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2-Methyl- and 2-Ethylamino-3-picoline *N*-oxide Complexes Formed from Various Copper(II) Salts

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Abstract

Copper(II) complexes with 2-methylamino-3-picoline *N*-oxide (3MMH) and 2-ethylamino-3-picoline *N*-oxide (3MEH) have been prepared from the following salts: tetrafluoroborate, nitrate, chloride, bromide and acetate. Solids of the general formula $[Cu(LH)_4](X_2)$ (where LH = either ligand when $X = BF_4^-$ and LH = 3MMH when $X = NO_3^-$); $[Cu(3MEH)_2(ONO_2)_2]$; $[Cu(LH)X_2]$ (where LH = either ligand and $X = Cl^-, Br^-$) and CuL_2 (where L = either ligand's conjugate base) were characterized using spectral methods (*i.e.*, IR, UV–Vis and ESR). Both coordinate as monodentate ligands via their *N*-oxide oxygen in their complexes with salts having polyatomic anions. They bond as neutral bidentate ligands in their halide complexes, but as anionic bidentate ligands in the complexes formed from copper(II) acetate. The bonding to Cu(II) centers via the *N*-oxide oxygen is the strongest for these two ligands based on spectral data than any of the 2-aminopyridine *N*-oxides or 2-aminopicoline *N*-oxides studied to date.

Introduction

2-aminopyridine *N*-oxide [1, 2], 2-aminopicoline *N*-oxides [3–6], 2-amino-4,6-lutidine *N*-oxide [7] and 2-alkylaminopyridine *N*-oxides [8–11] have all been found to bond to copper(II) primarily as monodentate ligands via the *N*-oxide oxygen. In addition, 2-methylamino-6-picoline *N*-oxide (6MMH) was also found to coordinate to copper(II) centers solely via its *N*-oxide oxygen [12]. In contrast, 2-dialkylaminopyridine *N*-oxides [13, 14] coordinate in a bidentate manner by including the amino group in the coordination sphere as does 2-dimethylamino-6-picoline *N*-oxide (6MDM) [12]. Loss of a proton from the 2-amino group (*i.e.*, amino or alkylamino groups) does allow for nitrogen coordination [1] in the same manner as an amide function [15] and a series of molecular bis(ligand)copper(II) complexes have been prepared and characterized [16]. Further examples of this type of complex have been included in some of our more recent reports [3, 7, 12].

The alkyl group(s), whether on the amine nitrogen or on the *N*-oxide ring, have altered both the stoichiometry and the stereochemistry of the various copper(II) complexes that have been isolated. In view of these variations, we have prepared and spectrally characterized a series of copper(II) complexes of the ligands 2-methylamino-3-picoline *N*-oxide (3MMH) and 2-ethylamino-3-picoline *N*-oxide (3MEH) which are shown in Fig. 1. Also shown in Fig. 1 is a representation of the deprotonated ligand, 3MM, along with the expected modes of bonding to copper(II). Comparisons with Cu(II) complexes of previously studied *N*-oxide ligands will be included in our discussion of the present complexes, which are thought to be the first prepared with 2-alkylamino-3-picoline *N*-oxides.

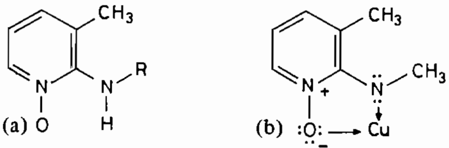

Fig. 1. (a) 3MMH and 3MEH, (b) 3MM bonding to Cu(II).

Experimental

The 3MMH and 3MEH ligands were prepared by amination of 2-chloro-3-picoline *N*-oxide in a steel bomb at 140 °C with the ensuing isolation of the products being carried out as reported previously [8, 13]. Oxidation of 2-chloro-3-picoline was accomplished using the method reported by Katritzky [17]. We prepared 2-chloro-3-picoline from 2-amino-3-picoline (Aldrich) following the procedure described by Jovanovic [18] using hydrochloric acid and sodium nitrite.

The copper(II) complexes were isolated from anhydrous ethanol solution, washed with anhydrous ether and stored in a vacuum desiccator over calcium

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TABLE I. Colors, Partial Elemental Analyses, Molar Conductivies and Magnetic Susceptibilities of some Copper(II) Complexes of 2-Methyl-amino-3-picoline *N*-oxide(3MMH) and 2-Ethylamino-3-picoline *N*-oxide(3MEH)

Compound	Color	%Found (Calc.)		Λ_M[a]	μ_{eff} (μ_B)
		C	H		
$[Cu(3MMH)_4](BF_4)_2 \cdot H_2O$	green	41.2(41.6)	4.9(5.2)	219[b]	2.0
$[Cu(3MEH)_4](BF_4)_2$	green	44.9(45.4)	5.3(5.7)	290[b]	1.6
$[Cu(3MMH)_4](NO_3)_2$	green	45.3(45.4)	5.7(5.5)	180[b]	1.6
$[Cu(3MEH)_2(NO_3)_2$	yellow	38.4(39.1)	4.4(4.9)	98[b]	1.9
$Cu(3MMH)Cl_2$	green	30.7(30.8)	3.1(3.7)	52[c]	1.8
$Cu(3MEH)Cl_2$	green	33.1(33.5)	4.2(4.2)	65[c]	1.9
$Cu(3MMH)Br_2$	olive	23.4(23.3)	2.6(2.8)	43[c]	1.9
$Cu(3MEH)Br_2$	olive	25.2(25.6)	3.2(3.2)	62[c]	1.6
$[Cu(3MM)_2]$	beige	49.8(49.3)	5.4(5.2)	17[b]	1.7
$[Cu(3ME)_2]$	tan	52.5(51.8)	6.1(6.2)	13[b]	1.8

[a] $ohm^{-1}\ cm^2\ mol^{-1}$. [b] *ca.* 10^{-3} CH_3CN. [c] *ca.* 10^{-3} DMF.

sulfate. Approximate magnetic susceptibility values were obtained with a Johnson Matthey, Inc. balance and the other methods of characterization of the complexes were the same as in previous studies from this laboratory [8].

Results and Discussion

The unique solids isolated with both ligands and the various copper(II) salts are shown in Table I along with their colors, partial elemental analyses, molar conductivities and approximate magnetic susceptibilities. The first three compounds listed in Table I involve *N*-oxide oxygen coordination of the ligand and not the polyatomic anions, which is consistent with their molar conductivities. Although $[Cu(3MMH)_4](NO_3)_2$ has a value below that expected for a 1:2 electrolyte in acetonitrile [19], this is probably due to some ion association with the nitrate ions. Along with the two molecular solids listed at the bottom of Table I, the remaining solids behave as non-electrolytes and therefore involve coordination of the anions. The yellow nitrate solid isolated with 3MEH may either be dimeric like $[Cu(IPH)_2(NO_3)_2]$ (IPH = 2-isopropyl aminopyridine *N*-oxide) [11], or a monomeric species such as was proposed for $[Cu(3MA)_2(NO_3)_2]$ (3MA = 2-amino-3-picoline *N*-oxide) [3]. The four solids isolated from halide salts are of a different color and stoichiometry than any of the previous halide solids formed with *N*-oxide ligands. That is, we have most often isolated CuL_2X_2 solids, and if $CuLX_2$ solids were isolated, they were brown as opposed to green or olive green. All the compounds of this study are monomeric based on their magnetic susceptibilities.

In Table II we have compiled the assignments of the infrared bands most useful for establishing the coordination mode of the ligands. Bands associated with the water molecule of the tetrafluoroborate solid isolated with 3MMH indicate it to be lattice water rather than coordinated water, and therefore, it is omitted from the rest of the Tables. For the first four complexes of Table II ν(NH) appears at higher energy than in the spectrum of the pure ligands, but the opposite is true for the four halide solids. The former complexes do not involve amine coordination, but the four halide solids apparently do since they are monomeric. The presence of strong bands at higher energy assignable to ν(NH) for the first four solids can be explained in terms of reduced hydrogen bonding in these solids compared to that found in the pure ligand. In the spectra of the four halide solids bands are observed at much lower energy indicating amine coordination [20]. Therefore, these halogen complexes represent the first examples of amine coordination by neutral 2-alkylaminopyridine *N*-oxide ligands (or 2-amino-n-picoline *N*-oxide ligands) of the many compounds studied [1–12].

In both series of complexes ν(NO) shifts to lower energy upon coordination, which indicates bonding to the copper(II) centers via the *N*-oxide oxygen [21]. The much greater shift of this band in the spectra of the halogen solids must be due to both the reduced steric requirements of halo ligands compared to *N*-oxide ligands and the chelation of the *N*-oxide ligand. As is usually the case, the δ(NO) mode undergoes only small shifts in energy upon complexation because of two opposing factors [22]. However, the halide solids have this band at significantly lower energy than the remaining complexes of this study as has been observed previously for chelating *N*-oxide ligands [23]. Similarly, the band that we have assigned as owing most of its intensity to the copper–oxygen stretching mode is also at substantially lower energy for the halide solids. While this band is usually found at lower energy for those complexes including ligands other than *N*-oxides in their coordination sphere the difference is usually much less pronounced [1–12].

TABLE II. Infrared Assignments (cm^{-1}) for the Copper(II) Complexes of 2-Methyamino-3-picoline *N*-oxide(3MMH) and 2-Ethylamino-3-picoline *N*-oxide(3MEH)

Compound	ν(NH)[a]	δ (NH)	ν(NO)	δ (NO)	ν(CuO)	ν(CuX)	ν(CuN)
3MM	3270s	1604s	1243s	825sh			
$[Cu(3MMH)_4](BF_4)_2$	3348s	1620s	1236s	830m	433m		
3ME	3258s	1602s	1240s	836s			
$[Cu(3MEH)_4](BF_4)_2$	3320m	1618s	1224s	840m	437m		
$[Cu(3MMH)_4](NO_3)_2$	3297m	1616s	1228m	828m	428m		
$[Cu(3MEH)_2(NO_3)_2]$	3331s	1613s	1225s	829m	438m	338s	
$[Cu(3MMH)Cl_2]$	3140m 3118sh	1598w	1169sh	824m	378m	314s 288s	288s 275sh
$[Cu(3MEH)Cl_2]$	3090m 3070sh	1597w	1174sh	822m	380m	322sh 310s	283m
$[Cu(3MMH)Br_2]$	3135m	1601sh	1172m	826m	375m	257m 248m 239m	290s 275sh
$[Cu(3MEH)Br_2]$	3095sh 3082m	1598w	1170sh	822m	380m	250m 243sh	280sh 274s
$[Cu(3MM)_2]$			1215s	838m	412m		338m 320m
$[Cu(3ME)_2]$			1199s	836m	439m		346m 320m

[a] The ν(NH) bands of the halogen solids were assigned from fluorolube spectra.

TABLE III. Electronic Spectral Band Assignments (cm^{-1}) for the Copper(II) Complexes of 2-Methylamino-3-picoline *N*-oxide (3MMH) and 2-Ethylamino-3-picoline *N*-oxide (3MEH)

Compound	Intraligand	Charge transfer	d–d
$[Cu(3MMH)_4](BF_4)_2$	32260	27620; 23260	16390
$[Cu(3MEH)_4](BF_4)_2$	31950	27320; 22830	16230
$[Cu(3MMH)_4](NO_3)_2$	31850	27620; 22730	16260
$[Cu(3MEH)_2(NO_3)_2]$	30960	26950; 21600	14640
$Cu(3MMH)Cl_2$	36760	28010	14730
$Cu(3MEH)Cl_2$	35970	28170	15900
$Cu(3MMH)Br_2$	32260	21650 (Br → Cu)	14730
$Cu(3MEH)Br_2$	31150	21370 (Br → Cu)	14900
$[Cu(3MM)_2]$	35910	28410; 26180; 23810	19230; 13700
In $CHCl_3$[a]		28820; 27700; 23200	18940; 13420
		(5540) (7130)	(67) (40)
$[Cu(3ME)_2]$	36630	27930; 26100; 23980	18420; 13530
In $CHCl_3$		29850; 27930; 23150	18730; 13590
		(5580) (4570) (6950)	(59) (39)

[a] Numbers in parentheses below the band energies are molar absorptivities.

We have tentatively assigned ν(CuN) bands in the spectra of all of the halide complexes as well as the molecular complexes. The latter complexes appear to have this band above 300 cm^{-1} which is consistent with the reported 342 cm^{-1} for an amide nitrogen [24]. For the halide solids we suggest that this band is in the 270–290 cm^{-1} region based in part on the assignment of ν(CuCl) and ν(CuBr) for a 4-coordinate Cu(II) complex at energies above 300 cm^{-1} and below 260 cm^{-1}, respectively [25]. The remainder of the infrared assignments will be considered in our discussion of the individual complexes. Also, the results of the electronic (Table III) and electron spin resonance (Table IV) spectra will be discussed as well as previously reported information for related complexes.

TABLE IV. Electron Spin Resonance Parameters of some Copper(II) Complexes of 2-Methylamino-3-picoline *N*-oxide(3MMH) and 2-Ethylamino-3-picoline *N*-oxide(3MEH)

Compound	Temperature	g_1 or $g_\parallel$	g_2	g_3 or $g_\perp$	g_{av} or g_{iso}
$[Cu(3MMH)_4](BF_4)_2$	RT[a]	2.245		2.059	2.121
	77 K	2.242		2.057	2.119
$[Cu(3MEH)_4](BF_4)_2$	RT	2.230		2.059	2.116
	77 K	2.241		2.059	2.120
$[Cu(3MMH)_4](NO_3)_2$	RT	2.247		2.061	2.123
	77 K	2.242		2.060	2.121
$[Cu(3MEH)_2(NO_3)_2]$	RT	(2.247)		2.059	(2.122)
	77 K	(2.258)		2.058	(2.125)
$Cu(3MMH)Cl_2$	RT	2.242		2.055	2.117
	77 K	2.242		2.054	2.117
$Cu(3MEH)Cl_2$	RT	2.191	2.115	2.054	2.120
	77 K	2.189	2.115	2.055	2.120
$Cu(3MMH)Br_2$	RT	2.200	2.083	2.035	2.106
	77 K	2.200	2.086	2.035	2.107
$Cu(3MEH)Br_2$	RT				2.152
	77 K				2.133
$[Cu(3MM)_2]$	RT				2.085
	77 K				2.087
$[Cu(3ME)_2]$	RT				2.077
	77 K				2.077

[a] RT, room temperature.

$[Cu(3MMH)_4](BF_4)_2$, $[Cu(3MEH)_4](BF_4)_2$ and $[Cu(3MMH)_4](NO_3)_2$

As with previous complexes prepared from $Cu(BF_4)_2$ and related ligands, there is no indication of coordination of the tetrafluoroborate anions. $\nu_3(BF_4)$ is observed as a broad, intense band at *ca.* 1070 cm^{-1} and $\nu_4(BF_4)$ as a sharp, medium intensity band at *ca.* 525 cm^{-1} in the spectra of both complexes. Likewise the nitrate ions are not bound directly to the Cu(II) center in $[Cu(3MMH)_4](NO_3)_2$ since none of the bands associated with coordinated nitrato ligands are observable in its spectrum. For example, there is a single, broad band at 1745 cm^{-1} assignable to $\nu_1 + \nu_4$ of an ionic nitrate and the ν_3 band is located at *ca.* 1370 cm^{-1}. Therefore, although the molar conductivity value found for this compound suggests it to be a 1:1 electrolyte, its infrared spectrum does not indicate the presence of coordinated nitrate ions. The observance of the ν(NH) band at considerably lower energy for this solid in comparison to that of $[Cu(3MMH)_4](BF_4)_2$ indicates greater hydrogen bonding to the nitrate ions and may explain, in part, the lower conductivity value for this solid.

The three solids all have comparable d–d transition energies and ESR parameters confirming the similarity of their bonding and stereochemistry. As with previously studied *N*-oxide complexes, the energies of the d–d band maxima are higher and the values of $g_\parallel$ lower than is normally found for a CuO_4 chromophore [26]. In Table V some spectral parameters of the two tetrafluoroborate solids are compared with those of a number of related tetrafluoroborate solids. Like the solid prepared with 2-amino-3-picoline *N*-oxide(3MAH), the energy of ν(CuO) is higher for both of the present solids showing the strongest bonding for the ligands having the methyl group in the 3-position compared to the 6-position or the absence of the methyl group. This effect must be in part due to steric factors hindering the interaction of the tetrafluoroborate anions with the Cu(II) center as well as interaction of the Cu(II) with *N*-oxide oxygens on adjacent Cu(II) centers. Both of these interactions would be expected to occur in the axial positions of the CuO_4 chromophore and would thereby increase the coordination number and reduce the strength of the four existing copper–oxygen bonds. This steric factor along with the ample electron density available in the ring allows the copper–oxygen bond to be extremely strong in this series of aromatic *N*-oxide complexes. This is confirmed by the high values found for the maximum of the d–d envelope and the low values found for $g_\parallel$.

$[Cu(3MEH)_2(NO_3)_2]$

We were unable to prepare a compound of this same stoichiometry with 3MMH, but have previously isolated compounds with two nitrato ligands and the

TABLE V. A Spectral Comparison of CuO_4 Chromophores formed by Various 2-Aminopyridine *N*-oxide Ligands[a]

Compound	ν(CuO) (cm^{-1})	ν(d–d) (cm^{-1})	$g_{\parallel}$	Reference
$[Cu(AH)_4](BF_4)_2$	408	16810	2.255	2
$[Cu(MH)_4](BF_4)_2$	408	15670	2.232	8
$[Cu(EH)_4](BF_4)_2$	398	16530	2.246	9
$[Cu(3MAH)_4](BF_4)_2$	432	17120	2.240	3
$[Cu(3MMH)_4](BF_4)_2$	433	16390	2.245	this work
$[Cu(3MEH)_4](BF_4)_2$	437	16230	2.230	this work
$[Cu(6MAH)_4](BF_4)_2$	424	15430; 14290 sh	2.236	6
$[Cu(6MMH)_4](BF_4)_2$	399	15870	2.227	12

[a] AH = 2-aminopyridine *N*-oxide; MH = 2-methylaminopyridine *N*-oxide; EH = 2-ethylaminopyridine *N*-oxide; 3MAH = 2-amino-3-picoline *N*-oxide; 6MAH = 2-amino-6-picoline *N*-oxide and 6MMH = 2-methylamino-6-picoline *N*-oxide.

following three *N*-oxide ligands: 2-isopropylaminopyridine *N*-oxide(IPH) [11], 2-amino-6-picoline *N*-oxide(6MAH) [6] and 2-amino-3-picoline *N*-oxide (3MAH) [3]. The former ligand yielded a dimeric species, presumably with bridging *N*-oxide ligands, while the latter two *N*-oxides gave 4-coordinate monomeric CuO_4 species with both monodentate nitrato and *N*-oxide ligands.

The appearance of a strong band at 1011 cm^{-1}, which can be assigned to $\nu_1(NO_3)$ [27], and a strong band at 338 cm^{-1}, which is assignable to ν(CuO) [28], as well as the remaining bands associated with a nitrato ligand, confirm its coordination. The 1700–1800 cm^{-1} region is often considered diagnostic for the mode of nitrate coordination [29]. The spectrum of the present compound has a weak band at 1745 cm^{-1} and a shoulder located at 1738 cm^{-1} and the difference of 7 cm^{-1} is indicative of monodentate coordination. This suggests that this complex is a 4-coordinate Cu(II) species with two *N*-oxide ligands and two monodentate nitrato ligands similar to the two $[CuL_2(ONO_2)_2]$ compounds formed previously [3, 6]. The spectral parameters of the three solids are comparable. The presence of only one ν(CuO) band for each ligand suggests a *trans* arrangement. The non-electrolytic behavior of this solid in solution as well as the magnetic susceptibility are consistent with the proposed stereochemistry. The ESR parameters and energy of the d–d envelope indicates the nitrato ligands to be bound more weakly than the aromatic *N*-oxide ligands when the values for this complex are compared to those reported in Tables III and IV for $[Cu(3MEH)_4](BF_4)_2$.

[Cu(3MMH)Cl_2], [Cu3MEH)Cl_2], [Cu(3MMH)Br_2] and [Cu(3MEH)Br_2]

As mentioned earlier the colors of these four solids are different than any of the previous compounds prepared from copper(II) halides [2–12]. All of these previously studied solids had a ν(NH) band observable in their spectra above 3250 cm^{-1} indicating an absence of coordination by the amine nitrogen. However, the spectra of the present four solids do not have any bands in that energy region and the ν(NH) bands were assigned from fluorolube mull spectra. We have confidence in our assignment based on a comparison of the fluorolube spectra of $Cu(3MM)_2$ and $Cu(3ME)_2$ with the spectra of these four solids. The ν(NH) bands are at an energy indicative of amine coordination [20] and the coordination sphere for these four solids can be represented by $Cu(ON)X_2$. These four solids are the first examples of Cu(II) complexes having coordination of the amine group, and therefore, bidentate coordination, when the neutral amine group possesses a hydrogen [2–12]. In all of the previous compounds the hydrogen(s) must be involved in hydrogen bonding thereby making the nitrogen's electron pair improperly positioned for coordination. However, the steric factor of the methyl group on the 3-position on the ring must alter that situation in the present compounds.

A second band in Table II associated with the coordination of the amine group is the δ(NH) mode which is at lower energy in the spectra of these four complexes by *ca.* 15 cm^{-1} than for the other solids of this study. In addition, we have tentatively assigned bands to ν(CuN) in the 275–290 cm^{-1} region of the spectrum. Further, there is an absence of bands in this region of the spectra of the complexes prepared with copper(II) salts having polyatomic anions.

Both bands associated with the *N*-oxide function are found at lower energy in the spectra of these halide solids than the previously discussed solids of this study. Chelation by 2-dialkylaminopyridine *N*-oxides [13, 14] caused these two bands to be found at lower energy than for the related 2-alkylaminopyridine *N*-oxides which are monodentate [8, 9]. In addition, the complexes having bidentate 2-dialkylaminopyridine *N*-oxide ligands have the ν(CuO) band at considerably lower energy than the complexes of 2-alkylaminopyridine *N*-oxides. They are found at

TABLE VI. A Comparison of Spectral and Covalency Parameters of a Series of Molecular Cu(II) Complexes

Compound	ν(d–d) (cm^{-1})	$g_\parallel$	$g_\perp$	$A_\parallel \times 10^{-4}$ (cm^{-1})	$k_\parallel$	$k_\perp$	α^2	Reference
[CuA_2]	17860 13120	2.183	2.054	173	0.60	0.75	0.72	16
[Cu(3MA)$_2$]	17700 13190			dimer				3
[Cu(4MA)$_2$]	17760 12820	2.187	2.054	170	0.61	0.74	0.72	16
[Cu(5MA)$_2$]	18120 13190	2.211	2.045	160	0.64	0.68	0.71	16
[Cu(6MA)$_2$]	17730 13120	2.196	2.044	167	0.63	0.69	0.72	16
[CuM_2]	17860 13040	2.199	2.043	169	0.63	0.68	0.73	16
[CuE_2]	18520 13300	2.191	2.047	177	0.62	0.70	0.74	16
[Cu(3MM)$_2$]	18940 13420			dimer				this work
[Cu(3ME)$_2$]	18730 13590	2.180	2.041	193	0.59	0.66	0.77	this work
[Cu(6MM)$_2$]	18830 13550	2.169	2.046	185	0.54	0.87	0.75	12

essentially the same energy as is found for these four solids (Table VI). The ν(CuX) bands for these four complexes are also found in the same region [13, 14] as well as at energies usually associated with terminal halogens of 4-coordinate copper(II) centers [25].

The energies of the d–d bands are somewhat higher than those reported for the $CuONX_2$ chromophores prepared with 2-dialkylaminopyridine *N*-oxides [13, 14], but both types of complexes have intense ESR signals consistent with their monomeric nature. Low solubility in nonpolar solvents and apparent reaction with polar solvents (*i.e.*, color change) have frustrated our attempts to grow crystals for structural studies to date. A weak ESR signal was obtained from a methanolic solution of Cu(3MMH)-Cl_2, but its $g_0 = 2.23$ and $A_0 = 58$ G are more likely those of a CuO_4 or CuO_3N chromophore indicating decomposition of the complex.

This bonding via the amine nitrogen is the first example of coordination by a 2-alkylamino (or 2-amino) group. These solids might be expected to have similar spectral parameters to those of Cu(DM)X_2 and Cu(DE)X_2 (DM = 2-dimethylaminopyridine *N*-oxide and DE = 2-diethylaminopyridine *N*-oxide). However, the considerably lower energy of the ν(CuN) band as well as the difference in the maximum of the d–d energy suggests stereochemical differences. However, the blue [Cu(DM)Cl_2] was thought to approach tetrahedral symmetry [13] while the yellow green [Cu(DE)Cl_2] and [Cu(6MDM)-Cl_2] (6MDM = 2-dimethylamino-6-picoline *N*-oxide) [12] were proposed to be more planar. Therefore, we expect that all of these solids would more closely approach planar symmetry, but that their lack of similarity to the previous solids [12–14] is due to the weaker bonding of the amino function.

[Cu(3MM)$_2$] and [Cu(3ME)$_2$]

As indicated earlier we have previously prepared and spectrally characterized a number of molecular solids of this type with related ligands [3, 7, 12, 16]. Most of these solids were tan or olive in color, all were non-electrolytes and were soluble in nonpolar solvents such as $CHCl_3$. The present solids have these same properties and our approximate magnetic susceptibility values confirm their monomeric nature. Compared to the other compounds of this study, these two solids have ν(NO) at a range intermediate between the halide compounds and the solids prepared with polyatomic anions. Similarly, the energies of the ν(CuO) bands are also intermediate in energy while the ν(CuN) band is at higher energy for these deprotonated amine groups than for the neutral amine groups of the halide complexes.

The separation of the two d–d bands in the electronic spectra of both compounds is an indication of an essentially square planar Cu(II) complex [30]. A preliminary report of the single crystal X-ray study for the related [CuE_2] (E = deprotonated 2-ethylaminopyridine *N*-oxide) shows it to be rigorously square planar [31]. [CuE_2] had d–d band energies of 18250 and 13550 cm^{-1} [16] which are comparable to the energies for these two compounds shown in Table III. Charge transfer bands to Cu(II) from lone pairs on both the coordinating oxygen and nitrogen atoms are expected in the 23000–30000 cm^{-1} region of the spectrum. In the spectra of the previously studied molecular compounds we were usually able to observe only two bands in this region and assigned the lower energy band to the transfer from oxygen based on observance of a band in this energy region of the spectra of Cu(II) complexes when *N*-oxide oxygens were the only donor atoms. However, in this study even those compounds (*i.e.*, the first three compounds in Table III) have two bands observable in the region. A comparison of the spectra of these two groups of compounds does lead us to suggest that the lowest energy band of the three is charge transfer from oxygen and that one of the two higher energy bands is from nitrogen.

Like many of the previously studied molecular solids involving chelation of the deprotonated 2-aminopyridine *N*-oxide (or picoline *N*-oxide), these two solids have a broad isotropic ESR signal suggesting considerable interaction between Cu(II) sites. In $CHCl_3$ solution the familiar four line spectrum with $g_o = 2.098$ and $A_o = 70$ G is observed for both compounds. In frozen $CHCl_3$ the two solids give very different spectra. [$Cu(3ME)_2$] has a typical axial Cu(II) spectrum of a monomer with the following parameters: $g_{\parallel} = 2.180$, $g_{\perp} = 2.041$, $g_{av} = 2.087$ and $A_{\parallel} = 190$ G. However, [$Cu(3MM)_2$] like [$Cu(3MA)_2$] [3] shows the spectrum of a dimer in frozen $CHCl_3$. The values for g_D and D are 2.130 and 357 G, respectively. The formation of a dimer (actually a mixture of a monomer and a dimer) in frozen chloroform by [$Cu(3MA)_2$] was the first example of this behavior among this group of compounds. The formation of a dimer is evidently favored by having a methyl group in the 3-position on the ring and it appears that the bulkiness of the ethyl group is sufficient to prevent dimer formation while the methyl on the amine nitrogen is not. It should be noted that the dimer spectrum is only observed with rapid freezing and not when the temperature is slowly lowered using a variable temperature apparatus. Slow cooling gives the typical axial signal of a solid copper-(II) complex.

The orbital reduction factors $k_{\parallel} = 0.59$ and $k_{\perp} = 0.66$ for [$Cu(3ME)_2$] have been calculated as reported previously [16] using equations based on the work of Figgis [32]. They and some of the spectral parameters involved in their calculation are shown in Table VI for this and related compounds. Although the parameters for [$Cu(3ME)_2$] are not as extreme as was found for [$Cu(6MM)_2$], they do suggest somewhat weaker σ-bonding, but stonger π-bonding for this solid. Therefore, there is some alteration of the coordination of the Cu(II) centers both by substitution on the ring as well as substitution on the amine nitrogen in this type of complex.

Conclusions

Both of these ligands show a strong tendency to resist the formation of dimeric or polymeric Cu(II) complexes. As opposed to the previously studied 2-aminopyridine or 2-aminopicoline *N*-oxide ligands possessing one or more hydrogens on the 2-amino group, these ligands acted as O, N bidentate ligands in their halide complexes. In addition, the bonding of the *N*-oxide oxygen to the various copper(II) centers was the strongest for these two ligands along with 3MA based on ν(CuO) as well as the energy of the d–d maxima and $g_{\parallel}$. Therefore, the position of the methyl group on the ring is significant both in the mode of coordination as well as the strength of the coordinate bond.

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