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Infra-red Spectroscopic Studies of Selected Pyridylamine Complexes by the Metal Isotope Technique

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Six complexes of di- and tri-(2-pyridyl)amine have been prepared for pairs of metal isotopes (^{63}Cu, ^{65}Cu; ^{54}Fe, ^{57}Fe).

*When the electronic ground state of the metal–tri-(2-pyridyl)amine complex ion is non-degenerate and the microsymmetry of the metal ligand array approximates closely to O_h, only one mode is metal sensitive (*e.g. *[Fe(II)(tripyam)$_2$] (ClO$_4$)$_2$). However, for [Cu(II)(tripyam)$_2$](PF$_6$)$_2$ the observation of two metal sensitive modes indicates a lower effective symmetry, which is reasoned to arise from a "tetragonal" distortion of the CuN$_6$ array. The isomeric [Cu(II)(tripyam)$_2$(ClO$_4$)$_2$], with bidentate ligands, gives shift data consistent with a* trans-*diperchlorato-complex.*

The structure of [Cu(II)(dipyam)$_2$](ClO$_4$)$_2$ is known and the shift data are in good accord with expectation. The trigonal bipyramidal structure previously proposed for [Cu(II)(dipyam)$_2$Cl]Cl is completely supported, but the structure of [Cu(II)(dipyam)$_2$(NO$_3$)$_2$] appears less regular than formerly believed.

All metal–nitrogen stretching frequencies are located below 300 cm^{-1} with the exception of the low spin bis-tri-(2-pyridyl)amineiron(II) perchlorate for which ν_{as}(FeN) = 307 cm^{-1}, a value in good agreement with proposed for low spin bis-tri-(2-pyridyl)-aminecobalt(II) using a different experimental approach to the assignment.

Introduction

We have published a range of papers [1] describing new complexes of di-(2-pyridyl)amine and tri-(2-pyridyl)amine with first row transition metals. In particular copper(II) has shown an ability to form a remarkable variety of complexes with these ligands [2, 3] which, judged by their electronic spectra, encompass a large range of stereochemical environments for the ion. Jacobsen and co-workers have published structures for some copper(II) di(2-pyridyl)amine complexes [4, 5] which show that predictions of co-ordination number and stereochemistry based on "sporting" data have been broadly correct. However, it has been clear for many years that it is far more satisfactory to use the structure of a complex as a starting point for the discussion of spectra – a point well illustrated in the present context by Hathaway's study [6] of bis-(di-2-pyridylamine)copper(II) perchlorate.

Nakamoto [7] has demonstrated that the application of the elegant metal isotope technique may solve in an unambiguous fashion the problem of assignment of metal–nitrogen stretching frequencies in complexes of pyridine derivatives. In particular his study of 2,2'bipyridyl complexes [8] suggested that the selection rules for the stretching modes were determined by the molecular symmetry of the complex. Thus there is at least the possibility that useful structural information could be available, given definitive assignments of metal ligand modes. Two previous attempts have been made to assign metal–nitrogen modes in pyridylamine complexes. An early empirical study [9] of di-(2-pyridyl)amine complexes must now be regarded as unsatisfactory but the rather more novel use of Raman and infra-red spectroscopy to study the spin cross-over system bis-(tri-2-pyridylamine)cobalt(II) perchlorate provides more definitive guidance for the present study [10]. We therefore undertook the study of selected pyridylamine complexes of copper(II) and iron(II) by the metal isotope technique to provide further physical data on these interesting compounds.

Experimental

Metal isotopes were supplied by the Electromagnetic Separation Group, A.E.R.E. Harwell (^{63}Cu, ^{65}Cu, ^{54}Fe, ^{57}Fe) as the metal. The following procedures were developed for the synthesis of milligramme quantities of three complexes of tri-(2-pyridyl)amine (synthesised by the method of Wibaut and La Bastide [11]) and three complexes of di-(2-pyridyl)amine.

Diperchloratobis(tri-2-pyridylamine)copper(II) (^{63}Cu and ^{65}Cu)

The pure copper isotope (5 mg) was weighed into a crucible and dissolved in the minimum quantity of nitric acid (70% w/w). The solution was heated to dryness and then more strongly to afford copper(II) oxide. The oxide was then dissolved in perchloric acid (27 mg, 60–62%) to give a solution which was heated gently to dryness to give crystalline copper(II) perchlorate which was transferred to a small flask with ethanol (2 ml). A solution of tri-(2-pyridyl)-amine (40 mg) in ethanol (2 ml) was added and the mixture was refluxed for 30 min. Yellow–green *crystals* were obtained on cooling, which were washed with ethanol, and dried *in vacuo*.

Bis(tri-2-pyridylamine)copper(II) Hexafluorophosphate (^{63}Cu and ^{65}Cu)

The blue isomeric form of the above diperchlorato-complex containing terdentate ligands and ionic perchlorate groups proved difficult to synthesise pure on a small scale, hence it was decided to synthesise the hexafluorophosphate salt in which the ligands are terdentate. The above preparation of the diperchlorato-complex was first repeated. The yellow–green crystals were dissolved in water and added to a solution of ammonium hexafluorophosphate in water. A white precipitate formed on setting the solution aside (identified as a tri-(2-pyridyl)amine salt), this was filtered off and further tri-(2-pyridyl)-amine in ethanol was added to the filtrate which was again set aside. After 10 min blue *crystals* of $[Cu(II)(tripyam)_2](PF_6)_2$ separated. These were filtered, washed with ethanol and dried *in vacuo*.

Bis(tri-2-pyridylamine)iron(II) Perchlorate (^{54}Fe and ^{57}Fe)

This preparation was carried out under nitrogen. Isotopically pure elemental iron (5 mg) was weighed into a small flask fitted with a nitrogen inlet and outlet. A graduated syringe was used to add 5 ml of a dilute perchloric acid solution (0.9 g in 250 ml water) which had been pre-saturated with nitrogen. When the iron had totally dissolved, a nitrogen saturated solution of tri-(2-pyridyl)amine (45 mg) in ethanol was added. The solution was refluxed for 15 min and cooled to afford orange brown *crystals* of the desired complex. The material was filtered, washed with ethanol, and dried *in vacuo*.

Bis(di-2-pyridylamine)copper(II) Perchlorate, Nitrate, and Chloride (^{63}Cu and ^{65}Cu)

A slightly different procedure was used. Isotopically pure elemental copper (25 mg) was dissolved in a slight excess of nitric acid (200 mg, 35% w/v). Water (1 ml) was added and the solution was made up to 25 ml with acetone. The solution was then divided into three equal parts which were each carefully evaporated to dryness. (*a*) One specimen was heated strongly to convert it to black copper(II) oxide which was then treated with a slight excess of hydrochloric acid (15 mg, 70% w/w) to afford cupric chloride. This was heated gently until dry, then dissolved in a few drops of ethanol. To this solution was added a slight excess of di-(2-pyridyl)amine (50 mg) in acetone (0.5 ml). A green *precipitate* of $Cu(dipyam)_2Cl_2$ was formed immediately. The crystals were dried in a vacuum desiccator. (*b*) A second specimen of cupric nitrate was dissolved in a slight excess of perchloric acid (45 mg, 60%) and gently fumed to dryness. The residue was dissolved in acetone (1 ml) and treated with di-(2-pyridyl)amine (50 mg) in acetone (0.5 ml) to afford the pale green di-acetone adduct $[Cu(dipyam)_2](ClO_4)_2$ acetone. The acetone was evaporated off using a jet of air and the addition of a few drops of water then afforded the deep blue–violet *material*, $[Cu(dipyam)_2](ClO_4)_2$ which was dried *in vacuo*. (*c*) The remaining specimen of copper(II) nitrate was treated directly with di-(2-pyridyl)-amine (50 mg) in acetone solution (1.5 ml) to afford the olive green *compound*, $[Cu(dipyam)_2(NO_3)_2]$ which was dried *in vacuo*. The identity and purity of the complexes prepared above were checked by comparison of infra-red spectra (taken on a Perkin Elmer 457 instrument) with those of authentic specimens containing metal of natural isotopic abundance.

The shift data were obtained between 600 cm^{-1} and 200 cm^{-1} with a Perkin Elmer 225 grating spectrophotometer. Each specimen was subjected to five replicate scans and it is believed that shifts in excess of 1 cm^{-1} could be detected with some confidence. The samples were prepared as polythene discs, 13 mm in diameter, pressed at 10–13 tons inch^{-2} for five minutes. Good agreement was obtained between the spectra of the isotopically pure compounds and those containing the metal in natural isotopic abundance.

Results and Discussion

The shift data are presented in Tables I (tri-(2-pyridyl)amine complexes) and II (di-(2-pyridyl)amine complexes). Numerical data for the isotope of lower mass are given, any shift to lower wavenumber in the spectrum of the isotope of higher mass being denoted as $\Delta\nu$.

Complexes with Tri-(2-pyridyl)amine

The true symmetry of an undistorted bis-tri-(2-pyridyl)amine metal cation, in which both ligands are terdentate, is D_{3d}; however there is some evidence from studies of the iron(II) [12] and nickel(II) [13] complexes that the microsymmetry of the [metal N_6] unit is close to O_h and that some spectroscopic

TABLE I. Infra-red Data (400–200 cm^{-1}, Cu; 600–200 cm^{-1}, Fe) for Tri-(2-pyridyl)amine Complexes Containing Isotopically Pure Metals.

[^{63}Cu(tripyam)$_2$](PF$_6$)$_2$	$\Delta\nu$(^{65}Cu)	[^{63}Cu(tripyam)$_2$(ClO$_4$)$_2$]	$\Delta\nu$(^{65}Cu)	[^{54}Fe(tripyam)$_2$](ClO$_4$)$_2$	$\Delta\nu$(^{57}Fe)
344	0.2	381	1.0	550	0
337	0.3	282	0.3	524	0
294	2.0	269	2.0	504	0
258	2.0	257	2.0	485	0
				381	0
				348	0
				307	1.5

TABLE II. Infra-red Data (400–200 cm^{-1}) for Di-(2-pyridyl)amine Complexes Containing Isotopically Pure Copper.

[^{63}Cu(dipyam)$_2$Cl]Cl	$\Delta\nu$(^{65}Cu)	[Cu(dipyam)$_2$(NO$_3$)$_2$]	$\Delta\nu$(^{65}Cu)	[Cu(dipyam)$_2$](ClO$_4$)$_2$	$\Delta\nu$(^{65}Cu)
		437	1.4		
354	2.1	375	0	361	0
346	0	352	0		
271	2.2	286	1.8	295	2.8
250	1.6	264	2.3	252	1.2
222	1.2	218	1.8		
205	0.5				

data may be interpreted in the higher symmetry. It is clear from the electronic spectrum of the [Cu(tripyam)$_2$]$^{2+}$ ion that the O_h model is inappropriate in this case [14]. However the nature of the distortion is not currently known since a model based on D_{3d} symmetry as well as one based on a distortion along one N–Cu–N axis (C_{2h} symmetry) could provide a plausible basis for the interpretation of some data, although the "tetragonal" model has been preferred.

The shift data were recorded for [Cu(tripyam)$_2$](PF$_6$)$_2$. Two bands (294 cm^{-1} and 258 cm^{-1}) undergo a significant shift and are assigned as the components of ν_{as} (CuN). This observation confirms the inadequacy of the O_h model and if anything supports the D_{3d} model for which we expect two i.r. active stretching modes (A_{2u} + E_u), rather than the C_{2h} model for which three modes are expected (Au + 2Bu). If, however, the microsymmetry were adequate to determine the activity of ν(CuN), we cannot differentiate the models since D_{4h} rather than C_{2h} would be the effective point group and two i.r. active Cu–N stretching modes anticipated.

It was of interest to examine a cation for which an O_h microsymmetry was more probable and [Fe(II)(tripyam)$_2$]$^{2+}$ was selected. If two bands undergo significant shift, then the true symmetry (D_{3d}) determines the selection rules for ν(FeN), whereas if one band shifts, the microsymmetry of FeN$_6$ (O_h) is adequate. Careful comparison of the spectra of the isotopically pure complexes (^{54}Fe and ^{57}Fe) revealed that only one band between 600 cm^{-1} and 200 cm^{-1} underwent a measurable shift, that at 307 cm^{-1} (^{54}Fe). Earlier work [10] has used the $^4T \nleftrightarrow {}^2E$ spin cross-over situation for [Co(tripyam)$_2$](ClO$_4$)$_2$ to assign ν(CoN) for both high spin (263 cm^{-1}) and low spin (301,312 cm^{-1} – split in Jahn–Teller distorted C_{2h} symmetry) isomers. Thus, the assignment of ν_{as}(FeN) at 307 cm^{-1} for the low spin iron(II) complex seems very reasonable and the two approaches to assignment are satisfyingly self consistent. The metal sensitivity of the band at 260 cm^{-1} for the series [M(II)(tripyam)$_2$](ClO$_4$)$_2$ (M = Co, Ni, Cu, Zn) was previously used to suggest the assignment of that mode as ν_{as} (MN) [10], the present work supports this. The iron(II) and cobalt(II) (high spin) data suggest that, in undistorted complexes the O_h symmetry rather than the D_{3d} symmetry of the cation determines the selection rules for ν(MN). However the distortion of the low spin cobalt(II) complex was detected and, hence, the C_{2h} model for the copper(II) complex is attractive with the greater separation between the components of ν_{as} in this case suggesting a greater distortion. The D_{4h} microsymmetry does, however, appear to dictate the selection rules for the copper(II) compound.

An isomeric form of [Cu(II)(tripyam)$_2$](ClO$_4$)$_2$, [Cu(II)(tripyam)$_2$(ClO$_4$)$_2$], may be prepared [2]. The visible absorption spectrum of this isomer with bidentate tri-(2-pyridyl)amine ligands is quite unlike that established [15] for examples of *cis*-distorted octahedral complexes or for trigonal bipyramidal complexes, thus a *trans* diperchlorato-complex has been postulated. A possible objection to this structure is the steric crowding of the hydrogen atoms on the pyridyl-groups of adjacent ligands. This could be relieved by retention of the pyramidal configuration about the amine nitrogen atom and co-ordination of the bidentate ligands in such a way as to conserve a centre of symmetry and affords a complex molecule of C_{2h} symmetry. Thus three infra-red active metal-ligand modes, which are also metal sensitive, would be anticipated (two ν(Cu–N) – Au + Bu, and one ν(CuO) – A_u). Isotopic studies show the bands at 381, 269 and 257 cm^{-1} to undergo measurable shifts. The latter two are obviously very reasonably assigned as ν(Cu–N) whereas that at 381 cm^{-1} is equally reasonably assigned as ν(CuO) for a weak copper to oxygen bond by comparison with well accepted assignments [16] for, say, pyridineN-oxide complexes (the N-oxide and perchlorate ion have similar masses) *e.g.* ν(CuO) for $[Cu(II)(C_5H_5NO)_6](ClO_4)_2$ is placed at 368 cm^{-1}. Thus the data are completely consistent with the C_{2h} model with *trans* perchlorato groups.

Complexes of Di-(2-pyridyl)amine

From the crystal structure [4] of $[Cu(II)(dipyam)_2](ClO_4)_2$ we know that the four CuN bonds define a distorted tetrahedron. The simplest model that we could use for interpretation of the shift data would be a cation of D_{2d} symmetry from which we would predict two infra-red active stretching modes (B_2 + E). The two bands undergoing isotopic shift are located at 295 cm^{-1} and 252 cm^{-1} (^{63}Cu) and provide convenient support for the model. Thus, as with the tri-(2-pyridyl)amine complexes, the copper nitrogen stretching frequencies are expected below 300 cm^{-1}.

The compound $[Cu(II)(dipyam)_2Cl]Cl$ has been designated trigonal bipyramidal on the basis of visible, i.r. and e.s.r. spectroscopic data [3]. If this is so, the isotopic shift data should be analysed in terms of a model of C_2 symmetry and all five metal-ligand stretching vibrations should be i.r. active (3A + 2B). Table II reveals significant shifts for four vibrations (354, 271, 250 and 222 cm^{-1}) and a more questionable shift for the band at 205 cm^{-1}. In fact the model is in excellent agreement with the data. The band at 354 cm^{-1} may clearly be assigned to ν(CuCl) for the short axial Cu–Cl bond (not 346 cm^{-1} as previously believed [3]) and the three remaining bands are ν(CuN) (A + 2B). The symmetric stretch of the axial N–Cu–N bonds (A) involves no movement of the metal atom unless coupling to the A mode of the equatorial CuN bonds occurs. Thus the very small shift of the 205 cm^{-1} may originate from this mode.

The information available for the bis di-(2-pyridyl)amine complex of copper(II) nitrate is less readily interpreted. Evidence available suggests that the nitrate groups are weakly co-ordinated [3] and the weak d $\nleftrightarrow$ d spectrum did suggest a centro-symmetric structure similar to that considered for $[Cu(II)(tripyam)_2(ClO_4)_2]$ above. The shift data show three isotopic sensitive bands at 286, 264 and 218 cm^{-1}. In addition a band at 437 cm^{-1} undergoes a shift of 1.4 cm^{-1}. All spectra of di-(2-pyridyl)amine complexes show a band in this region which has been assigned as the ligand ϕ(CC) mode [17]. That it should shift in this spectrum alone may be due to one of two causes: (a) coupling with some metal ligand mode or (b) accidental degeneracy with a metal sensitive copper–oxygen (nitrate) mode. In view of the comparable magnitude of the shift to others observed in this work, we rather favour the latter explanation although this would place ν(CuO) much higher than observed for other copper nitrate complexes [18]. This would in turn lead to the assignment of the remaining three metal sensitive modes as ν(CuN) with the clear implication that the symmetry about copper(II) is less in this complex than for $[Cu(II)(tripyam)_2(ClO_4)_2]$. Clearly a crystallographic investigation would be welcome in this case.

We have made no attempt to discuss bending modes since those generally give rise to immeasurably small shifts unless coupled with some low frequency stretching mode [7]. It will however be observed that extremely small shifts of some "ligand" modes have been recorded in Tables 1 and 2 (~0.2–0.3 cm^{-1}). We have taken the view that these shifts are too small to be called significant, and if they are real they probably reflect the coupling of internal ligand modes to the metal ligand stretching vibrations.

It is concluded that the study has provided useful support for much that has previously been written about the nature of these pyridylamine complexes.

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