

2-Amino-4-picoline N-Oxide Complexes Formed from Various Copper(II) Salts

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Received September 1, 1982

Copper(II) complexes have been prepared with 2-amino-4-picoline N-oxide (2am4PicO) employing the perchlorate, tetrafluoroborate, chloride and bromide salts. Preparative molar ratios of 4:1 and 2:1 ligand to Cu(II) salt yielded solids having the following empirical formulas: $\text{Cu}(\text{2am4PicO})_4\text{X}_2$ ($\text{X} = \text{ClO}_4$, BF_4) $\text{Cu}(\text{2am4PicO})_2\text{X}_2$ ($\text{X} = \text{ClO}_4$, Cl and Br) and $\text{Cu}(\text{2am4PicO})\text{X}_2$ ($\text{X} = \text{Cl}$, Br). The green solids of the first group appear to be tetrahedrally distorted four-coordinate species while the latter two groups are likely dimeric solids containing some monomeric centers. 2am4PicO functions as a monodentate ligand coordinating via the N-oxide oxygen or apparently using this function to bridge two Cu(II) centers.

reported the preparation and the infrared spectra of the various transition metal ion complexes of 2-aminopyridine N-oxide employing the perchlorate salts. Because of an interest in 2-substituted pyridine N-oxide complexes, studies of this ligand were extended to include other copper(II) salts [4]. In such studies we have varied not only the competing anion, but also the ligand to Cu(II) preparative mole ratio. A similar study is reported here with the ligand 2-amino-4-picoline N-oxide (2am4PicO) and comparisons of the properties of derived solids with those of 2-aminopyridine N-oxide (2-APO) [4] are included. It is believed that this is the first report on the metal ion complexes of 2am4PicO.

Introduction

N-alkyl substituted 2-aminopyridine N-oxides have been shown to bond to copper(II) centers primarily via the N-oxide oxygen as monodentate ligands [1]. In contrast, the N,N-dialkylaminopyridine N-oxides coordinate most commonly as bidentate ligands involving amine bonding as well as the N-oxide function [2]. Previous workers [3] have

Experimental

The 2am4PicO was prepared by oxidizing 2-amino-4-picoline (Aldrich) with m-chloroperoxybenzoic acid (Aldrich) in acetone. The preparation of the complexes was performed in an analogous manner to the Cu(II) complexes in previous studies from this laboratory [1, 2, 4].

TABLE I. Colors and Parital Elemental Analyses of Some Copper(II) Complexes of 2am4PicO.

Compound	Color	% Calcd		% Found	
		C	H	C	H
$\text{Cu}(\text{2am4PicO})_4(\text{ClO}_4)_2$	green	37.98	4.25	37.13	4.11
$\text{Cu}(\text{2am4PicO})_2(\text{ClO}_4)_2$	forest green	28.22	3.16	27.66	3.25
$\text{Cu}(\text{2am4PicO})_4(\text{BF}_4)_2$	green	39.29	4.40	39.41	4.54
$\text{Cu}(\text{2am4PicO})_2\text{Cl}_2$	orange-brown	37.66	4.21	36.45	4.26
$\text{Cu}(\text{2am4PicO})\text{Cl}_2$	brown	27.87	3.12	28.01	3.22
$\text{Cu}(\text{2am4PicO})_2\text{Br}_2$	red brown	30.56	3.42	29.07	3.50
$\text{Cu}(\text{2am4PicO})\text{Br}_2$	dark brown	20.74	2.32	20.31	2.20

TABLE II. IR Assignments (cm^{-1}) for 2am4PicO and its Copper(II) Complexes.

Compound	$\nu_{\text{NH}}(\text{asy})$	$\nu_{\text{NH}}(\text{sym})$	ν_{NO}	$\nu_{\text{CuO}}^{\text{a}}$	ν_{CuX}
2am4PicO = L	3325w	3260w	1191s		
CuL ₄ (ClO ₄) ₂	3482m	3362m	1199s	416m 355m	
CuL ₂ (ClO ₄) ₂	3430m	3310m	1202s	420m 353m	
CuL ₄ (BF ₄) ₂	3500m	3386m	1201s	419m 364m	
CuL ₂ Cl ₂	3382m	3280m	1200s	423m 381m	302m 288sh
CuLCl ₂	3422m	3308m	1192s	418m 365m	314m 291sh 253m
CuL ₂ Br ₂	3395m	3300m	1198s	422s 380s	252m 230m
CuLBr ₂	3390m	3280m	1190w	418s 363s	247m 228m

^aSee text.

TABLE III. Solid State Electronic Spectra (kK) for the Copper(II) Complexes of 2am4PicO.

Compound ^a	Charge Transfer		d-d
	O(π) \rightarrow Cu(II)	X(π) \rightarrow Cu(II)	
CuL ₄ (ClO ₄) ₂	25.64		16.72, 14.08sh
CuL ₂ (ClO ₄) ₂	24.69		15.45, 13.46sh
CuL ₄ (BF ₄) ₂	25.32		16.31, 14.04sh
CuL ₂ Cl ₂	23.42	21.65	12.35
CuLCl ₂	22.79	20.58	13.51, 6.83
CuL ₂ Br ₂	22.57	20.40	12.47, 7.35
CuLBr ₂	—	20.00	12.99, 6.71

^aL = 2am4PicO.

Results and Discussion

The unique solids isolated with 2am4PicO and the various Cu(II) salts are shown in Table I along with their colors and partial elemental analyses. In comparison with the solids derived with 2-APO, there is a general trend to incorporate fewer ligands per metal ion in these complexes presumably due to the presence of the methyl group. For example, we did not isolate a 2:1 perchlorate complex with 2-APO and 1:1 complexes were not formed with the copper halide salts [4]. A complex having less than a 4:1 ligand to Cu(II) ratio with Cu(BF₄)₂ has also been isolated, but satisfactory elemental analyses have not been achieved.

The colors shown in Table I are similar to the colors found for the corresponding 2-APO complexes

[4] as well as the N-alkyl substituted 2-aminopyridine N-oxide complexes [1]. Therefore, the complexes isolated with 4:1 ligand to Cu(II) mole ratios would be expected to have the four ligands bound via the N-oxide oxygens to give CuO₄ chromophores while the remaining complexes may involve bidentate ligand bonding, participation of the anion in the coordination sphere, polynuclear complex formation or some combination of these. The results of the spectral studies, which have been limited primarily to the solid state due to the tendency of the N-oxide complexes to undergo a change in their nature upon dissolution, are shown in Tables II (infrared), III (electronic) and IV (esr).

The two stretching modes associated with the amine function are found at lower frequencies than normal in the spectrum of the ligand due to its

TABLE IV. ESR Spectral Parameters of the Copper(II) Complexes of 2am4PicO.

Compound ^a	Temp., K	ESR Parameters			
CuL ₄ (ClO ₄) ₂	298	g ₃ = 2.190	g ₂ = 2.112	g ₁ = 2.055	g _{av} = 2.119
	77	g ₃ = 2.184	g ₂ = 2.110	g ₁ = 2.053	g _{av} = 2.116
CuL ₂ (ClO ₄) ₂	298	g _⊥ = 2.191	g _∥ = 2.056		g _{av} = 2.146
	77	g ₃ = 2.188	g ₂ = 2.111	g ₁ = 2.055	g _{av} = 2.118
CuL ₄ (BF ₄) ₂	298	g ₃ = 2.191	g ₂ = 2.111	g ₁ = 2.056	g _{av} = 2.119
	77	g ₃ = 2.184	g ₂ = 2.103	g ₁ = 2.055	g _{av} = 2.114
CuL ₂ Cl ₂	298	A _∥ = 127G	g _∥ = 2.221	g _⊥ = 2.051	g _{av} = 2.108
	77	A _∥ = 165G	g _∥ = 2.204	g _⊥ = 2.048	g _{av} = 2.100
CuLCl ₂	298		g _∥ = ?	g _⊥ = 2.057	g _{av} = ?
	77	A _∥ = 146G	g _∥ = 2.264	g _⊥ = 2.061	g _{av} = 2.129
		A _⊥ or A(Cl) = 26 G			
CuL ₂ Br ₂	298		g _i = 2.091	Δpk - pk = 265 G	
	77	A(?) = 30G	g _i = 2.091	Δpk - pk = 210 G	
CuLBr ₂	298		g _i = 2.079	Δpk - pk = 237 G	
	77	A(Br) = 36 G	g _i = 2.087	Δpk - pk = 232 G	

^aL = 2am4PicO.

intermolecular hydrogen bonding [5]. In the 4:1 complexes with the polyatomic anions these bands appear to be at energies which suggest that the amine function is not coordinated at the copper(II) center while the halo solids as well as the 2:1 perchlorate solid have their bands at somewhat lower frequency. Association with the anions by the amine hydrogens is more likely to be the cause of this difference than coordination of the function in that coordinated amines generally have their bands at somewhat lower energies (e.g., $\nu_{N-H(asy)} = 3250 \text{ cm}^{-1}$ when complexed to Cu(II) [6]).

Generally, coordination of the N-oxide function lowers the N-O stretching mode but the intermolecular hydrogen bonding of the ligand has shifted this band to much lower energy (i.e., $\nu_{N-O} = 1243 \text{ cm}^{-1}$ in pyridine N-oxide [7]) so that it is found at somewhat higher energy in the spectra of the complexes. These energies are consistent with coordination of the oxygen in that they are at comparable energies to those found for the Cu(II) complexes of 2-APO [4] and the N-alkyl-2-aminopyridine N-oxides [1]. Additionally, all bands are relatively strong and unsplit, except for CuLBr₂, suggesting a single type of coordination for the N-O function. The N-O bending mode assignments are omitted from Table II in that they are not much shifted in the complexes from the 846 cm^{-1} position in the spectrum of the ligand.

At this point the various spectral results of Tables II-IV will be discussed for the different compounds (or pairs of compounds). The initial compounds discussed will be used as models and only differences

in properties of the later compounds will be indicated rather than duplicate the discussion.

Cu(2am4PicO)₄(ClO₄)₂ and Cu(2am4PicO)₄(BF₄)₂

Both the esr and electronic spectra of these two compounds suggest that they have identical Cu(II) centers and that the anions are not coordinated or semicoordinated to the Cu(II) or interacting with the coordinated ligands. Confirming this is the presence of a relatively broad band at 1075 cm^{-1} and a sharp band at 608 cm^{-1} in the spectrum of perchlorate solid and similarly shaped bands at 1035 cm^{-1} and 508 cm^{-1} in the spectrum of the tetrafluoroborate solid with the two pairs of bands assignable to ν_3 and ν_4 of approximately tetrahedral AX₄ species. Note also that the amine stretching frequencies are at the highest energy in these two substances suggesting little interaction with either anion by the amine function.

The ν_{Cu-O} modes are assigned to a band at $415-420 \text{ cm}^{-1}$ and it is also possible that the band found in the $350-380 \text{ cm}^{-1}$ range owes some of its intensity to this stretching mode. The 2-APO complexes showed similar bands in this spectral region with the higher energy band at approximately 405 cm^{-1} and the lower energy band at about 360 cm^{-1} . This latter band, which is at an energy which could possibly be associated with a ν_{Cu-N} mode [8], is likely to be primarily associated with a ligand mode because none of the N-alkyl-2-aminopyridine N-oxide complexes of Cu(II) showed a band in this region of the spectrum [1]. Lending support to this suggestion is that aniline shows the C-NH₂ (in plane) deforma-

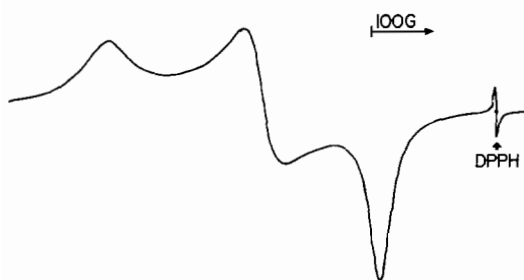


Fig. 1. Room temperature powder ESR spectrum of $\text{Cu}(\text{2am4PicO})_4(\text{ClO}_4)_2$.

tion at this same wavelength [9]. The higher energy of the band due primarily to $\nu_{\text{Cu-O}}$ when compared to the analogous band at the 2-APO complexes is probably due to both the greater electron density due to the methyl group as well as the steric hindrance of the ligand to the bonding of the polyatomic anions. This stronger coordination occurs because of the closer approach to a 4-coordinate rather than 4 + 2 (or 4 + 1) Cu(II) center.

Previous complexes [1, 2, 4] with these anions yielded the typical axial esr spectra normally associated with a $d_{x^2-y^2}$ ground state. However, the esr spectrum of both of these solids (Fig. 1) shows a loss of axial symmetry presumably caused by a distortion of the four bonding oxygens toward a tetrahedral arrangement. The appearance of a similar, but not identical, spectrum in the recent literature [10] for a Cu(II) species having a distorted trigonal bipyramidal structure casts some doubt on this assignment. Additionally, a powder anisotropic spectrum, with the same spectrum occurring in the analogous Cu(II)-doped zinc powder and in solvent glasses, had been reported previously for another distorted trigonal bipyramid [11]. While the g -values of the two previously reported spectra are considerably different due to different chromophores, there appear to be other differences.

Prior to discussing these spectral differences it should be pointed out that solution spectra of the perchlorate solid were recorded at room and liquid nitrogen temperatures in a variety of solvents. With methanol and *N,N*-dimethylformamide the low temperature spectra showed a minimum of three different Cu(II) species indicating decomposition of the complex. With pyridine as the solvent the typical spectrum [12] of $\text{Cu}(\text{py})_4^{2+}$ was observed indicating complete decomposition of the $\text{Cu}(\text{2am4PicO})_4^{2+}$. In nitromethane at liquid nitrogen temperature a typical axial spectrum associated with a $d_{x^2-y^2}$ ground state with $g_{\parallel} = 2.264$, $g_{\perp} = 2.060$ and $A_{\parallel} = 158$ G was found. However, the average g -value of 2.128 is significantly different from the 2.116 value

of the solid's g_{av} and also different from the solution spectrum g_0 of 2.110 obtained at room temperature. Also, both of the spectra obtained from the nitromethane solution showed superhyperfine splitting on the low g -value feature with an A -value of approximately 14 G which is probably due to one nitrogen coordinated to Cu(II). Therefore, again the nature of coordination sphere has been altered either by solvent coordination (*i.e.*, through nitrogen) or by bidentate formation using one of the amine nitrogens. Speculation about the nature of the species in solution is probably inadvisable although it would appear that, at least at liquid nitrogen temperatures, the change in coordination is probably due to axial coordination because of the presence of the nitrogen hyperfine splitting on the perpendicular feature as well as the shift to higher g -value of g_{\parallel} . With acetonitrile a color change occurs within $\frac{1}{2}$ hour but a rapidly frozen solution gave the following esr parameters: $g_{\parallel} = 2.258$, $g_{\perp} = 2.060$ and $A_{\parallel} = 171$ G. It should be noted that with this solvent no 'nitrogen' superhyperfine splitting was observed at either temperature. It is possible that this spectrum is representative of $\text{Cu}(\text{2am4PicO})_4^{2+}$. Nevertheless, in none of the solvents, as opposed to the previous compounds [10, 11], was the non-axial symmetry reproduced. This would seem to suggest the possibility of the non-axiality of the solid spectrum being caused by a steric effect of the lattice packing rather than a distorted trigonal bipyramidal structure. That is, a lattice-caused distortion of a 4-coordinate species.

A method of comparing the present orthorhombic esr spectra with those obtained by previous authors is by evaluation of the orbital reduction factors, k_2 . The electronic spectrum showed only a broad unresolved envelope for the $d-d$ transitions of the complexes of 2-APO while the solids reported on here show a resolvable shoulder on the low energy side of the main band. Resolution of the shoulder suggests that these complexes have less tetragonal distortion (*i.e.*, are closer to 4-coordinate) than those formed with 2-APO [13]. Coupling the energy of the shoulder to the lowest g -value feature (g_1) and the energy of the large peak to the other two g -values and employing the equations used by previous authors [11] yields the following values: $k_1^2 = 0.40$, $k_2^2 = 1.07$ and $k_3^2 = 0.53$. There is probably little significance to the fact that k_2^2 is greater than one in that the third $d-d$ band was not resolved in the spectrum. The values found for the other two parameters are consistent with the metal-ligand bonding being primarily σ in nature [14]. The lack of confidence in the high value for k_2^2 led me to evaluate the energy which would give k_2^2 a value of about 0.50, and consequently, a careful recording of the reflectance spectrum of the solid in the near infrared region. A broad, very weak peak may be centered

at 1128 nm (8.87 kK) which if used to calculate k_2^2 gives a value of 0.58. If this peak is real, then the symmetry about the Cu(II) is D_{2d} with the distortion from square planar toward tetrahedral being small [15].

$Cu(2am4PicO)_2(ClO_4)_2$

Only rarely have we been able to isolate a second solid when employing $Cu(ClO_4)_2$ or $Cu(BF_4)_2$ in our studies [1, 4]. Most often we simply get an impure sample of the 4-coordinate species which appears to be the case with the tetrafluoroborate salt mentioned earlier because its spectral properties are essentially identical to those of $Cu(2amPicO)_4(BF_4)_2$. However we have isolated a dark green solid with copper(II) perchlorate which appears to be unique. Differences are the following: the two ν_{N-H} bands are found at lower energy by some fifty cm^{-1} , the ligand to Cu(II) charge transfer band is about 1 kK lower in energy, the d-d band maximum is more than 1 kK lower in energy and although the low temperature esr spectra are essentially identical, the room temperature spectra are not. The bands assignable to the perchlorate ion are little different from the bands in the spectrum of $Cu(2amPicO)_4(ClO_4)_2$ with the following exception: the region of about 930 cm^{-1} contains two sharp bands in the spectrum of the latter compound, one of which is presumably due to $\nu_1(ClO_4)$ which is probably activated due to a minor distortion from tetrahedral symmetry by interaction with an amino hydrogen. However, the dark green solid has a much broader, but also weak, single band at this energy. Because the band is rather weak and there is no indication in the spectrum of splitting of either ν_3 or ν_4 , no strong bonding of ClO_4 to the Cu(II) center is indicated. Therefore, this compound may involve some bridging N-oxide ligands, partial amine coordination or both of these. Its 'reversed' esr spectrum at room temperature is probably due to antiferrodistortively coupled elongated chromophores [16]. When freezing to liquid nitrogen temperature the three g-value spectrum observed is essentially identical to that found for the two 4-coordinate salts discussed earlier. While surprising in itself, even more surprising is the agreement between g_{\perp} and g_3 as well as g_{\parallel} and g_1 for the room and low temperature spectra, respectively. At present a low temperature electronic spectrum is not obtainable with our facilities but on cooling there is no doubt that the forest green color of the solid goes to the green of the former compounds. A possibility is a tetrahedral distortion (*i.e.*, to D_{2d} as previously suggested) of the four strongly held ligands with the forcing out of the coordination sphere of the two ligands at the axial positions that are presumably present at room temperature.

$Cu(2am4PicO)_2Cl_2$ and $Cu(2am4PicO)_2Br_2$

Although we were unable to isolate compounds of this stoichiometry with the 2-APO ligand [4], a pair of compounds of the same stoichiometry were isolated with 2-methylaminopyridine N-oxide. However, the chloride solid with that ligand was brick red and the bromide solid was green in contrast to the colors shown in Table I. It should be noted that the energies of the ν_{N-H} bands in these complexes are consistent with non-coordination of the amine function but are suggestive of hydrogen bonding probably to the chloro (bromo) ligands. Of importance is that the infrared bands assigned to ν_{N-H} of the 2-methylaminopyridine N-oxide complexes suggested that the amine was coordinated [4].

Of interest in the spectra of both solids is the appearance of two bands which may have ν_{Cu-O} character suggesting two types of coordination of the ligand. Since bidentate formation has been ruled out, the only other likely method of coordination for the N-oxide function is a bridging ligand. The lower energy band (*ca.*, 380 cm^{-1}) in the spectra of both solids could be assignable to this type of N-oxide bonding. Note, however, that only one band was found for ν_{Cu-Cl} , but for the bromide solid two possible ν_{Cu-Br} bands have been assigned. The position of these bands is near the edge of the detection level of the instrument, as well as the salt plates employed, which makes their assignment less convincing.

Very recently a single crystal X-ray study of the chloride solid formed with 2-methylaminopyridine N-oxide has been reported [17] and it was found, upon recrystallization from a mixture of methanol and triethylorthoformate, to have a dimer structure. Briefly, the two copper atoms are bridged by two N-oxide ligands and each Cu(II) has one monodentate N-oxide ligand and one chloride ligand completing its planar portion. A second chloro ligand is in an axial position yielding a distorted square pyramid and the two pyramids are related by an inversion center. The recrystallization yielded amber crystals which may be significant since the original solid was brick red. The original solid gave an esr spectrum with a resolved g_{\parallel} feature suggesting it to be a mixture of monomer and dimer, the dimer evidently serving to dilute the monomer sufficiently to allow the spectrum to be resolved. The dimer gave no detectable signal either in the $g = 2$ or 4 region of the spectrum at either room or liquid nitrogen temperature and the recrystallized solid in this laboratory using the same solvent system still gives a resolved monomer spectrum.

Very possibly the same situation, that is, the presence of a monomer impurity in a dimeric solid, has occurred with the chloride solid since again its g_{\parallel} feature is resolved. Both g_{\parallel} and A_{\parallel} are changed

considerably, as is the color to yellow, upon cooling; the changes suggest a more planar structure for the monomer at the lower temperature [18]. Therefore, it appears that a CuO_2Cl_2 4-coordinate structure is likely for this monomer with no indication of the nature of the bromide solid from the esr spectrum. The dimer is likely the principle constituent so that the electronic spectrum is probably representative of a dimer, presumably similar in structure to the one reported by Pavkovic [17]. Attempts to recrystallize this solid led to a mixture of amber and green crystals, the green probably representing a Cu(II) center similar to that achieved with the polyatomic anion salts. This mixture did not give a resolved g_{\parallel} feature but instead gave an axial, normal monomer signal with $g_{\parallel} = 2.193$ and $g_{\perp} = 2.064$.

That the monomer is in fact an impurity in these solids, rather than being the primary species, can be derived from the intensity of the esr signal for these solids compared to the monomer signals of the solids with polyatomic anions. The latter signals are 100 times as intense. Further, dissolution in a solvent does not allow detection of the monomer signal, its concentration now being too dilute. Again as with the 2-methylaminopyridine N-oxide solid there has been no feature that is assignable to the dimer in the spectra of either solid.

Finally, the broad isotropic spectrum of the bromide solid shows some partially resolved features in its high field region. Also, the lower energies of the $\text{O}(\pi) \rightarrow \text{Cu}(\text{II})$ charge transfer bands in these complexes are consistent with less steric crowding about the Cu(II) and therefore stronger copper-oxygen bonds for the non-bridging N-oxide function. This is confirmed by the higher energies found for $\nu_{\text{Cu-O}}$ in the spectra of these solids. The lower energy for the $\text{X}(\pi) \rightarrow \text{Cu}(\text{II})$ in the spectrum of the bromide compared to the chloride solid is expected due to its better π -donor ability.

Cu(2am4PicO)Cl₂ and Cu(am4PicO)Br₂

While there have certainly been a number of dimers of the $(\text{CuL}_2\text{X}_2)_2$ stoichiometry [19], there have also been a large number of polymeric species of the stoichiometry CuLX_2 . In some cases these species include a solvent molecule in their coordination to reach a 5-coordinate center at each Cu(II) [20], while in other cases a chain of dimers, often one-dimensional, has been found [21]. With this in mind it should be pointed out that again for these two compounds there is no indication of amine coordination based on the infrared spectra of the two solids. We again observe two bands which could be assigned to $\nu_{\text{Cu-O}}$ but as with the solids with polyatomic ions these peaks are centered in the region where a primary amine group possesses a deformation mode. From the stoichiometry of the complexes it is unlikely that there are two different

types of N-oxide functions so that it is likely that the band in the 365 cm^{-1} owes much of its intensity to the amine group. For the chloro complex there are three bands which may be due to $\nu_{\text{Cu-Cl}}$ while the bromo complex shows only two bands which are assignable to $\nu_{\text{Cu-Br}}$. The electronic spectra of both solids show a band in the NIR region usually associated with a Cu(II) center having tetrahedral character. It should be noted that there are considerable differences in the literature concerning the electronic spectrum and its ability to distinguish unambiguously between the various stereochemistries [22]. However, Cu(II) species having tetrahedral or approaching tetrahedral symmetry seem to possess bands below 10 kK in their spectra [23]. Therefore, based on the spectral evidence, it is likely that these two solids are in fact dimeric with the chloro compound again possessing some monomeric impurity because of the esr signal at low temperature.

If one accepts that the two solids possess a dimeric structure, the nature of the bridging group (*i.e.*, halogen or N-oxide) should be able to be determined. The presence of bands in the 420 cm^{-1} region that have been assigned to the ν_{NO} mode would suggest nonbridging N-oxide functions in these two solids. On the other hand, the spectrum of the chloro complex shows a band at 253 cm^{-1} which is definitely in the range associated with bridging chloro ligands [24]. Less information is available on bridging bromide ligands although bands as low as 188 cm^{-1} for a bridging, 6-coordinate complex have been reported [25]. These same authors have given assignments with energies as high as 240 cm^{-1} [26] for Cu(II) centers having lower coordination numbers. Based on the above assignments it appears logical that both of these solids possess halide bridges with the band at the lower energy being associated with the bridging ligands and the bands at the higher energy in Table II to terminal halogens. Given the above assignment, the most likely structure for these two solids is that of a dimer with two halogen bridges and each Cu center then contains these two atoms, a terminal halogen and an N-oxide ligand arranged in a distorted tetrahedral environment. Very possibly the 'terminal' atoms interact with other dimers to give a chain or sheet structure, but only an X-ray and detailed low temperature magnetic study, neither of which is available at the author's institution, would validate these predictions.

The esr results for these two solids are of interest. The presence of a monomeric species in the chloride solid that has a resolved g_{\parallel} feature suggests the presence of a diamagnetic dimer. Additionally, the monomeric species for this compound is rather different from that observed for the other chloro solid in that g_{\parallel} is considerably larger and A_{\parallel} smaller. Both of these changes are consistent with either a higher coordination number (*e.g.*, six) or greater

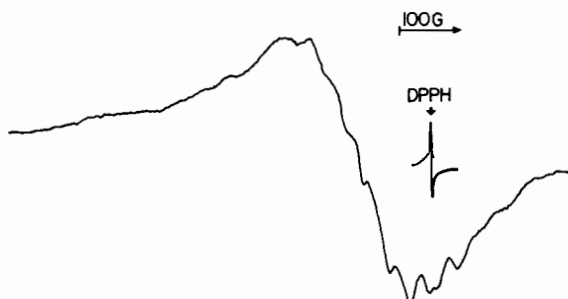


Fig. 2. Powder ESR spectrum of $\text{Cu}(\text{2am4PicO})\text{Br}_2$ recorded at 77 K.

distortion from a strong planar symmetry (e.g., toward tetrahedral). Finally the resolution of super-hyperfine structure in the g_{\perp} region of the spectrum of the chloro solid and throughout the spectrum of the bromo solid (Fig. 2) confirms the bonding of the halogen ligands. It is likely that this splitting is due to the halogens rather than the copper atom in that powder samples rarely show resolution of the g_{\parallel} feature and even when diluted often the g_{\perp} is unresolved. When comparing the two bromide solids the larger A value for CuLBr_2 shows stronger copper–bromine bonding which may suggest a lower coordination number.

In conclusion, the ligand appears not to function as a bidentate group in any of the complexes, the solids isolated from copper halide salts appear to yield dimeric products with monomeric impurities and salts of polyatomic anions give monomeric solids showing significant distortion from planarity. When one compares the complexes of 2-amino-4-picoline N-oxide with those of 2-aminopyridine N-oxide [4], it is surprising that the methyl substituent in the four position has exercised such a dramatic change in the nature of the complexes. Studies on the Cu(II) complexes of other 2-aminopicoline N-oxides are presently under way to determine whether the position of the methyl substituent is of importance.

References

- D. X. West and W-H. Wang, *J. Inorg. Nucl. Chem.*, **41**, 1719 (1979); **42**, 1656 (1980); D. X. West and K. Duffield, *J. Inorg. Nucl. Chem.*, **43**, 1517 (1981); D. X. West and J. B. Sedgwick, *J. Inorg. Nucl. Chem.*, **43**, 2307 (1981).
- D. X. West and W-H. Wang, *J. Inorg. Nucl. Chem.*, **42**, 985 (1980); **43**, 1511 (1981).
- H. Sigel and H. Brintzinger, *Helv. Chim. Acta*, **46**, 701 (1963).
- D. X. West, *J. Inorg. Nucl. Chem.*, **43**, 3169 (1981).
- M. C. R. Symons and D. X. West, unpublished results.
- N. B. Singh and J. Singh, *J. Inorg. Nucl. Chem.*, **40**, 919 (1978).
- S. Kida, J. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).
- L. Antolini and L. Menabue, *Trans. Metal Chem.*, **6**, 377 (1981).
- F. F. Bentley, L. D. Smithson and A. L. Rozek, 'Infrared Spectra and Characteristic Frequencies' ~700–300 cm^{-1} , p. 68, Interscience, New York (1968).
- R. P. Bonomo, E. Rizzarelli, N. Bresciani-Pahor and G. Nardin, *J. Chem. Soc., Dalton Trans.*, 681 (1982).
- J. R. Wasson, D. M. Klassen, H. W. Richardson and W. E. Hatfield, *Inorg. Chem.*, **16**, 1906 (1977).
- K. Wuthrich, *Helv. Chim. Acta*, **49**, 1400 (1966).
- I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. (A)*, 1678 (1968); D. E. Billing and B. J. Hathaway, *J. Chem. Soc. (A)*, 1516 (1968); J. I. Bullock, R. J. Hobson and D. C. Povey, *J. Chem. Soc. (Dalton)*, 2037 (1974) and D. E. Billing and A. E. Underhill, *J. Inorg. Nucl. Chem.*, **30**, 2147 (1968).
- R. S. Naidu and R. R. Naidu, *J. Inorg. Nucl. Chem.*, **41**, 1625 (1979).
- A. G. Karipides and T. S. Piper, *Inorg. Chem.*, **1**, 970 (1962); E. J. Solomon, J. W. Hare, D. W. Dooley, J. H. Dawson, P. J. S. Stephens and H. B. Gray, *J. Am. Chem. Soc.*, **102**, 168 (1980) and R. M. Gaura, P. Stein, R. D. Willett and D. X. West, *Inorg. Chim. Acta*, **60**, 213 (1982).
- I. Bertini, D. Gatteschi and A. Scozzafava, *Coord. Chem. Rev.*, **29**, 67 (1979).
- S. F. Pavkovic and S. L. Wille, *Acta Cryst.*, **B38**, 1605 (1982).
- G. D. Shields, S. Christiano and R. D. Bereman, *J. Inorg. Nucl. Chem.*, **40**, 1953 (1978).
- W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, **21**, 2679 (1982) and references therein.
- E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **348**, 15 (1976) and D. A. Krost and G. L. McPherson, *J. Am. Chem. Soc.*, **100**, 987 (1978).
- D. D. Swank and R. D. Willett, *Inorg. Chem.*, **19**, 2321 (1980).
- S. E. Livingstone and J. E. Oluke, *Trans. Met. Chem.*, **2**, 190 (1977).
- G. L. Seebach, D. K. Johnson, H. J. Stoklosa and J. R. Wasson, *Inorg. Nucl. Chem. Lett.*, **9**, 295 (1973); Y. Muto and T. Tokii, *Bull. Chem. Soc. Japan*, **51**, 139 (1978); and G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Coord. Chem.*, **9**, 141 (1979).
- Z. Karwecka and L. Pajdowski, *Pol. J. Chem.*, **52**, 2053 (1978). M. Biddau, M. Massacesi, R. Pinna and G. Ponticelli, *Trans. Met. Chem.*, **3**, 153 (1978); and *J. Inorg. Nucl. Chem.*, **41**, 1239 (1979).
- J. R. Allan, G. M. Baillie and N. D. Baird, *J. Coord. Chem.*, **10**, 171 (1980).
- J. R. Allan, N. D. Baird and A. L. Kassyk, *J. Therm. Anal.*, **16**, 79 (1979).