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THE COORDINATION BEHAVIOUR OF SOME CHELATING LIGANDS CONTAINING NON- OR WEAKLY CONJUGATED 2-PYRIDYL-GROUPS

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CONTENTS

ABBREVIATIONS

2-ampy	2-aminopyridine
bipy	2,2′-bipyridyl
dipyam	di-(2-pyridyl)amine
DPEA	bis(2-pyridylethyl)amine
dpm	di-(2-pyridyl)methane
DPMA	bis(2-pyridylmethyl)amine
dpds	di-(2-pyridyl)disulphide
dppa	di-(2-pyridyl)phenylamine
dpe	1,2-di-(2′-pyridyl)ethane

dpso	di-(2-pyridyl)sulphoxide
dps	di-(2-pyridyl)sulphide
en	ethylenediamine
phen	1,10-phenanthroline
py	pyridine
pyCO COpy	di-(2-pyridyl)ketone
tripyam	tri-(2-pyridyl)amine

A. INTRODUCTION

Organic ligands based on pyridine derivatives continue to be of importance in the development of coordination chemistry. The familiar 2,2′-bipyridyl and the closely related molecule 1,10-phenanthroline are probably the most versatile ligands known, forming as they do a wide variety of complexes with all classes of element in a wide variety of oxidation states. The chemistry of these ligands, together with that of 2,2′,2″-terpyridyl has been comprehensively reviewed[1]. It is the purpose of this article to summarise the increasing number of reports dealing with other ligands which may be bi- or ter-dentate by virtue of the presence in the ligand molecules of two or more 2-pyridyl groups separated by a bridging group.

To keep the length of the article within reasonable limits and to maintain some degree of cohesion the ligands to be considered are those of the general class $(2\text{-py})_2X$ (Fig. 1), where X may be (a) a single atom bridge, *e.g.* $>$NH, $>$NPh, $>$N(2-py), $>$C=O, $>$S, $>SO_2$, $>CH_2$, (b) a diatomic bridge, *e.g.* –CO · CO–, $>$C = C$<$, –N = N–, or rarely (c) a triatomic bridge, *e.g.* –NHCSNH–, $-CH_2 \cdot NH\ CH_2-$.

B. THE STEREOCHEMICAL REQUIREMENTS OF THE COORDINATED LIGANDS

2,2′-Bipyridyl and 1,10-phenanthroline form five-membered chelate rings which are most usually, but not invariably[1], planar. One consequence of this fact is that, with the bizarre exception of the bis(1,10-phenanthroline)palladium(II) cation[1], no *trans*-bis complexes have been satisfactorily characterised[2,3,4]. This is undoubtedly due to unfavourable steric factors which lead to interference between the 6 and 6′ protons of the two bipyridyl molecules in the *trans* complex. The introduction of a monatomic bridging group X such as $>$NH, $>CH_2$ or $>$S between the two pyridine rings (Fig. 1) leads to the formation of a flexible six-membered chelate ring which need not be, and in a strain free conformation will not be, planar; thus *cis–trans* isomerism for bis complexes should be possible. Molecular models indicate that when such ligands coordinate a first row dipositive transition metal ion in a strain free conformation they cause remarkably little distortion of the octahedral angles subtended by the metal in a six coordinate complex. Indeed for the case where X = >N(2-py), *i.e.* tri-(2-pyridyl)amine-(tripyam), the Mössbauer spectrum of the low spin iron(II) complex $[Fe(tripyam)_2](ClO_4)_2$ indicates that the microsymmetry about the metal ion is accurately cubic ($\Delta E_Q = 0.00$ mm · sec^{-1})[5,6].

For the bidentate ligands where X = >NH, >CH_2, >S *etc.* coordination in a strain free conformation may not be favourable if π bonding involving the π* obitals of the pyridyl-group is important for a given complex, since, in the case of an octahedral complex, the rings will be inclined at an angle approaching 45° to the σ_h planes of the octahedron. Also if the group X possesses a lone pair of electrons *e.g.* >NH or >S, conjugation involving these electrons will be less easy when the ligand coordinates such as to cause the minimum distortion of the bond angles subtended by the metal. Thus the detailed stereochemistry of the coordinated ligands is likely to be determined by the interplay of a number of factors, the chelate rings being sufficiently flexible to accomodate to a particular set of requirements. Di-2-pyridylketone (p. 303) is likely to be an exception since there is reason to believe that a planar six membered chelate ring may be favoured[7]; however, even in this case there is probably more flexibility in the chelate rings than some authors have allowed[8]. In this connection it is relevant to point out that the potentially aromatic 2,2'-dipyridyliminato-group in bis(2,2'-dipyridyliminato)palladium(II) is distorted to a non-planar structure whereas the palladium(II) ion is in a strictly square planar environment with normal palladium–nitrogen bond lengths (0.202 nm)[9], thus strong conjugation within the ligand need not be an overriding factor in determining the stereochemistry of the complex.

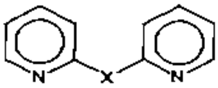

Fig 1.

When X (Fig. 1) is a di- or tri-atomic group a different situation may arise since the ligand itself may exist in isomeric forms, *e.g.* *cis*- and *trans*-2,2'-diazopyridine and the bridging group may coordinate or undergo rearrangement in the presence of the metal. It is thus more difficult to define general patterns of behaviour.

Unfortunately this section must of necessity be speculative since, with the exception of the 2,2'-dipyridyliminato complex mentioned above, structural investigations are lacking. It is to be hoped that this will be remedied in the near future.

C. SPECTROSCOPIC AND OTHER PHYSICAL CHARACTERISTICS OF THE LIGANDS

The vibrational spectra of the general class of ligands $(2\text{-py})_2X$ have not been the subject of a detailed investigation but it is well established that small shifts of frequency for the ν(CN), γ(CH) and φ(CC) vibrations of the 2-pyridyl groups which occur in the presence of metal ions are usefully diagnostic of coordination[10,11,12]. The high local symmetry of terdentate tri-(2-pyridyl)amine is well illustrated by the comparatively simple IR spectrum of the terdentate as compared with that of the bidentate base[13]. The high symmetry of the terdentate ligand (C_{3v}) is also demonstrated by the comparatively simple ^{1}H NMR spectrum, *e.g.* in Tl(tripyam) Br_3 the 100 MHz ^{1}H NMR trace approximates to a first order spectrum[14].

The UV spectra of the pyridylamines have been the subject of a number of papers[10,15,16,17], the earliest being that by Spiers and Wibaut[15]. In the case of 2-aminopyridine[17] and of di-2-pyridylamine[10] the presence of copper(II) ions caused only slight modifications to the ligand spectra the most marked change being the splitting of the 310-nm band of di-2-pyridylamine[10]; protonation has a similar effect[16]. There is as yet no evidence that studies in this region of the spectrum will be valuable in elucidating the nature of the metal complexes although confirmation that 2-aminopyridine coordinates to copper(II) in the amino form was obtained[17].

There is little information on the relative basicities of the more simple ligands $(2\text{-py})_2X$ and such data as are available are once more relevant to the pyridylamines. A crude comparison of basicities[18] for 2-aminopyridine, di-2-pyridylamine and tri-2-pyridylamine gave the order of basic strength as: dipyam > 2-ampy > tripyam. pK_1-Values are now available for 2-aminopyridine (6.86)[19] and di-2-pyridylamine (6 99)[20]. There is some evidence from pK_a studies of the 3,3′- and 4,4′-di-pyridylamines[20] and also from methylation and protonation studies with (2-pyridyl)amines, phosphines and arsines that there is some conjugative effect in the case of the amines but not when the central atom is P or As. Thus, for example, it is only possible to methylate two pyridyl-groups of $N(2\text{-py})_3$ but all three may be methylated for $P(2\text{-py})_3$ and $As(2\text{-py})_3$[21], this point may have some bearing on the fact that tri-(2-pyridyl)amine functions more often as a bidentate than as a terdentate ligand (page 301).

D. THE COORDINATION COMPOUNDS OF $(2\text{-py})_2X$ WHERE X IS A MONATOMIC BRIDGING GROUP

(*i*) *Coordination compounds of the 2-pyridylamines and related ligands*

A 2-pyridylamine is represented in Fig. 2, thus the parent compound may be considered to be 2-aminopyridine ($R_1 = R_2 = H$). This is a compound of

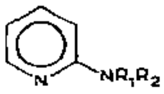

Fig 2.

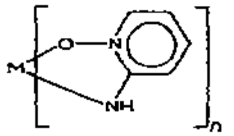

Fig 3. The inner complex formed by deprotonation of ligated 2-aminopyridine-*N*-oxide.

fundamental importance in pyridine chemistry: yet comparatively little use has been made of the base as a ligand. Although it is not strictly an example of $(2\text{-py})_2X$, it is considered that a brief survey of the complexes formed by the parent 2-pyridylamine is in order at this point.

Generally the pyridine nitrogen atom of 2-aminopyridine coordinates to the metal ion although it has been claimed that with silver(I) it is possible to achieve some replacement of the amino-group protons, *e.g.* $[(2\text{-py–NH} \cdot \text{Ag})_2\text{Ag}]_n(\text{NO}_3)_n$[22]; it is also known that 2-aminopyridine-*N*-oxide functions as a monodentate ligand[23], but deprotonation affords inner complexes of the type illustrated in Fig. 3 with copper(II) ($n = 2$) and iron(III) ($n = 3$)[24]. Platinum(II) complexes containing 2-aminopyridine have been extensively examined by Russian workers. The majority of complexes reported are mixed ligand compounds[25,26,27] although a tetrakis complex has also been prepared[27,28]. The greater thermal stability of *trans*-$[\text{Pt(2-ampy)}_2\text{Cl}_2]$ compared with *trans*-$[\text{Pt(py)}_2\text{Cl}_2]$ has been attributed to hydrogen bonding of the non-coordinated amino-group to the chloride ligands[29]. The *trans* effect of 2-aminopyridine is estimated to be similar to that of ammonia[30].

There have been reports that 2-aminopyridine may function as a bidentate ligand, thus it is suggested that in the complex $[\text{Pt(NH}_2\text{OH)}_2\text{(2-ampy)}]\,[\text{PtCl}_4]$ the 2-amino-pyridine chelates in the imino form[26]; this appears unlikely and the compound may reward re-investigation Compounds of stoichiometry $\text{Fe(2-ampy)}_3 \cdot \text{Fe}_2\text{(CO)}_8$[31] and (2-ampy)PtCl_2[32] have also been reported, the latter is probably dimeric.

The compounds of 2-aminopyridine with copper(II) nitrate and perchlorate are dimeric, of the form $[\text{(2-ampy)}_2\text{Cu(OR)}_2\text{Cu(2-ampy)}_2]\text{X}_2$ ($X = \text{NO}_3$ or ClO_4, $R = \text{H,Me, Et}$)[17] and have sub-normal effective magnetic moments at ambient temperatures[33]. Evidence for the formation of a 1:1 complex of copper(II) chloride with the base in ethanolic solution was obtained and also one tetrakis complex was isolated *viz.* $[\text{Cu(2-ampy)}_4]\text{Cl}_2$. There have been occasional reports of the formation of 2-aminopyridine complexes with other elements, *e.g.* with Me_3Au[34], TiBr_4[35], SeCl_4[36], TeCl_4[37], VCl_4[38] and WBr_5[39]. In the latter case $[\text{W(2-ampy)}_5\ \text{Br}_3]\text{Br}_2$ was claimed[39].

Di-2-pyridylamine ($X = \text{NH}$, Fig. 1) is one of the most extensively investigated ligands in this class. It is available relatively cheaply* and this has

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* Reilly Tar Distillation Corp , Indianapolis, U S A.

encouraged the study of the metal complexes of the base. It finds some measure of use as an anti-oxidant for lubricating oils[40], and in at least one case a metal complex is utilised.

Although the ligand is potentially tribasic, no evidence is available to show that the >NH group possesses basic properties. The base generally chelates to the metal ion but one of the earliest reports of the use of this ligand claims that it may catenate *viz.* $Br_3Au \cdot (2py)NH(2py) \cdot AuBr_3$; stoichiometry was the only evidence for this formulation but the suggestion is not unreasonable[41]. More recently Kirschner[42] drew attention to the possible use of the base as a ligand by reporting a number of simple preparations; also brief mention was made of a spectroscopic study of copper(II) and nickel(II) complexes[43].

At the present time complexes containing the ligand in 1:1, 2:1 and 3:1 ratio with the metal ion are known. Iron(II)[5,44] cobalt(II),[11] nickel(II)[5,45,46], rhodium(III)[47] and iridium(III)[47] all form *tris* complexes whereas copper(II)[10] and zinc(II)[10] do not. To date no *tris* di-2-pyridylamine complex of chromium(III) has been prepared[48] possibly due to the insolubility of the *bis* complex under some preparative conditions and the tendency to form alkoxo- and hydroxo-bridged dimers under other experimental conditions[48]. Values of Δ (10 Dq) of 11,000 cm^{-1} with respect to cobalt(II)[11] or 11,100 cm^{-1} with respect to nickel(II)[46] have been estimated. Using the rule of average environment for the complex *cis*-$[Cr(dipyam)_2Cl_2]Cl$ a value[48] of 19,800 cm^{-1} for Δ with respect to chromium(III) has been obtained. The fact that the iron(II) complex is spin free[5,44] is consistent with these values since it has been suggested that only ligands with values of Δ towards nickel, in excess of the range 11,630–11,700 cm^{-1} should stabilise the $^1A_{1g}$ term of iron(II) as the ground state in octahedral symmetry[49]; the complex $Fe(dipyam)_2(CN)_2$ is however diamagnetic[44]. There is some difference of opinion as to which point group is appropriate to the discussion of the electronic spectra of the *tris* (di-2-pyridylamine) complexes, thus O_h was selected for $[Co(dipyam_3)]^{2+}$ whereas assymmetry in the $^5T_{2g} \rightarrow {}^5E_g$ band in the spectrum of $[Fe(dipyam)_3]^{2+}$ led to the selection[44] of D_3. An alternative point of view for the iron(II) case considers that the microsymmetry around iron(II) may be close to O_h and that the Jahn–Teller effect removes the degeneracy of the ^5E_g level[5]; both sets of workers claim an adequate interpretation of experimental data.

A range of *bis* (di-2-pyridylamine) complexes are known. No case of *cis–trans* isomerism has been reported but individual representatives of each of these stereochemical arrangements have been claimed. Structural assignments have relied heavily on IR spectroscopy thus $Fe(dipyam)_2(CN)_2$[44] and $[Cr(dipyam)_2Cl_2]Cl$[48] are believed to be *cis* complexes whereas $[Rh(dipyam)_2X_2]X$ (X = Cl, Br, I)[47], $Ni(dipyam)_2X_2$ (X = Cl, Br)[45,46] and $Fe(dipyam)_2X_2$ (X = Cl, Br)[5,44] are considered to be *trans* complexes. The rhodium(III) complexes are of interest since the stereochemistry, if *trans*, could imply that catalytic amounts of rhodium(I) are involved in the preparative procedure[50]. There is no evidence that di-2-

pyridylamine will stabilise rhodium(I); treatment of $[Rh(dipyam)_2X_2]X$ ($X = Cl$, Br, I) with sodium borohydride under hydrogen and subsequent treatment with sodium perchlorate affords the paramagnetic material $Rh(dipyam)H_n \cdot ClO_4$ ($n = 1$ or 2) which has to date defied complete characterisation[51].

The deep blue bis(di-2-pyridylamine)copper(II) perchlorate shows interesting behaviour[10]. The complex readily forms a diacetone adduct and dissolves in polar solvents such as dimethylformamide and water to give solutions the spectra of which suggest the presence of copper(II) ions in a pseudo D_{4h} environment. However, solutions in nitromethane absorb strongly and there is evidence of an equilibrium involving at least one non-planar species[10]. Di-2-pyridylsulphide (dps) forms a similar blue complex with copper(II) perchlorate and Driver and Walker[52] suggest a non planar arrangement of ligands in the solid state for both $[Cu(dps)_2]\,(ClO_4)_2$ and $[Cu(dipyam)_2]\,(ClO_4)_2$. Some further support for this view is obtained from the fact that the X-ray powder photographs of $[Cu(dipyam)_2](ClO_4)_2$ and $[Zn(dipyam)_2]\,(ClO_4)_2$ are identical and the ESR spectrum of the microcrystalline copper complex appears isotropic; however, the major $d \rightarrow d$ band appears at a surprisingly high frequency (17,900 cm^{-1}) if the complex is genuinely tetrahedral[10a]. The above chemistry is in contrast to that of pale green $[Cu(dipyam)_2](NO_3)_2$ which is considered to be planar with very weakly interacting nitrate groups Other complexes of copper(II) to be prepared are of the form $Cu(dipyam)_2X_2$ ($X = Cl^{-}$ [42], Br^{-} [10], I^{-} [10], NO_2^{-} [10a]) and $[Cu(dipyam)_2Y](ClO_4)$ ($Y = I^-$, NCS^-)[10]. The variety of stereochemical behaviour is greater[10a] than at first thought[10] and includes the possibilities of *cis*-octahedral, square based pyramidal and trigonal bipyramidal structures. A crystalline green complex now known to be $Cu_2(dipyam)_3(HF_2)_2(PF_6)_2$ has been prepared in which the copper ions appear to be in a distorted octahedral environment involving two chelating and one catenating dipyridylamine together with HF_2^{-} [10a].

Complexes with a metal-to-ligand ratio of 1.1 are freely formed by di-2-pyridylamine, *e.g.* with iron(II) ($Fe(dipyam)X_2$, $X = Cl$, Br)[44], cobalt(II) ($Co(dipyam)X_2$, $X = Cl$[42], Br[11]), nickel(II) ($Ni(dipyam)X_2$, $X = Cl$, Br, I)[45] copper(II) ($Cu(dipyam)Cl_2$)[42] and zinc(II) ($Zn(dipyam)X_2$, $X = CN$,[54] CH_3COO (Ref. 54), Cl[54], Br[53], I[10]. When X is a halogen the electronic spectra[11 44,45], magnetic susceptibilities[44] and far infra-red spectra[53] indicate pseudo tetrahedral stereochemistry for all complexes except for $Ni(dipyam)Cl_2$ and $Cu(dipyam)Cl_2$. The reaction of di-2-pyridylamine with copper(II) perchlorate in slightly alkaline media affords $[Cu(dipyam)OH]ClO_4$ which is considered to be a hydroxo-bridged dimer[10]. A study[55] of the thermal stabilities of a closely related series of cobalt(II) complexes has produced the following stability order: $Co(dipyam)Cl_2 > Co(bipy)Cl_2 > Co(py)_2Cl_2$; the observed order was related to the sterically more favourable six membered chelate ring and the greater basicity of the pyridylamine ligand. Similar thermal studies have been made with some zinc complexes where the observed stability order was: $Zn(dipyam)Cl_2 > Zn(dipyam)\,(OOC \cdot CH_3)_2 >$

$Zn(dipyam)(CN)_2$, which was said to be inversely proportional to the strength with which the anion X^- bridges the zinc ions in ZnX_2[54].

The comparative ease with which coordinated di-2-pyridylamine may be deprotonated was noted for $[Pd(dipyam)_2](ClO_4)_2$[56] but Black[57] was unable to remove protons from the coordinated base in the complex said to be $[Ni(dipyam)_2(H_2O)_2]Cl_2$. Hurley and Robinson[46] have however managed to deprotonate the ligand when coordinated to nickel(II); thus $[Ni(dipyam)_2Cl_2]$ was deprotonated to $[Ni(dipyam\text{-}H)_2]$ which is a three dimensional polymeric complex with involvement of the third nitrogen atom. Deprotonation of $[Ni(dipyam)_2Cl_2]$ at 185° in naphthalene gives $[Ni_3(dipyam\text{-}H)_4Cl_2]$ the structure of which is believed to contain nickel(II) ions in both planar and tetrahedral environments (Fig. 4). Utke and Sanderson[58] have reacted calcium with di-2-pyridylamine in liquid ammonia and have isolated solids of the composition $Ca(dipyam)(NH_3)_{0\cdot 33}$ and $Ca(dipyam)_2(NH_3)_{0\cdot 33}$; the possibility that di-2-pyridylamine is present as $(dipyam)^-$ exists.

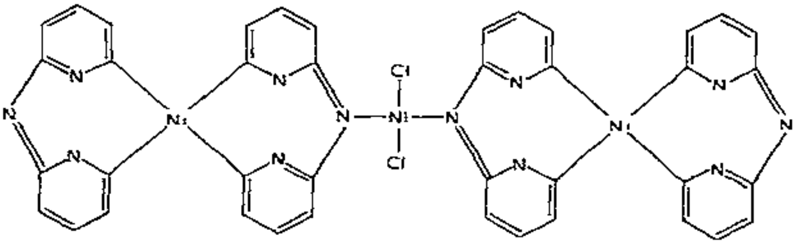

Fig 4. Postulated structure for $[Ni_3(dipyam\text{-}H)_4Cl_2]$ (after Ref. 46)

There has to date been little quantitative discussion of the mode of interaction between ligands such as di-2-pyridylamine and the metal ion A crude attempt[59] has been made to establish a spectrochemical series of "π-acidity" for some chelating ligands by comparing the IR spectra of $[Mo(chelate)(CO)_4]$, to the extent that this is meaningful (the method rests upon an alarming number of assumptions) the following order was obtained: di-2-pyridylamine < 2,2′-bipyridyl ~ 1,10-phenanthroline.

Reports of complexes of di-2-pyridylamine with non-transition metals are sparce. Apart from the compounds with zinc(II) the only representatives seem to be $[Sn(SCH_2 \cdot CH_2S)_2(dipyam)]$[60], $[Ph_2SnX_2(dipyam)]$ (X = Cl, Br)[61], $[Et_2SnX_2(dipyam)]$ (X = Cl, Br)[61] and $[TlCl_3(dipyam)]_n$[62] (see p. 302).

Black[57] has synthesised a range of ligands $(py)_2X$, where X = >NH, >S, $>SO_2$(dpso), $>CH_2$(dpm), which he has used to prepare a limited number of complexes with cobalt(II), nickel(II) and copper(II). The following order of stability for complexes of a given ion with the above ligands was inferred from the properties of the compounds isolated, together with the observed failure of some ligands to afford certain complexes: dipyam > dps > dpm > dpso. Black relates the order to three factors: (*a*) the angle of twist of the pyridine rings with respect to the metal ion in a strain free structure, (*b*) the distance between the ring nitrogen atoms when the ligand has a planar conformation and (*c*) the possibility of the lone pairs of electrons entering into delocalisation in the cases of $(2\text{-py})_2NH$ and $(2\text{-py})_2S$. Whilst all these factors are indeed likely to affect the stability of the complexes, the number and variety of compounds examined by Black was limited and it is still premature for positive conclusions to be reached.

Block and Simkin[63,64] have attempted to prepare coordination polymers containing di-2-pyridylamine. A metarial having the composition $[Zn_2(\text{dipyam})(RPO_3)_2]_n$ was obtained by the reaction of zinc aryl and alkyl phosphites with the base. The compound with $R = Ph$ has been examined in some detail but the thermal stability is not good[63].

Tri-2-pyridylamine is virtually unique amongst terdentate ligands in that with ions comparable in size to Fe(II) ($^1A_{1g}$) it will cause virtually no distortion of the octahedral angles in a six coordinate complex[5]. The spectra of the bis(tri-2-pyridylamine) complexes with the dipositive ions of the first transition series may therefore be discussed using O_h symmetry (the true symmetry of such cations is D_{3d})[65]. There are however more examples of complexes in which the ligand is bidentate than in which it is terdentate. This is superficially surprising since the ligand field strength of the terdentate ligand is greater ($\Delta = 12{,}820\ \text{cm}^{-1}$ w r.t. Ni(II))[66] than that estimated ($11{,}000\ \text{cm}^{-1}$ w.r.t. Ni(II)) for the bidentate base; also entropy considerations might be expected to favour terdentate coordination. However the conformation of the base is rigidly constrained to C_{3v} symmetry in the terdentate complex whereas the conformational entropy must be greater when the ligand is bidentate. Also it is known from methylation and protonation studies that the basicity of the third pyridyl group is lowered when the other rings are quaternised[21] (p. 296); consequently coordination of a metal ion with two rings may possibly lower the basicity of the third pyridyl-nitrogen atom with the result that it may be thermodynamically favourable for a solvent molecule or an anion to preferentially coordinate. Some support for this view is obtained from the fact that introduction of the electron withdrawing nitro-group to one ring affords a ligand which is invariably bidentate[57]. It is unlikely that the corresponding arsine and phosphine would show identical behaviour but an additional complication may be the tendency of As and P to act as ligand atoms.

A number of isomeric pairs of compounds which differ only in the coordination behaviour of tri-2-pyridylamine are known, *e g.* $[Cu(\text{tripyam})_2](ClO_4)_2$ and $[Cu(\text{tripyam})_2(ClO_4)_2]$[13]; $[Cu(\text{tripyam})_2I](ClO_4)$ and $[Cu(\text{tripyam})_2I \cdot ClO_4]$[13]; $[Co(\text{tripyam})_2](NO_3)_2$ and $[Co(\text{tripyam})_2(NO_3)_2]$[68]. In each case the complex in which the base is terdentate will convert on standing to the other isomer.

The first pair of isomers have been most closely examined. The yellow green perchlorato-complex, $[Cu(\text{tripyam})_2(ClO_4)_2]$, has similar spectroscopic properties to the corresponding compound of di-(2-pyridyl)phenylamine (dppa), for example both compounds give intensely absorbing solutions in nitromethane (*cf.* Cu(dipyam)$_2$(ClO$_4$)$_2$, p. 299). In solvents such as water the perchlorate groups are not coordinated and a di-solvato species with a planar arrangement of nitrogen ligands is considered to be present. A similar structure is envisaged for the solid state with the difference that perchlorato-groups replace the solvent molecules. The perchlorate groups should probably be regarded as being "semi-coordinated"[69]. When the electronic spectrum of the blue isomer, [Cu(tripyam)$_2$](ClO$_4$)$_2$, is examined under high resolution it is apparent that at least two $d \rightarrow d$ transitions are present; yet at ambient temperature the ESR spectrum shows an isotropic g-value[65]. It has been suggested[65] that a dynamic Jahn–Teller effect is operative; this accounts for the optical and room temperature ESR spectra together with the observed[13] isomorphism with [Ni(tripyam)$_2$](ClO$_4$)$_2$ but the postulate is not yet proven.

A series of papers describing the reaction of the ligand with various salts of Mn(II)[66], Fe(II)[5], Co(II)[13,66,68*], Ni(II)[13,66,68*], Cu(II)[13,66,68], Zn(II)[56], Rh(III)[66], Ir(III)[66] and Sn(IV)[61] have been published. The products in which the base is terdentate are of the general types [M(tripyam)$_2$]X$_2$, [M(tripyam)$_2$][MX$_4$] (Mösshauer spectroscopy has provided an elegant confirmation of [Fe(tripyam)$_2$][FeCl$_4$][5]) or [M(tripyam)X$_3$] (X is an anionic group); [Mo(tripyam)(CO)$_3$][13] is also known General types of compounds in which the ligand is bidentate are [Cu(tripyam)$_2$][CuX$_4$] (X = Cl, Br)[66], [M(tripyam)$_2$X$_2$][66,68] and [M(tripyam)X$_2$][66,68]. The spectroscopic properties of these compounds are discussed in the references cited. The compound of tri-2-pyridylamine with copper(II) thiocyanate may be prepared in three isomeric forms[68,70]. These have been suggested to be the three possible thiocyanate linkage isomers[70] *viz* [Cu(tripyam)(NCS)$_2$], [Cu(tripyam)(NCS)(SCN)] and [Cu(tripyam)(SCN)$_2$] This identification is subject to the normal reservations when solid state IR spectra are the major supporting experimental evidence.

In the presence of a coordinating solvent terdentate tri-2-pyridylamine may on occasion become bidentate allowing a solvent molecule to coordinate A well defined example occurs in thallium chemistry where [Tl(tripyam)X$_3$] (X = Cl, Br) reacts with DMF to give [Tl(tripyam)X$_3$DMF] which presumably has a *cis*-arrangement of halide ligands. The complexes Tl(dipyam)Cl$_3$ (p. 300), Tl(chelate)Cl$_3$ (chelate = bipy, phen) also gives DMF complexes [Tl(chelate)Cl$_3$ ·DMF]; the similarity of far IR spectra with that of [Tl(tripyam)Cl$_3$ · DMF] suggest that the chloride groups are also *cis* in these cases[14].

Recent attempts have been made to synthesise compounds of chromium(III) with di- and tri-2-pyridylamine. The only compounds to be satisfactorily characterised are *cis*-[Cr(dipyam)$_2$Cl$_2$]Cl and [Cr(tripyam)Cl$_3$][48,65]. Estimates of the ligand field splitting parameter Δ have been made using Jørgensen's "Rule of Average Environment"[71], *i.e.* tri-2-pyridylamine = 18,800 cm^{-1} (see also p. 298). The

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[*] Note added in proof the existence of a spin equilibrium ($^4T \rightleftharpoons {}^2E$) was recently established for [Co(tripyam)$_2$](ClO$_4$)$_2$[91].

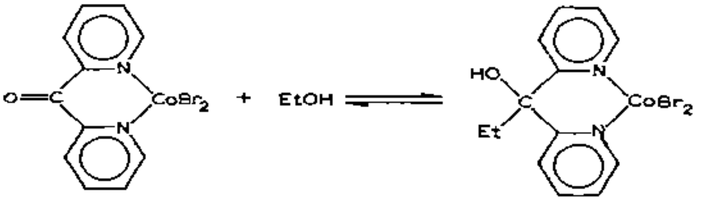
spectrochemical series with respect to chromium(III) is therefore: $F^- < H_2O < NCS^- <$ py ~ tripyam < dipyam $< NH_3 <$ en $< CN^-$; this is in contrast to that with respect to nickel(II): $F^- < H_2O < NH_3 \sim$ py < dipyam ~ en < tripyam. It is considered that the lower position of tri-2-pyridylamine in the chromium series reflects the smaller size of Cr^{III} and the consequent weaker σ-bonding of the rigid terdentate tri-2-pyridylamine with Cr^{III} than with the larger M^{II} ions. The geometry of di-2-pyridylamine allows that base to accomodate more easily to changes in size of the central ion π-Bonding considerations are not believed to be predominant.

Compounds of di-(2-pyridyl)phenylamine have been briefly considered mainly as steric analogues of corresponding compounds of bidentate tri-2-pyridylamine[13,68]. $[Co(dppa)Cl_2]$ was noted to show three apparent cobalt–chlorine stretching frequencies; this was attributed to the Fermi resonance of the symmetric stretching mode with the first overtone of a lower frequency fundamental[72].

(ii) *Di-2-pyridylketone*

To date only three reports have appeared in which the base has been used as a ligand[7,73,74]. It is likely that the coordination chemistry of di-2-pyridylketone will prove to be of some complexity.

The base may potentially coordinate through both nitrogen atoms (N, N) or through one pyridyl-group together with the carbonyl group (N, O) It was at one time believed that the two modes of coordination had been characterised with some compounds of copper(II)[73], thus the pairs of compounds $[Cu(pyCOpy)_2(ClO_4)_2]$ (N, N) and $[Cu(pyCOpy)_2(H_2O)_2](ClO_4)_2$ (N, O) together with $[Cu(pyCOpy)Cl_2]$ (N, N) and $[Cu(pyCOpy)Cl_2 \ EtOH]$ (N, O) were considered to constitute examples. The above pairs of compounds may be readily interconverted and the observations were rationalised in terms of the lower basicity of the carbonyl group compared to the 2-pyridyl-group which would in turn increase the affinity of copper(II) for solvent molecules when the ligand was coordinated N, O. However, difficulty was experienced in assignment of ν(CO) in the supposed N,O-complexes. The compound $CoBr_2(pyCOpy)$ (green) will react with ethanol to afford $CoBr_2(pyCOpy)EtOH$ (blue)[8]. Both compounds are shown by their spectroscopic and magnetic properties to be pseudo tetrahedral complexes of cobalt(II) and Osborne considered this reaction as possibly:



and also suggested a similar scheme to provide an alternative explanation for the copper(II) data. An alternative view of the cobalt(II) case is to consider the ethanol to be hydrogen bonded to the free pyridyl group[8], however it seems unacceptable that the ligand field strength of an N,O-complex should be greater than that of the N,N-case.

Other workers[7] have also re-interpreted the copper(II) data in terms of hydration or ethanolation of the carbonyl group and Morgan[74] has independently reached similar conclusions. Both Morgan[74] and Feller and Robson[7] report a wider range of complexes including some with Mn, Fe, Co, Ni, Pd and Pt, but much work remains to be done. There is little positive information on the stereochemistry of compounds such as $M(pyCOpy)_2Cl_2$ which are considered *cis* by Morgan but not by others; $[Rh(pyCOpy)_2Cl_2]^+$ is said to be *trans* in $[Rh(pyCOpy)_2Cl_2][Rh(pyCOpy)Cl_4]$[75] but this is on the basis of IR spectroscopy. The reversible hydration process is not well understood and the ligand field parameters of the ligand are unknown.

E. THE COORDINATION COMPOUNDS OF $(2\text{-}py)_2X$ WHERE X IS A DIATOMIC BRIDGING GROUP

The choice of ligands to be considered at this juncture becomes more arbitrary and is restricted to those related to ones earlier discussed in Section D together with information for others, *e.g.* 1,2-di-(2-pyridyl)ethylene in which some degree of conjugation between the pyridine rings is theoretically possible.

(i) 2,2'-Dipyridil-py CO · COpy

The ligating properties of 2,2'-dipyridil, the 2-pyridyl analogue of benzil, have been investigated by Black[76]. The base undergoes rearrangement to pyridylic acid in the presence of nickel, cobalt or calcium acetates In the case of the nickel and cobalt salts the products are inner complexes of the type illustrated in Fig 5. The rearrangement does not occur for salts other than acetates.

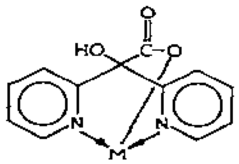


Fig 5 Terdentate anion derived from 2-pyridylic acid (after Ref 76)

(ii) 1,2-*Di(2'-pyridyl)ethylene and related ligands*

There have been some reports of the use of these compounds as gravimetric reagents, *e.g.* for cadmium[77], however, the most systematic studies are those by Brierley and Geary[78,79]. The *trans* isomers of the organic compounds have been used and there is no example in which both pyridine rings coordinate to the same metal ion; this would however be unlikely on steric grounds. Cobalt, nickel and copper(II) halides (MX_2) give polymeric complexes $[MX_2 \cdot L]_n$ (L = 1,2-di-(2'-pyridyl)ethylene) in which the metal ions are in pseudo tetrahedral or square planar environments or, when the halogen atoms function as bridging groups, in a distorted octahedral environment. Nickel(II) reacts less readily with the ligand than do the other metal ions; $[NiBr_2 \cdot L]_n$ is polymeric but nickel(II) chloride affords the dimer $[Ni_2Cl_4L]$ in which the ligand was considered to bridge the nickel(II) ions to complete the distorted tetrahedral arrangement. However, the results of a recent far IR spectroscopic study (400–80 cm^{-1}) do not support this view[79a] but no alternative structure was put forward. The same IR study generally supports the broad stereochemical conclusions reached in the original study[78]. The acetates of copper and nickel give the polymeric products $[\text{–Cu(OAc)}_4\text{Cu–N–N}]_n$, in which the copper–copper interaction is retained, and $[\text{–Ni(OAc)}_2\text{–N–N–}]_n$

Comparison has been made with other isomers of the ligand, *e.g.* 1,2-di-(4-pyridyl)ethylene[78] and 1-(2-pyridyl)-2-(3- or 4-pyridyl)ethylene[79] where the observations roughly parallel those of the previous paragraph. Again IR studies (Ref. 79*a*), which also debate the assignment of ν(metal–halogen) and ν(metal–nitrogen), generally support the structural conclusions based on electronic spectroscopy without in any way amplifying them[79a]. The copper(II) complexes of the less symmetric ligands are considered to retain the chain structure of CuX_2 (X = Cl, Br). There is no evidence that conjugation between the pyridyl groups is an important factor determining the coordination behaviour of the ligand, nor is there evidence of any bonding interaction between the alkene linkage and the di-positive metal ions.

"Pyridoin", *i.e.* 1,2-di-(2-pyridyl)ethylenediol also gives compounds of high molecular weight (> 2500–3000) with nickel(II), copper(II) and zinc(II)[80], *e.g.* $M_7L_8 \cdot nH_2O$ ($M = Ni, n = 14$; $M = Cu, Zn, n = 0$; L = pyridoin); in addition monomeric $NiL_2 \cdot 2H_2O$ is obtained. Methyl substitution of the pyridyl groups in the 6-position has little influence on the stoichiometry of the polymeric materials formed with the exception that zinc gives Zn_8L_9 rather than Zn_7L_8.

(iii) *2,2'-Azopyridine*

A preliminary report[81] outlined the properties of some cobalt(II) and copper(II) halide (MX_2) complexes of this ligand (L): LMX_2, L_2MX_2 and

$L(MX_2)_2$. As the ratio of metal to ligand increases in the copper series evidence of antiferromagnetic interactions is seen in the lowering of the room-temperature magnetic moments, e g. for $[(CuBr_2)_2 \cdot L]$, $\mu_{eff} = 1.53$ B.M. at ambient temperature.

More recently a comprehensive survey of the use of 2,2′-azopyridine as a ligand has appeared[82], in which six coordinate complexes of iron(II) and nickel(II) were reported together with four and six coordinate derivatives of cobalt(II) and copper(II). A detailed discussion of the IR spectra of the complexes is given.

Of five possible modes of coordination, three are observed (Fig 6). There is some disagreement between the two reports[81,82] concerning CoL_2Cl_2 the earlier identification as a tetrahedral species[81] appears invalid[82]; however $L(CuCl_2)_2$ does contain copper(II) ions in a tetrahedral environment although the agreement between the reported room-temperature magnetic moments for this compound is not good The effective magnetic moment of $L(CoCl_2)_2$ is rather low (4.18 B.M.)[82].

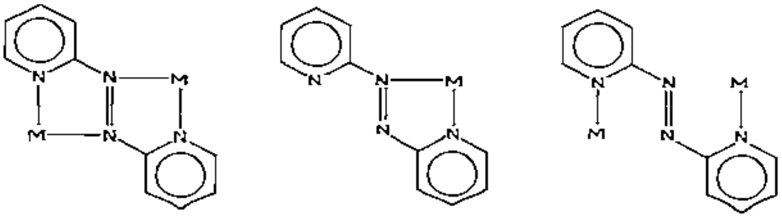


Fig 6 The observed coordination modes of 2,2′-azopyridine (after Ref 82).

Examination of other spectroscopic properties of the complexes yields interesting information. The diamagnetic $FeL_2(NCS)_2$ is deep blue; the profile of the charge transfer band is shifted to the red compared with that of the familiar $Fe(bipy)_3^{2+}$; indeed the frequency of the maximum (13,950 cm^{-1}) is the lowest yet recorded for a $t_{2g} \rightarrow \pi^*$ transition in a diamine complex of iron(II) The compounds $Fe(phen)_2(NCS)_2$ and $Fe(bipy)_2(NCS)_2$ are known[1] to be examples of compounds where the average value of Δ (10 Dq) allows an equilibrium between the ${}^1A_{1g}$ and ${}^5T_{2g}$ ground states of iron(II), it is surprising[49] therefore to find that a value of Δ as low as 10,900 cm^{-1} has been estimated for $NiL_2(NCS)_2$[82].

(iv) Di(2-pyridyl)disulphide (dpds) and 1,2-di-(2′-pyridyl)ethane (dpe)

Keeton and Lever[82a] have recently completed a study of the above ligands with cobalt(II), nickel(II), copper(II), zinc(II) and mercury(II). With the exception of mercury(II), when the sulphur atoms of dpds coordinate in preference to the pyridyl groups, the disulphide functions as a bidentate ligand via the ring nitrogen atoms.

The IR spectra of the complexe prepared fall into three separate classes (series I, II and III) with the complexity increasing for I to III, however, in no case is there evidence of an uncoordinated 2-pyridyl-group for a compound of either ligand. The characteristic pyridyl band close to 400 cm^{-1} ($\varphi(CC)$) has been used in attempt to gain insight to the conformation of the coordinated ligand; thus it is argued that the series I spectra are characteristic of the *cis* conformation and series II of the *gauche* conformation whereas for the series III compounds the pyridyl groups are chemically non-equivalent. Although not as yet supported by X-ray structural studies the arguments become compelling when it is considered that for complexes $Co(dpds)X_2$ and $Co(dpe)X_2$ ($X = Cl^-, Br^-, I^-, NCS^-$), which from their electronic and far IR spectra appear to be pseudo tetrahedral compounds, the ligands adopt the *gauche* form when $X = Cl^-$, *i.e.* minimisation of intra ligand repulsions whereas when $X =$ the larger Br^-, I^- or NCS^- the *cis* form is preferred, *i.e.* minimisation of interligand repulsions. It is however surprising that the corresponding zinc(II) compounds, although apparently tetrahedral, give series III spectra. These observations may be rationalised in terms of a polymeric structure with bridging ligands but the difference from cobalt(II) remains puzzling since quite often the behaviour of these two ions is very similar with the class of ligand considered in this article

The behaviour of the two ligands with nickel(II) is not quite identical, thus $Ni(dpe)X_2$ ($X = Br^-, I^-$) but only $Ni(dpds)I_2$ are tetrahedral with the ligands in the *cis* conformation (series I spectra) whereas $Ni(dpds)X_2$ ($X = Cl^-, Br^-, NCS^-$) and $Ni(dpe)X_2$ ($X = Cl^-, NCS^-$) give series III spectra. The isothiocyanato complexes are convincingly argued to be five coordinate with one terminal and one bridging NCS^- group, the halogeno complexes are similar. If the IR criteria are accepted the fact that all the five coordinate complexes give series III spectra must imply chemically non-equivalent 2-pyridyl groups, *i e.* the ligands span equatorial and axial positions in a five coordinate structure; accepting this the axial interaction appears stronger with dpds than with dpe.

Diamagnetic $Ni(dpe)_2(ClO_4)_2$ is reported[82a]. This must imply square planar geometry around the nickel(II) ion, a fact which supports the contention of section B (p. 294) that given some flexibility in the chelate rings, a *trans* disposition of two ligands of the class considered here is quite possible.

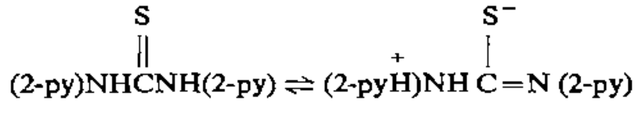
An analysis of the far IR spectra yields an assignment for $\nu(MN)$, *i e* the stretching of the metal–pyridine bond in the range 225–262 cm^{-1} which is in agreement with tentative proposals made for other ligands of this type[53].

F. THE COORDINATION COMPOUNDS OF $(py)_2X$ WHERE X IS A TRIATOMIC BRIDING GROUP

For consistency examples of X in this section are restricted to those which have some relationship to those considered in Section D, *e.g.* $X = -CH_2NHCH_2-$. It is evident that such molecules will function as terdentate ligands and it is in this respect they differ from those considered in Section D.

(i) Ketonic ligands and related molecules

The fusion of ethyl methane with 2-aminopyridine affords symmetrical dipyridylureas[83] which may well reward study as ligands. Also a simple preparation of 1,3-di-(2-pyridyl)acetone was recently reported[84], complexes of which should provide an interesting parallel with those of di-(2-pyridyl)ketone. At least one recent paper reports the use of *N,N′*-di-(2-pyridyl) thiourea as a ligand[85]. The base is claimed to show a variety of coordination behaviour and, with copper, a tautomeric form(II) is said to coordinate:



$$\mathrm{(2\text{-}py)NH\overset{S}{\overset{\|}{C}}NH(2\text{-}py)} \rightleftharpoons \mathrm{(2\text{-}py\overset{+}{H})NH\,\overset{S^-}{\overset{|}{C}}{=}N\,(2\text{-}py)}$$

I II

Examples of complexes of (I) are claimed, *e.g.* $[Pd(I)_2]Cl_2 \cdot 4H_2O$ (bidentate N, S) together with $[Rh(I)(OH)_3]$ (terdentate N, S, N) However, the characterisation of the compounds could be more complete

(ii) Complexes of bis(2-pyridylmethyl)amine and related ligands

Synthetic routes to bis(2-pyridylmethyl)amine (DPMA) are available[86]. Nelson and Rodgers[49] find the base to afford spin paired complexes with iron(II), $[Fe(DPMA)_2]X_2 \cdot nH_2O$, yet replacement of the proton on the aliphatic nitrogen atom by a methyl group produces a ligand (L) which gives spin free FeL_2^{2+} complexes. The spin paired iron(II) complexes of DPMA show intense charge transfer bands similar in profile to those of the familiar $Fe(bipy)_3^{2+}$ but displaced to higher wave number. It is suggested that the t_{2g} electrons interact to some extent with the pyridine rings despite the fact that a high degree of conjugation is absent from the chelate rings[49]. This point has also been made for $Fe(tripyam)_2^{2+}$ and $Ni(tripyam)_2^{2+}$ [66]. Nelson and Rodgers point out that replacement of aliphatic by pyridyl nitrogen atoms about nickel(II) increases the ligand field strength; the data for tri-2-pyridylamine[66] appears in complete accord with this hypothesis[49]. The failure of bis(2-pyridylmethyl)methylamine to give low spin iron(II) complexes is attributed to steric factors. The electronic influence of the methyl group would be expected to increase the basicity of the ligand, and indirectly Δ; however with respect to nickel(II) the values of Δ are 12,550 cm^{-1} (DPMA) and 10,500 cm^{-1} (DPMA–Me).

Bis(2-pyridylethyl)amine (DPEA) is a related ligand; six rather than five membered chelate rings being formed. The ligand field strength is however much less than that of DPMA and five coordinate complexes, *e g.* $Ni(DPEA)X_2$ (X = halogen)[87] or $Co(DPEA)X_2$[88] are often formed. Indeed no example of M-

$(DPEA)_2^{2+}$ is known. The related bis(2-pyridylethyl)sulphide behaves similarly[87]. DPEA will function on occasion as a bidentate ligand, one pyridine ring remaining uncoordinated, *e.g.* $Zn(DPEA)X_2$[88]. The failure of DPEA to give *bis* complexes is attributed mainly to steric factors.

Very recently two papers have appeared which discuss pK_a determinations for ligands such as DPMA[89,90] and closely related polydentate species[89]. Some stability constants were also recorded[89,90].

G. CONCLUDING REMARKS

This article has attempted to survey a class of pyridyl ligands which has been of interest to the author over a number of years. It is clear that many potentially interesting ligands, *e.g.* pyCOpy and $pyCH_2py$, have received somewhat scant attention, whereas the survey of others, *e.g.* pyNHpy, which have been more extensively investigated reveals that further progress is severely hampered by lack of structural data and quantitative thermodynamic data; mechanistic studies are non-existent. With few exceptions the studies with ligands dealt with here have been confined to the right hand side of the transition metal series. The fact that the group –X– in $(py)_2X$ is often a potentially reactive functional group could render those ligands of value in some catalytic processes; again this possibility has yet to be considered.

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