $[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$ was re-run, there was no indication of splitting of ν_3 and acetone was shown to be present. From these observations one can suggest that the colour difference is due to slight variation in bonding of the acetone molecules to the metal ion, but is insufficient to effect noticeable changes in the physical data obtained. However, the identical values for ν(C-O) for the mauve and grey complexes are not consistent with stronger co-ordination in the grey complex. It is not possible, therefore, to resolve the problem adequately with the data available at the present time.

Physical data for complexes with 5npdpa

The infra red spectra of the diaquo and diperchlorato complexes $[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$ and $[Cu(5npdpa)_2(ClO_4)_2]$ were found to be very similar over the whole region (4000 - 250 cm^{-1}) apart from the expected differences for the water and perchlorate anion absorptions. This suggested that the structural environment around the metal or more particularly the orientation of the ligand molecules is similar in both cases. However, the similarity did not extend to the visible spectra. The visible spectrum of $[\mathrm{Cu(5npdpa)_2(H_2O)_2}](\mathrm{ClO_4})_2$ is similar to the spectra of the diperchlorato complexes of 6mpdpa, 4mpdpa and tri-2-pyridylamine whereas the spectrum of $[\mathrm{Cu(5npdpa)_2(ClO_4)_2}]$ is similar to the spectra observed for the complexes $[\mathrm{Cu(4mpdpa)_2}](\mathrm{ClO_4})_2$ and $[\mathrm{Cu(6mpdpa)_2}](\mathrm{ClO_4})_2$ in which the ligands are co-ordinated terdentate to the metal. It is possible that two different structural environments are present in the two complexes. However, it is considered more likely that the dissimilarity of the spectra is the result of differing ligand interactions with the metal ion resulting in (a) a shift in the charge transfer absorption and (b) a shift of the d-d transition. The weak nature of the interaction of the perchlorate ion with the metal ion, when the anion is co-ordinated, is indicated from the infra red spectrum. However, the interaction between the co-ordinated water molecules and the metal ion is stronger and an absorption to higher energy might be expected for the complex $[\mathrm{Cu(5npdpa)_2(H_2O)_2}](\mathrm{ClO_4})_2$. The esr spectra of $[\mathrm{Cu(5npdpa)_2(ClO_4)_2}]$ (Fig. 4.7) and $[\mathrm{Cu(5npdpa)_2(H_2O)_2}](\mathrm{ClO_4})_2$ were both indicative of a two g factor stereochemistry, although there is a degree of broadening in the spectrum of the diaquo complex, probably due to misalignment of the tetragonal axes.

It is worth noting, however, that only three complexes, $[\mathrm{Cu(6mpdpa)_2(ClO_4)_2}]$, $[\mathrm{Cu(5npdpa)_2(ClO_4)_2}]$ and $[\mathrm{Cu(5npdpa)_2(H_2O)_2}](\mathrm{ClO_4})_2$ gave esr spectra indicative of two g factors. It has been suggested earlier that the substituted ring is unco-ordinated in these

The esr spectrum of a microcrystalline sample of $[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$

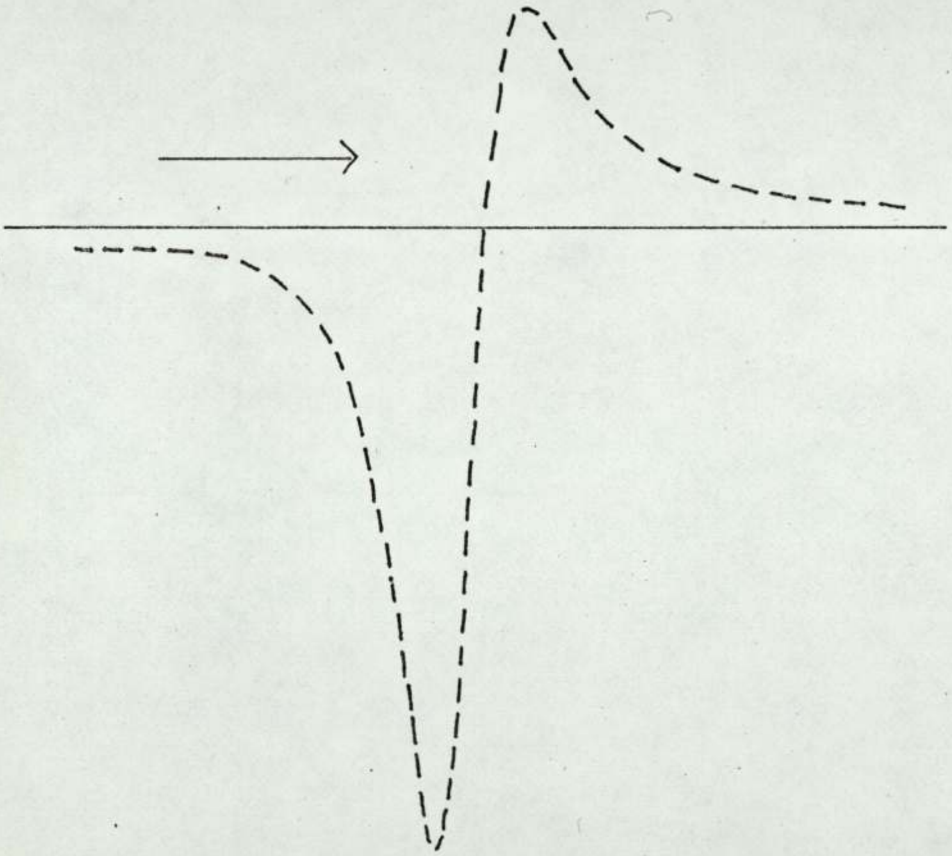


Fig. 4.8

three complexes. It is possible, therefore, that the two g factor spectra are obtained because the substituents hinder the misalignment of the molecular axes in these complexes.

The mauve and grey diacetone complexes $[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$ were found to give identical infra red spectra, X-ray powder photographs, esr spectra and visible spectra. The esr spectra were pseudo isotropic (Fig. 4.8) in nature, g average being 2.062 in both cases. It is possible that the isotropic nature could be due to a regular tetrahedral environment around the metal but other data is not consistent with this. The visible spectra indicate a tetragonally distorted octahedral structure with a strong absorption at 17,350 cm^{-1}; this strong absorption is not suggestive of a tetrahedral stereochemistry. Infra red evidence also suggests that the copper ion is six co-ordinate rather than four co-ordinate. The shift of ν(C-O) in acetone to 1690 cm^{-1} in these complexes from 1720 cm^{-1} in free acetone is consistent only with a complex where the acetone molecules are actually co-ordinated to the metal ion rather than held in the lattice. It is considered likely, therefore, that a tetragonally distorted octahedral stereochemistry is present in these complexes.

4.3 Electron spin resonance spectra of complexes with di-2-pyridylamine

The electron spin resonance work was extended to the study of the stereochemistry of copper(II) complexes with di-2-pyridylamine, which was being carried out by Pat Welham[64,67]. As indicated earlier for the complexes with tri-2-pyridylamines, the esr spectra were of little use in many cases, the electronic spectra correlating more positively with change of stereochemical environment.

$Cu(dipyam)_2(ClO_4)_2$ and $Cu(dipyam)_2(PF_6)_2$ gave electronic spectra consisting of a strong absorption at 17.9 kK and a weak absorption at about 10 kK. The esr spectra of these complexes were found to be sharply isotropic in both cases. $Zn(dipyam)_2(ClO_4)_2$ was synthesised and dilute crystals of composition $Cu(dipyam)_2(ClO_4)_2$: $Zn(dipyam)_2(ClO_4)_2$ (1:100) were grown. The X-ray powder photographs of these two Zn containing complexes and that of $Cu(dipyam)_2(ClO_4)_2$ were obtained and found to be identical. As the structure of the zinc complex is reasonably considered to be tetrahedral, the similarity of the powder photographs suggested a stereochemistry close to T_d for the copper complex. It is worth noting that the more intense reflections in the photographs will result from the relative spacings of the heavier elements, i.e. the copper and chlorine atoms (in the case of the perchlorate complex). It is evident therefore that the X-ray powder data were in agreement with the esr data. However, a regular tetrahedral environment in copper(II) complexes is most unlikely due to the Jahn Teller effect, the degeneracy of the orbitals in the excited state (^2E) being removed. The esr spectrum of $Cu(dipyam)_2(ClO_4)_2$ (Fig. 4.9) is isotropic suggesting an environment close to tetrahedral

The esr spectrum of $Cu(dipyam)_2(ClO_4)_2$

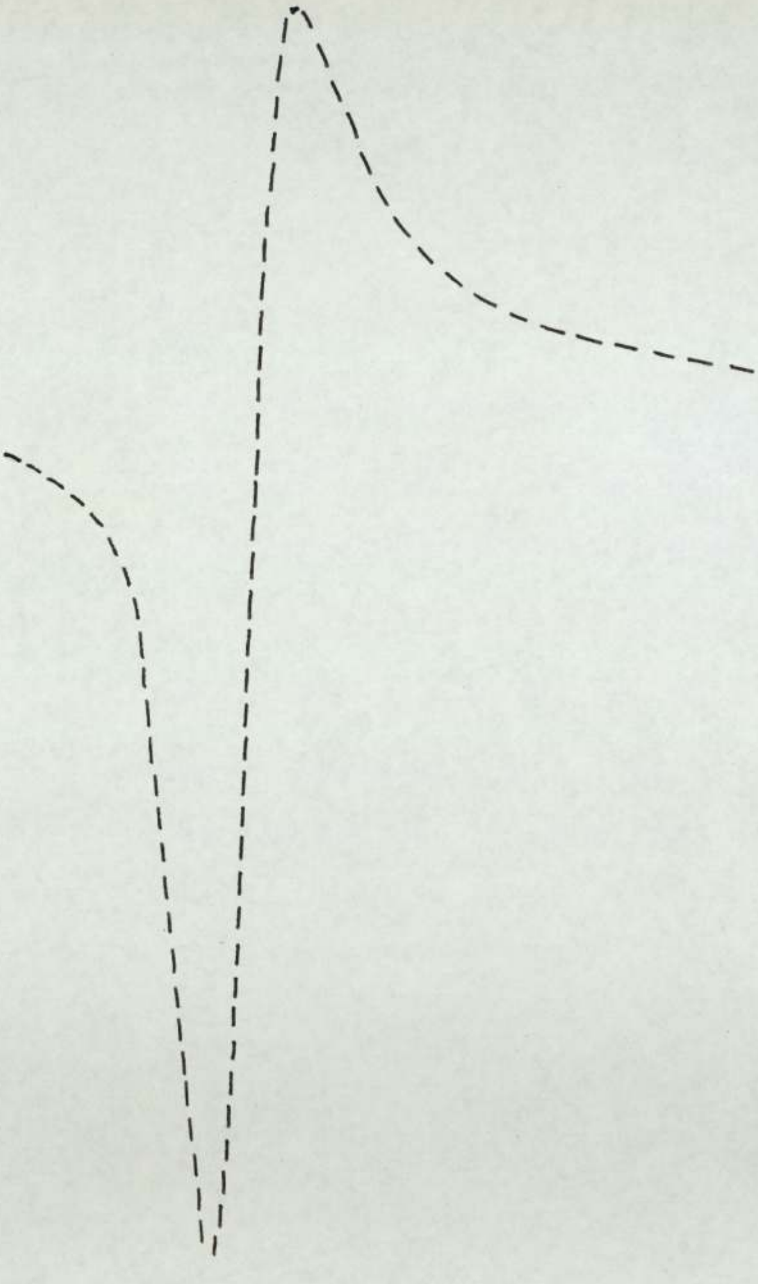


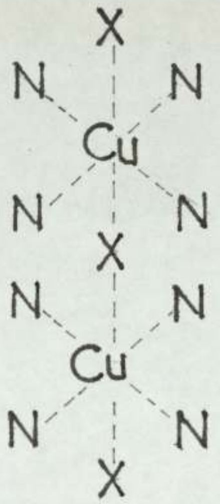
Fig. 4.9

with a dynamic Jahn Teller effect where distortion takes place in all three axial directions (equivalent in T_d symmetry). However, the esr spectrum of the dilute crystals was obtained and found to be characteristic of a two g value spectrum. This is not consistent with a tetrahedral stereochemistry or the dynamic Jahn Teller effect. It is suggested, therefore, that the stereochemistry is a distorted tetrahedral stereochemistry. A recent study of the crystal structure of $Cu(dipyam)_2(ClO_4)_2$ by Jacobson[63] confirms the distorted tetrahedral nature of the environment around the copper(II) ion. It is evident, therefore, that the isotropic spectrum obtained for $Cu(dipyam)_2(ClO_4)_2$ resulted from a misalignment of molecular axes rather than a dynamic distortion.

The diffuse reflectance spectra of $Cu(dipyam)_2(NO_3)_2$ and $Cu(dipyam)_2Br_2$ show a broad low intensity band with a maximum at 17.6 and 17.0 kK respectively. This type of spectrum is considered to be consistent with a square planar arrangement of the di-2-pyridylamine ligands about the copper(II) ion. Complexes of the form $Cu(en)_2X_2$ show spectra which contain a broad maximum in the region 19.4 to 16.7 kK and have been shown to contain an approximately square pyramidal arrangement of the ethylene diamine ligands around the copper(II) ion.

The esr spectra of $Cu(dipyam)_2Br_2$ and $Cu(dipyam)_2(NO_3)_2$ contain only one broad absorption, not consistent with the planar arrangement suggested by the electronic data. However, cooling the samples to liquid nitrogen temperature did not result in resolution of the spectra.

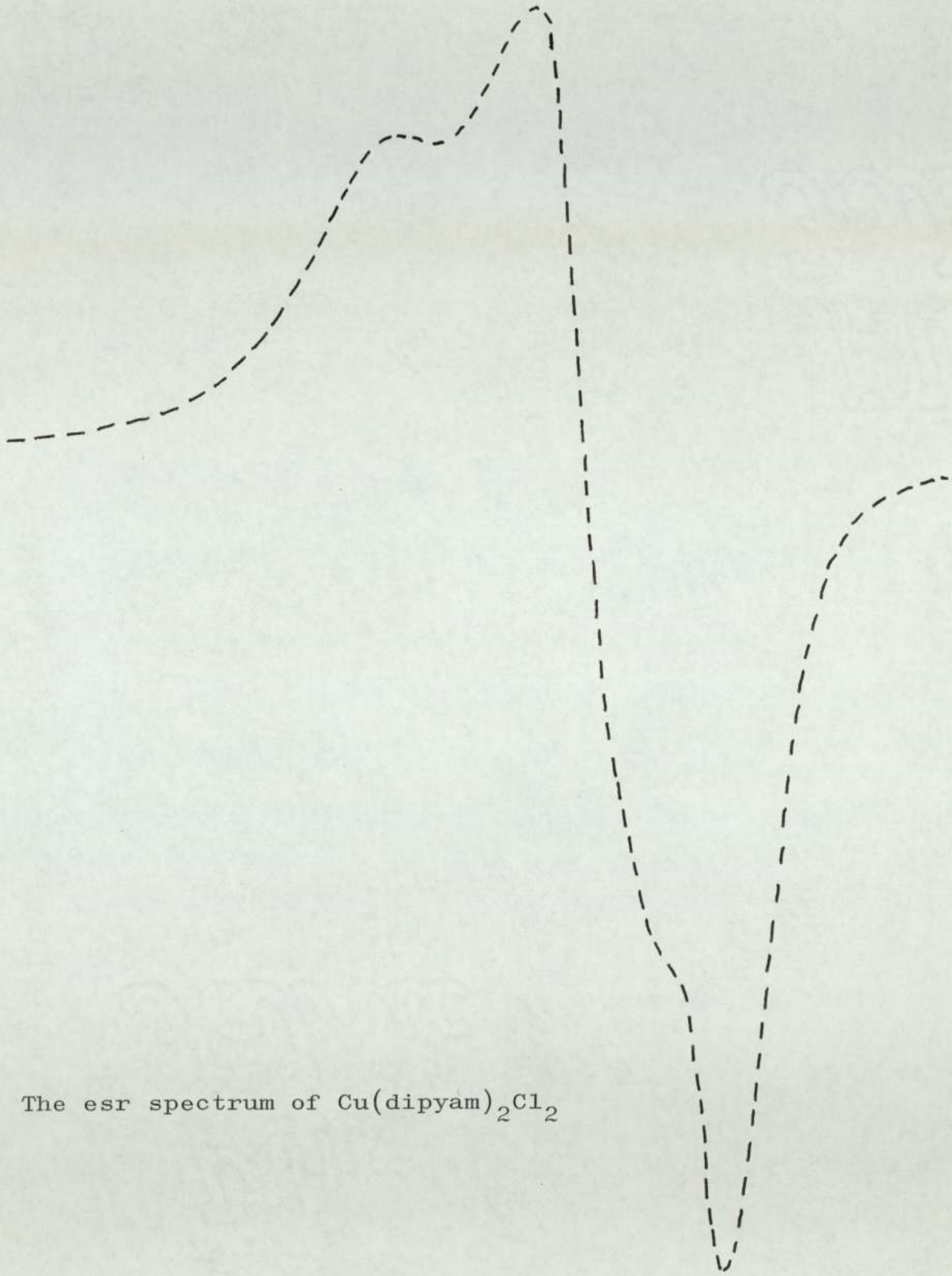
Therefore, misalignment of the molecular axes within the crystal or exchange interaction between adjacent copper ions can be suggested to explain the esr spectra. The latter is possible because, with a planar arrangement around the copper the anions occupy the axial positions and the complex could be of the form:



where X = NO_3 or Br

where interaction between adjacent paramagnets is feasible.

Esr data were more useful in the case of $Cu(dipyam)_2(Cl)_2$ (Fig. 4.10) where a three g value spectrum was indicated. The electronic spectrum consists of two intense, clearly resolved bands separated by 2.7 kK. This is intermediate between the spectra observed for a distorted trigonal bipyramidal stereochemistry and a cis distorted octahedral stereochemistry. The infra red spectrum contained a band at 346 cm^{-1} which can most convincingly be assigned to copper chlorine stretching. The high frequency of this vibration is compatible with a short copper chlorine bond in a cationic species. It has been suggested, therefore, that a trigonal bipyramidal stereochemistry is present in $[Cu(dipyam)_2Cl]Cl$,



The esr spectrum of $Cu(dipyam)_2Cl_2$

Fig. 4.10

similar to the structure of $[Cu(bipy)I]I$.

The electron spin resonance data on the remainder of the complexes was inconclusive, the spectrum of $Cu(dipyam)_2(NO_2)$ containing only a single pseudo isotropic peak. Conductivity data indicated that the complex is a 1:1 electrolyte and both electronic and esr data are similar to that for $[Cu(bipy)_2(ONO)]NO_2$ suggesting that a cis distorted octahedral stereochemistry is present.

4.4 Electron spin resonance spectra of $[Cu(py)_4(PF_6)_2]$ and $[Cu(py)_4(ClO_4)_2]$

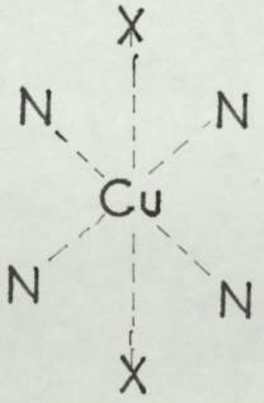
The weak co-ordinating nature of the perchlorate anion is well understood but many complexes containing partially co-ordinated perchlorate have been prepared since 1961. However, the hexafluoro-phosphate anion is a weaker ligand and is commonly used to precipitate cationic species when a non-co-ordinating anion is required. Attempts have been made using several ligands to isolate a complex involving a partially co-ordinated hexafluoro-phosphate anion. Tri-2-pyridylamine, which readily forms a diperchlorate complex with copper(II) perchlorate was used but it was only possible to isolate the ionic hexafluoro-phosphate complex. It was then decided to use 5npdpa which, as shown earlier, only functions as a bidentate ligand, no terdentate complexes having been isolated. Unfortunately, on complex formation, infra red data indicated the presence of a diaquo species, the hexafluoro-phosphate anions remaining ionic.

However, when pyridine was used as a ligand, S. Bell[65,66] isolated a tetra pyridine complex $[Cu(py)_4(PF_6)_2]$, the infra red spectrum suggesting co-ordination of the anion. Co-ordination is likely to take place via one of the fluorine atoms bonding to the metal ion, resulting in a lowering of the anion symmetry from O_h to C_{4v}. This results in the removal of some of the degeneracies and an alteration of the selection rules. The vibrational modes in O_h symmetry alter and span the irreducible representations $4A_1 + 2B_1 + B_2 + 4E$ of C_{4v} of which A_1 and E modes are active in the infra red, (fig. 4.11)

The spectrum obtained for $Cu(py)_4(PF_6)_2$ is in agreement with the above predictions except that further splitting of the E modes derived from ν_3 and ν_4 has occurred. This could be attributed to low symmetry of the lattice site within the crystal. The intensity of the A_1 mode at 742 cm^{-1} and the appearance of the A_1 mode at 572 cm^{-1} which is expected to be of weak intensity in the infra red, together with clear splitting of ν_3 suggest a relatively strong perturbation of the PF_6^- group as would occur if it were semi-co-ordinated to copper(II).

Comparison of the electronic and esr data of the perchlorate and hexafluorate complexes indicates a tetragonal environment in both cases, a stronger interaction being evident in the case of the perchlorate complex. The esr spectra consisted of two g factors in both cases, with a significant difference in g_{11} for the two complexes. The differing ligand potential of perchlorate and hexafluoro-phosphate anions is known and therefore the interaction of the anions with the copper(II) ion is likely to differ. The difference in g_{11} is a reflection of the differing interactions of the anions in the axial direction.

In conclusion, complexes with substituted tri-2-pyridylamine ligands co-ordinated terdentate to the transition metal ions are considered to have a tetragonally distorted octahedral stereochemistry on the basis of the electronic spectra. On consideration of all the data available it is likely that complexes in which the ligands are co-ordinated bidentate to the metal ion possess a trans stereochemistry. However, the complexity of the visible spectra of the bidentate complexes with 6mpdpa and 4mpdpa is not completely understood. The visible spectra of the diacetone complexes with 5npdpa suggest a tetragonal environment around the metal. Therefore all the complexes are considered to be of the form:-



X = py
solvent or
anion

Complexes with di-2-pyridylamine provided a wider variety of stereochemistries, electronic spectra again being the most informative. However, where reasonable esr spectra were obtained for $\mathrm{Cu(dipyam)_2Cl_2}$ and $[\mathrm{Cu(dipyam)_2(ClO_4)_2/Zn(dipyam)_2(ClO_4)_2}]$ the data were useful.

Overall, the results obtained from the esr spectra were disappointing. However, for $[\mathrm{Cu(py)_4(ClO_4)_2}]$ and $[\mathrm{Cu(py)_4(PF_6)_2}]$ esr data played an important role in demonstrating differing interactions between the axial ligands in the two complexes and similar interactions in the plane of the copper(II) ion.

Attempts have been made to illustrate the use of the various physical techniques in the determination of stereochemical environments around copper(II) ions. However, it was also evident that the applicability of the techniques, particularly, esr, is limited. More detailed stereochemical analysis would require the spectroscopic analysis of single crystals of the complexes. In many of the complexes discussed in this chapter, this would not be possible because the solids are powdery rather than crystalline. When the overall size and shape of the molecules is considered the inability to form crystals is easy to understand.

CHAPTER V

A study of the complexes of Cobalt (II) perchlorate with substituted tri-2-pyridylamines

The spectroscopic analysis of the iron(II), nickel(II), and copper(II) complexes with substituted tri-2-pyridylamines forms the basis of this work. However, earlier studies of cobalt(II) complexes with tri-2-pyridylamine (tripyam) prompted the preparation and preliminary investigation of cobalt (II) complexes with substituted tri-2-pyridylamines.

$[Co(tripyam)_2](ClO_4)_2$ was studied initially by Kulasingam, who observed a room temperature effective magnetic moment of 4.8 B.M. When compared with a moment of 5.2 B.M. for $[Co(tripyam)_2(NO_3)_2]$ he considered the value of 4.8 B.M. to be low for a high spin cobalt (II) complex, the micro symmetry of which was considered to be high. As a result, he postulated the presence of a spin doublet-quartet equilibrium. Subsequent work by Barnard, who studied the variation of magnetic susceptibility with temperature, confirmed the postulation. The effective magnetic moment of $[Co(tripyam)_2](ClO_4)_2$ at 77^oK was found to be 2.1 B.M. Barnard also studied the variation of magnetic properties of $Co(tripyam)_2(PF_6)_2$ with temperature and observed little change of moment on lowering the temperature, the Curie-Weiss Law being obeyed. The difference in behaviour between the perchlorate and hexafluorophosphate complexes was attributed to a lattice effect. It was suggested that the anion dependence was attributable to the different abilities of the two lattices to accommodate the predicted Jahn Teller distortion in the low spin isomer.

Prior to Barnard's work, necessary requisites for the formation of low spin cobalt(II) complexes with chelating heterocycle ligands were (a) distortion from octahedral symmetry or (b) extensive conjugation. However, X-ray powder photography indicated isomorphism between Co(tripyam)$_2$(ClO$_4$)$_2$ and Fe(tripyam)$_2$(ClO$_4$)$_2$ which had previously been shown to be almost exactly octahedral from the Mössbauer spectrum (ΔEq = 0.00).

Similarly extensive conjugation was not possible because the ligand does not contain an α di-imine function and the chelating rings in the complex are not planar; indeed, when the base functions as a terdentate ligand, the lone pair orbital of the amino nitrogen atom must be almost orthogonal to pyridine ring π systems.

Complexes of Cobalt (II) perchlorate with 6mpdpa, 5mpdpa, 4mpdpa and 5npdpa were synthesised (Chapter I) and the magnetic properties studied to determine whether earlier observations with $[Co(tripyam)_2](ClO_4)_2$ are common to the tri-2-pyridylamine series of ligands.

As mentioned in Chapter III, Δ values with respect to nickel(II) for 4mpdpa and 5mpdpa are slightly greater than for tri-2-pyridylamine. In the event of a spin equilibrium being present the increase in Δ is likely to increase the population of the low spin state. The properties of the cobalt complexes were examined in an attempt to determine whether such an equilibrium existed in all cases.

Table 5.1

Physical data for Cobalt (II) perchlorate complexes with substituted tri-2-pyridylamines

	Electronic Spectra		
5npdpa	20,650	19,000	9,700
5mpdpa	22,050	18,800	11,700
6mpdpa	22,900	18,850	10,800

Data not available for $Co(4mpdpa)_2(ClO_4)_2$

Table 5.2

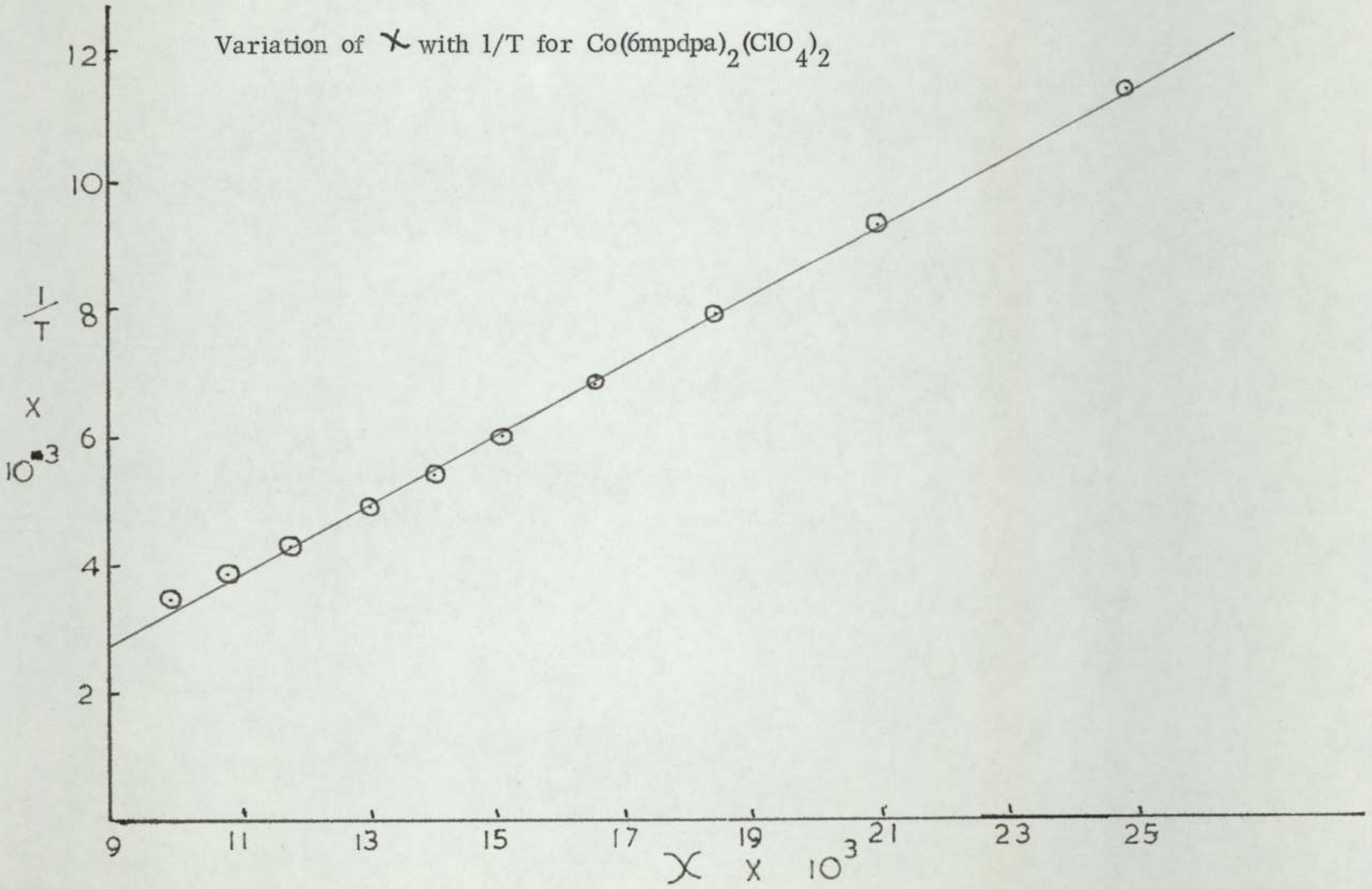
Variation of Magnetic Susceptibility Data with temperature for $Co(6mpdpa)_2(ClO_4)_2$

Temp ^oK	$1/T \times 10^3$	$\chi \times 10^6$	$1/\chi$	μ eff B.M.
293	3.448	9935	100.7	4.85
263	3.802	10844	92.25	4.80
234.7	4.261	11834	84.51	4.73
205.5	4.866	13074	76.51	4.67
186.5	5.361	14064	71.13	4.60
167	5.988	15134	66.10	4.51
148	6.757	16624	60.17	4.45
128	7.813	18484	54.10	4.38
108.5	9.215	21054	47.51	4.29
89	11.24	24954	40.07	4.23

Table 5.3

Variation of Magnetic Susceptibility Data with temperature for $Co(5mpdpa)_2(ClO_4)_2$

Temp ^oK	$1/T \times 10^3$	$\chi \times 10^6$	$1/\chi$	μ eff B.M.
293	3.448	7169	1395	4.12
273	3.663	7498	1333	4.06
243.5	4.107	8271	1210	4.03
215	4.651	9270	1077	4.01
192	5.208	10032	9971	3.98
176.5	5.666	11244	8900	3.99
157	6.369	12344	8103	3.95
138	7.246	14094	7100	3.96
118	8.475	15424	6485	3.83
99	10.10	17744	5636	3.76



Variation of χ with 1/T for $Co(6mpdpa)_2(ClO_4)_2$

Fig. 5.1

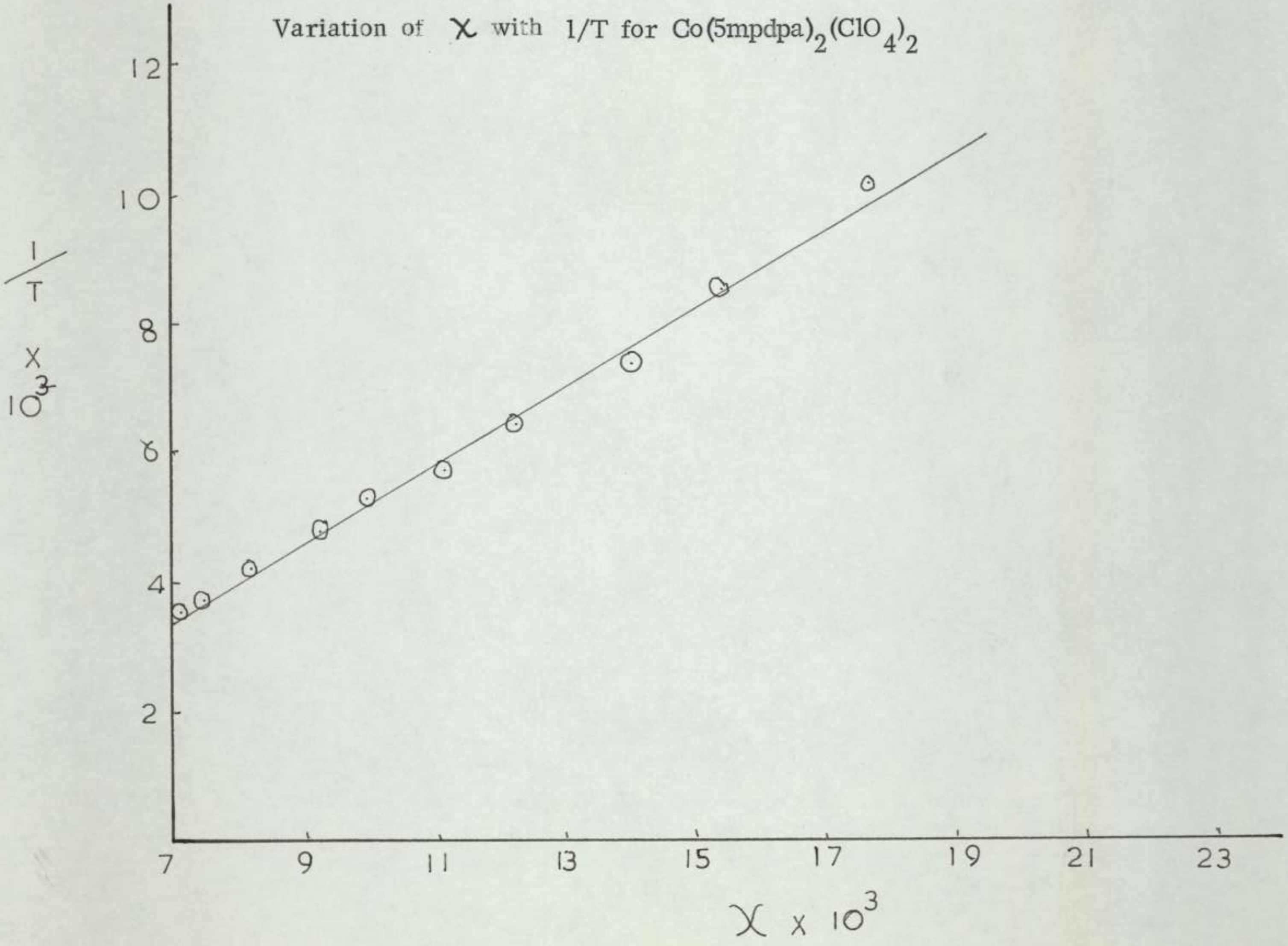

Variation of χ with 1/T for $Co(5mpdpa)_2(ClO_4)_2$

Fig. 5.2

For $[Co(6mpdpa)_2](ClO_4)_2$ the room temperature magnetic moment was found to be 4.85 B.M. However, the form of the ligand is such that on terdentate co-ordination of the ligand to the metal ion, a considerable strain is present in the complex due to non-bonded interactions between the metal ion and the methyl substituent. It is, therefore, possible to explain the low moment in terms of a reduction in the orbital contribution to the magnetic moment. Alternatively, the value of 4.85 B.M. is consistent with a tetrahedral environment around the metal ion. The tendency for 6mpdpa to co-ordinate bidentate rather than terdentate to the metal ion was apparent from studying the nickel and copper complexes. However, the electronic spectrum of $[Co(6mpdpa)_2](ClO_4)_2$ contains the longest wavelength band at 10,800 cm^{-1} with strong absorption at 22,900 cm^{-1}. This is not consistent with tetrahedral environment but suggests an octahedral environment around the metal ion. A study of the variation of μ eff. with temperature revealed a value μ eff = 4.23 B.M. at 89^oK, not consistent with the occurrence of spin doublet quartet equilibrium.

The distortion experienced in $[Co(6mpdpa)_2](ClO_4)_2$ is not present in complexes with 5mpdpa and 4mpdpa. However, the room temperature moments were found to be 4.12 and 4.8 B.M. respectively. The visible spectrum of $Co(5mpdpa)_2(ClO_4)_2$, like that of $Co(6mpdpa)_2(ClO_4)_2$, is not consistent with a tetrahedral environment but suggests an octahedral environment around the metal ion. It was not possible to obtain the spectrum of $Co(4mpdpa)_2(ClO_4)_2$ due to an instrumental breakdown.

The low value for μ eff for $Co(5mpdpa)_2(ClO_4)_2$ prompted the low temperature study of this complex. However, the results obtained were not consistent with the occurrence of spin cross-over in the temperature range examined.

Plots of $1/\chi$ versus temperature are close to straight lines for both $Co(6mpdpa)_2(ClO_4)_2$ and $Co(5mpdpa)_2(ClO_4)_2$ and therefore deviations from the Curie Weiss Law are small for both complexes. It is evident, therefore, that within the temperature range studied, there is no evidence to support the occurrence of spin isomerism in the complexes examined. However, it is possible that examination over an extended temperature range, in particular below $77^{o}K$, might be more informative. Unfortunately, it was not possible to study all complexes at low temperatures due to the limited time available for using the low temperature Gouy balance.

However, the data obtained suggests that $Co(6mpdpa)_2(ClO_4)_2$ and $Co(5mpdpa)_2(ClO_4)_2$ may exist in two isomeric forms, a low spin and a high spin form. The complexes examined may contain a mixture of the two isomers, the high spin form predominating in both cases. For $Co(6mpdpa)_2(ClO_4)_2$ an explanation in terms of a reduction in a spin-orbit coupling is feasible. However, the noticeably lower moment observed for $Co(5mpdpa)_2(ClO_4)_2$, where the distortion from O_h symmetry is considered to be small, cannot be explained reasonably on these grounds. Hence, the presence of two isomeric forms in the complexes is suggested.

Evidence in support of the mixture of isomers is not complete, but examination of the far infra red spectra of $Fe(5mpdpa)_2(ClO_4)_2$, $Co(5mpdpa)_2(ClO_4)_2$ and $Ni(5mpdpa)_2(ClO_4)_2$ resulted in the following observations. Bands present in the iron complex (low spin) at 482 cm^{-1} are present in the spectrum of the cobalt complex but not the nickel complex (high spin). Similarly, the nickel and cobalt complexes contain bands at 525 and 524 cm^{-1} respectively which do not occur in the spectrum of the iron complex. It is possible that the bands noted are characteristic of the spin state of the metal ion. X-ray powder photography indicated the isomorphous nature of the three complexes. Therefore, the spectroscopic differences cannot be explained on structural factors. However, a more detailed spectroscopic analysis, together with assignment of bands considered, is required before more positive suggestions are postulated.

The diffuse reflectance spectra of the complexes are all consistent with an octahedral environment around the metal ion, although definite assignments are not possible. However, the following tentative assignments are made:

$$\left.\begin{array}{ll} {}^4T_{2g}\,(F) \longleftarrow {}^4T_{1g}(F) & 9.70\text{ kK} \\ {}^4A_{2g}\,(F) \longleftarrow {}^4T_{1g}(F) & 19.00\text{ kK} \\ {}^4T_{1g}\,(P) \longleftarrow {}^4T_{1g}(F) & 20.65\text{ kK} \end{array}\right) \quad \text{for } Co(5npdpa)_2(ClO_4)_2$$

However, it is possible that the band at 19,00 kK is due to spin forbidden transition, the third band in the electronic spectrum being concealed by charge transfer and ligand absorptions above 21.00 kk.

Finally, the variation of magnetic susceptibility with temperature was examined for a diluted sample of Co(tripyam)$_2$(ClO$_4$)$_2$ (diluted with Zn(tripyam)$_2$(ClO$_4$)$_2$, which is known to be isomorphous with Co(tripyam)$_2$(ClO$_4$)$_2$) in an attempt to determine whether a change of lattice environment effected the occurrence of spin isomerism. However, it was noted that the spin cross-over was not effected by the lattice change involved.

In conclusion, it has been demonstrated that spin isomerism over the temperature range studied is not common to the tri-2-pyridylamine series of ligands but characteristic of Co(tripyam)$_2$(ClO$_4$)$_2$ only. It is suggested that deviations of μ eff from the expected high spin value for Co(II) may be due to the presence of Co(II) in two distinct forms, high spin and low spin. A more detailed spectroscopic analysis, in particular far infra red spectroscopy, is suggested.

APPENDIX

An exploratory investigation of the use of several physical techniques for structural investigations of silver (II) complexes

The chemistry of copper(II) perchlorate with pyridylamine type ligands afforded a wide variety of structural arrangements around the copper(II) ion and a series of isomers were reported. The interesting nature of the chemistry of the d^9 copper(II) ion prompted an extension of the work to study the preparation and morphology of complexes of Ag(II). The ability of certain pyridyl ligands to stabilize silver has been reported but detailed studies of the complexes formed are limited. Both tetrahedral and octahedral stereochemistries have been reported for Ag(II) complexes and the nature of tri-2-pyridylamine ligands, in particular their ability to co-ordinate both bidentate and terdentate, prompted the study of complexes.

Two methods were used in an attempt to prepare complexes of Ag(II) and 2-pyridylamines.

1. Oxidation of Ag(I) complexes by potassium persulphate. A saturated solution of potassium persulphate was added to an aqueous slurry of the Ag(I) complex. The mixture was left to stand for twelve hours, no reaction taking place.

2. Anodic oxidation of the Ag(I) complex in a divided cell. The cell consisted of platinum electrodes, a 12 volt battery supplying a current of 3-4 amps for several hours (up to 6). Oxidation did not take place.

Both methods failed to produce any Ag(II) complexes with -2-pyridylamine ligands.

Unfortunately, it is impossible to explain the observations satisfactorily with the data available. 2,2 bi-pyridyl 1,10 phenanthroline and pyridine are capable of stabilizing Ag(II). The basicity of pyridine is greater than that for di-2-pyridylamine and tri-2-pyridylamine whereas 1,10 phenanthroline and 2,2' bipyridyl contain α di-imine functions allowing greater conjugation between the pyridine rings than in pyridylamines. Alternatively, the conformation of the complexes may be the critical factor in determining whether a ligand stabilizes Ag(II) or not. A greater understanding of the stabilization of Ag(II) complexes may be gained by studying series of ligands. For instance, electronic effects may be studied by introducing substituents into pyridine and 2,2' bipyridyl and noting effects on stability of Ag(II) complexes, if any.

It is known that $Cu(py)_4X_2$ deviates greatly from planarity and it is expected that $Ag(py)_4X_2$ will be distorted. However, the increase in size of Ag(II) over copper(II) must reduce the distortion to a degree whereby there is sufficient delocalization between the pyridine rings and the metal ion for $Ag(py)_4X_2$ to be stabilized.

Unfortunately, the form of pyridylamine ligands prevents an appreciable overlap of $p\pi - d\pi$ electrons and consequently the silver(II) ion is not stabilized by them.

The sparsity of physical data and detailed structural analyses for Ag(II) complexes prompted the exploratory study of the potential of physical techniques for stereochemical investigation of Ag(II) complexes. Complexes of the form

$Ag(L)_2X_2$ where L = bipy or phen and X = ClO_4^- or NO_3^- were synthesised and the following physical techniques utilized:

(a) Infra Red Spectroscopy

(b) Electronic Spectroscopy

(c) Electron Spin Resonance Spectroscopy

(d) X-ray Powder Photography

(a) Infra Red Spectroscopy

The infra red spectra were of good quality although there was evidence of scattering. Vibrations due to the pyridine type rings were observable and the perchlorate bands at 1100 cm^{-1} for $Ag(L)_2(ClO_4)_2$ were both sharp and indicative of an ionic perchlorate anion.

However, it was not possible to locate absorptions indicative of No_3^- due to overlap with pyridine ring absorption bands.

(b) Electronic Spectroscopy

The electronic spectra did not contain bands below 20,000 cm^{-1}; however, absorption did occur to high wave number ($>$ 20,000 cm^{-1}) but it is considered that bands in this region are of charge transfer origin. It was evident, therefore, that electronic spectroscopy would be of limited use for studying Ag(II) complexes.

(c) Electron Spin Resonance Spectroscopy

Electron spin resonance spectra were all indicative of a two g factor stereochemistry consistent with axial assymmetry around the metal ion. It has been suggested that the stereochemistry for these complexes is planar, the electron spin resonance spectra being consistent with this stereochemistry. However, the esr data are not conclusive. $Cu(bipy)_2(ClO_4)_2$ givesan esr spectrum indicative of two g factors but is considered to be non-planar with a 5 co-ordinate stereochemistry. Therefore, in spite of the form of the esr spectra, the planarty of the Ag(II) complexes is not proven.

(d) X-ray Powder Photography

The X-ray powder photographs were obtained for the four silver complexes and their copper analogues. It was evident from the photographs that the silver and copper complexes are not isomorphous. However, this does not necessarily indicate a near planar arrangement around the silver ion.

In conclusion, the physical techniques discussed in this chapter are of limited use for structural studies of silver (II) complexes. However, it is possible that X-ray diffraction and single crystal esr studies would be more informative. These were unfortunately beyond the scope of this work.

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