Inorganica Chimica Acta, 104 (1985) 161–169

2-Methyl- and 2-Dimethylamino-6-picoline N-oxide Complexes Formed from Various Copper(II) Salts

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Received February 14, 1985

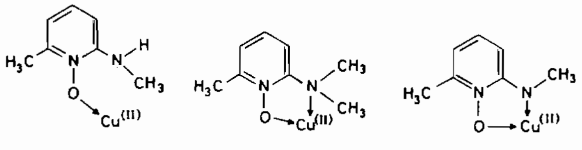
Abstract

Copper(II) complexes with 2-methylamino-6-picoline N-oxide (6MM) and 2-dimethylamino-6-picoline N-oxide (6MDM) have been prepared from the following salts: perchlorate, tetrafluoroborate, nitrate, chloride and bromide. A number of different ligand to copper(II) preparative stoichiometries were attempted and the isolated solids were characterized using spectral methods (*i.e.*, IR, UV–Vis and ESR). The 6MDM ligand coordinates via both the N-oxide oxygen and the amine nitrogen, but 6MM bonds to the various copper(II) centers solely by its N-oxide oxygen. However, deprotonation of 6MM does allow this ligand to bind in a bidentate fashion.

Introduction

2-aminopyridine N-oxide [1, 2], 2-aminopicoline N-oxides [3–5] and 2-alkylaminopyridine N-oxides [6–9] have all been found to bond to copper(II) primarily as monodentate ligands via the N-oxide oxygen. In contrast, 2-dialkylaminopyridine N-oxide ligands [10] coordinate in a bidentate manner by including the amino group in the coordination sphere. 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 [11] and a series of molecular bis(ligand)copper(II) complexes have been prepared and characterized [12]. The alkyl group(s), both on the amine nitrogen and 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-6-picoline N-oxide (6MM) and 2-dimethylamino-6-picoline N-oxide (6MDM) which are shown in Fig. 1. Also shown in Fig. 1 is a representation of the deprotonated ligand, (6MM-H). Comparisons with previous Cu(II) complexes of related N-oxide ligands will be included in our discussion of this series of complexes which are thought to be the first involving alkyl- and dialkyl-substituted 2-aminopicoline N-oxide ligands.



6MM 6MDM 6MM-H

Fig. 1. The ligands 6MM, 6MDM and 6MM-H with their bonding to Cu(II) illustrated.

Experimental

The 6MM and 6MDM ligands were prepared by amination of 2-chloro-6 picoline N-oxide. The amination process and the ensuing isolation of the products was carried out as reported previously [6, 10]. Oxidation of 2-chloro-6-picoline (Aldrich) was accomplished by following the procedure of Katritzky [13]. The copper(II) complexes were isolated from anhydrous ethanol solution, washed with anhydrous ether and stored in a vacuum desiccator over calcium sulfate. The method of characterization of the complexes was the same as in previous studies from this laboratory [6].

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 and molar conductivities. In addition, we have prepared solids with copper(II) perchlorate of both ligands but the violet solid formed with 6MDM **violently exploded** during an elemental analysis determination. We presume that the stoichiometries for both perchlorate solids are identical to the analogous tetra-

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0020-1693/85/$3.30

TABLE I. Colors, Partial Elemental Analyses and Molar Conductivities for Copper(II) Complexes 2-Methyl- and 2-Dimethylamino-6-Picoline N-oxides, 6 MM and 6MDM, respectively.

Compound	Color	% Calculated (% Found)			ΛM[a] (ohm^{-1} cm^2 mol^{-1})
		C	H	N	
$[Cu(6MMO_4](BF_4)_2 \cdot H_2O$	green	41.6(40.9)	5.2(5.1)	13.9(13.5)	206
$[Cu(6MM)_3(NO_3)](NO_3)$	green	41.9(41.5)	5.0(5.0)	18.6(18.4)	168
$[Cu(6MM)Cl_2]$	dark brown	30.8(32.2)	3.7(3.8)	10.3(10.5)	16
$[Cu_2(6MM)_3Br_4]$	dark violet	29.3(28.7)	3.5(3.7)	9.3(8.4)	94
$[Cu(6MM\text{-}H)_2]$	beige	49.8(49.6)	5.4(5.5)		2
$[Cu(6MDM)_2](BF_4)_2 \cdot H_2O$	violet	34.3(34.4)	4.7(4.3)	10.0(9.8)	221
$[Cu(6MDM)_2(NO_3)_2] \cdot H_2O$	light blue	37.7(38.4)	5.1(5.6)	16.5(16.1)	142
$[Cu(6MDM)Cl_2]$	yellow green	33.5(33.7)	4.2(5.0)	9.8(9.1)	8
$[Cu(6MDM)Br_2]$	orange	25.6(25.7)	3.2(3.1)	7.5(7.4)	13

[a] *ca.* 10^{-3} M acetonitrile solutions.

TABLE II. Infrared Band Assignments (cm^{-1}) for 6MM and 6MDM and their Copper(II) Complexes.

Compound	ν(NH)	ν(NO)	δ(NO)	ν(CuO)	ν(CuN)	ν(CuX)
6MM	3325s	1219s	830s			
$[Cu(6MM)_4](BF_4)_2 \cdot H_2O$	3465m	1203s	832s	399vs		
$[Cu(6MM)_3(NO_3)](NO_3)$	3390s	1204s	830s	399s 391sh		307s
$[Cu(6MM)Cl_2]$	3439s 3400s	1200s 1193sh	835s	400s		329s 309s
$[Cu_2(6MM)_3Br_4]$	3310mb	1197sh 1189s	827s	392s		253m (225s)
$[Cu(6MM\text{-}H)_2]$		1183s	820s	435m	328s	
6MDM		1236sh	839s			
$[Cu(6MDM)_2](BF_4)_2 \cdot H_2O$		1222s	838m	388m	336s	
$[Cu(6MDM)_2(NO_3)_2] \cdot H_2O$		1219m	831s	394m	338m	317s
$[Cu(6MDM)Cl_2]$		1214s	832s	382s	343m	328s 318sh
$[Cu(6MDM)Br_2]$		1214s	833	384s	340m	259m 221s

fluoroborate solids of this study based on the various spectral measurements. As was found with similar ligands of previous series [2–10], complexes prepared from tetrafluoroborate salts of copper(II) involve only the ligand in the coordination sphere of the metal ion which is consistent with their 1:2 electrolytic behaviour [14]. With the exception of $[Cu(6MM\text{-}H)_2]$ the remaining solids of this study involve coordination of the anions and behave as either 1:1 electrolytes (*e.g.*, both nitrate solids) or non-electrolytes. The stoichiometries of the compounds shown in Table I suggest that the coordination of the ligands occurs in the manner indicated in Fig. 1.

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 water molecules in three of the complexes indicate the presence of lattice rather than coordinated water. For this reason we need not consider the water molecules again in this report and their formulas have been omitted from the rest of the Tables. For the majority of the 6MM complexes ν(NH) appears at higher energy than in the spectrum of the pure ligand. This indicates non-coordination of the amine nitrogen and a reduction in hydrogen bonding in comparison to the free ligand.

Similar to the relationship between 2-methylaminopyridine N-oxide and 2-dimethylaminopyridine N-oxide, M and DM respectively, the spectrum of 6MM shows ν(NO) at lower energy than the spectrum of 6MDM due to the former ligand's involvement in hydrogen bonding. Since both M and 6MM are solids and M yields trapped radical pairs upon exposure to γ-radiation [15], the hydrogen bonding is also expected to be intermolecular for 6MM. It should be noted that ν(NO) for both DM and 6MDM are found at lower energies than in the spectrum of pyridine N-oxide due to the electron donating capability of the amino groups [16]. In both series of complexes studied in this work, ν(NO) shifts to lower enrgy upon coordination, which indicates bonding to the Cu(II) centers via the N-oxide oxygen [17]. As shown in Table II the magnitude of the energy change upon coordination is approximately the same for the two ligands. It should be pointed out that the lowest energy ν(NO) band occurs for $[Cu(6MM\text{-}H)_2]$. This is consistent with this substance being a planar, 4-coordinate CuO_2N_2 chromophore similar to $[Cu(E\text{-}H)_2]$ [18] (*i.e.*, E = 2-ethylaminopyridine N-oxide). The δ(NO) mode usually undergoes no shift in energy upon complexation due to opposing factors [19]. However, even though the shifts in energy are small, there is generally an increase in energy for the complexes of 6MM (coordination via the N-oxide only) and a decrease when there is bidentate ligand formation (*i.e.*, 6MDM and 6MM-H). Previous bidentate ligands have shown a slight increase in the energy of this mode [20], but a reduction in steric factors due to less crowding must be more important than the chelation for this series of complexes.

Consistent with the lower energy of the ν(NO) band for the complexes of 6MM, the ν(CuO) bands are found at higher energy, when compared to 6MDM. This indicates stronger bonding via the N-oxide oxygen for 6MM than for 6MDM. For the 6MDM complexes the accompanying coordination of the amine nitrogen yielding bidentate ligands presumably weakens the oxygen coordination. Coordination of the amine nitrogen is confirmed by an infrared band in the 335–345 cm^{-1} region in the spectra of the 6MDM complexes [10]. The ranges of ν(CuN) for the complexes of DM and DE were 310–351 and 305–358 cm^{-1}, respectively. Similarly, $[Cu(6MM\text{-}H)_2]$ has a band in its spectrum at 328 cm^{-1} assignable to ν(CuN) that is in good agreement with a band at 342 cm^{-1} proposed for an amide nitrogen complexed to Cu(II) [21].

TABLE III. Electronic Spectral Band Assignments (cm^{-1}) for the Cu(II) Complexes of 6MM and 6MDM.

Compound	ν(C.T.)	ν(d–d)
$[Cu(6MM)_4](BF_4)_2$	22730	15870
$[Cu(6MM)_3(NO_3)](NO_3)$	22370	13930
$[Cu(6MM)Cl_2]$	20410	12990
$[Cu_2(6MM)_3Br_4]$	21740 19610	13160
$[Cu(6MM\text{-}H)_2]$	27620 26180	18830 13550
$[Cu(6MDM)_2](BF_4)$	27020sh	18520 15870sh
$[Cu(6MDM)_2(NO_3)_2]$	17020sh	16390 14080sh
$[Cu(6MDM)Cl_2]$	26180 23580	12660
$[Cu(6MDM)Br_2]$	27030 22220	11900

The complexes having coordinated anions have one or more bands assignable to ν(CuX) modes and will be considered in our discussion of the individual complexes. Also, the results of the electronic (Table III) and electron spin resonance (Table IV) studies

TABLE IV. Electron Spin Resonances Parameters for the Copper(II) Complexes of 6MM and 6MDM.

Compound	Temperature	$g_{\parallel}$ or $g_{\perp}$	g_2	$g_{\perp}$ or g_3	g_{av}
$[Cu(6MM)_4(BF_4)_2$	RT	2.227		2.052	2.110
	77 K	2.218		2.050	2.106
$[Cu(6MM)_3(NO_3)]NO_3$	RT	2.270		2.051	2.124
	77 K	2.260		2.066	2.131
$[Cu(6MM)Cl_2]$	RT	2.232	2.074	2.032	2.103
	77 K	2.269	2.072	2.029	2.100
$[Cu_2(6MM)_3Bi_4]$	RT			g_{iso} = 2.138	
	77 K			g_{iso} = 2.122	
$[Cu(6MM\text{-}H)_2]$	RT	2.143		2.068	2.093
	77 K	2.142		2.067	2.092
$[Cu(6MDM)_2](BF_4)_2$	RT	(2.210)	2.078	2.048	(2.112)
	77 K	(2.205)	2.080	2.051	(2.112)
$[Cu(6MDM)_2(NO_3)_2]$	RT	2.173	2.109	2.050	2.111
	77 K	2.181	(2.134)	2.054	(2.123)
$[Cu(6MDM)Cl_2]$	RT	2.279		2.072	2.141
	77 K	2.273		2.067	2.136
$[Cu(6MDM)Br_2]$	RT	2.250	2.086	2.053	2.130
	77 K	2.249		2.062	2.124

will be discussed as well as previously reported information for related complexes.

[Cu(6MM)$_4$](BF$_4$)$_2$

As with previous complexes prepared from Cu(BF$_4$)$_2$ and related ligands, there is no indication of coordination of the tetrafluoroborate ions. $\nu_3(BF_4)$ is observed as a broad, intense band at 1068 cm^{-1}, and $\nu_4(BF_4)$ is found in combination with another band at *ca.* 565 cm^{-1}. In addition, the molar conductivity value is consistent with this solid behaving as a 1:2 electrolyte [14]. Therefore, this CuO$_4$ chromophore can be expected to be similar in nature to the complexes [Cu(M)$_4$](BF$_4$)$_2$ [6] and [Cu(6MA)$_4$](BF$_4$)$_2$ [5] where M refers to 2-methylaminopyridine N-oxide and 6MA to 2-amino-6-picoline N-oxide. A comparison of the spectral parameters for these and related complexes [2], as well as the present tetrafluoroborate solid are shown in Table V. With the exception of [Cu(A)$_4$](BF$_4$)$_2$, there is a decrease in the energy of ν(CuO) with increasing substitution. This is apparently due to steric hindrance affecting the coordination of the N-oxide oxygen. Since [Cu(6MA)$_4$](BF$_4$)$_2$ has the highest energy for the ν(CuO) band followed by the 4MA complex, it can be suggested that an electron donating effect by the methyl group in these positions strengthens the metal–ligand bonding. Lending credibility to this suggestion is the knowledge that the analogous compounds prepared with 3MA and 5MA have ν(CuO) at essentially the same position in their spectra as [Cu(A)$_4$](BF$_4$)$_2$. Although the alkyl groups on the ring appear not to provide a measurable steric effect, alkyl substitution on the amino function does sterically hinder the metal–ligand bonding since ν(CuO) is lowered to 391 cm^{-1} for [Cu(P)$_4$](BF$_4$)$_2$ (P = 2-propylaminopyridine N-oxide) [8].

TABLE V. A Spectral Comparison of CuO$_4$ Chromophores with Various 2-aminopyridine N-oxide Ligands.

Compound	ν(CuO)^a	ν(d–d)^a	$g_\parallel$
[Cu(A)$_4$](BF$_4$)$_2$	408	16,810	2.255
[Cu(6MA)$_4$](BF$_4$)$_2$	424	15,430 14,290sh	2.236
[Cu(M)$_4$](BF$_4$)$_2$	408	15,670	2.232
[Cu(6MM)$_4$](BF$_4$)$_2$	399	15,870	2.227

^{a}Units are cm^{-1}.

Although the ν(d–d) band maxima of copper(II) complexes is often cited as an indicator of coordinate bond strength, it is important to note that this is a combination of three d–d transitions and, therefore, may not be as sensitive to the strength of the bonding as other spectral parameters. It is known that distortion from square planar toward tetrahedral symmetry as well as an increased coordination number, such as bonding in the axial positions of an essentially square planar species, lowers the energy of the d–d envelope maximum. Substitution on the amino group with increasingly larger alkyl substituents was cited as a hindrance to axial bonding and, therefore, the reason for the increase in ν(d–d) with increasing size of the alkyl substituent [8]. However, the complex formed with A (A = 2-aminopyridine N-oxide) had its ν(d–d) maximum at approximately the same energy as the complex of the more sterically hindered P (2-propylaminopyridine N-oxide). A plausible explanation for this behavior is the greater possibility of hydrogen bonding by the A ligand's two hydrogens to the BF$_4^-$ ions which would reduce the tendency of the anion to interact with the Cu(II) center in the axial positions. Substitution on the pyridine N-oxide ring must also cause steric hindrance to the axial bonding of the anions since their d–d spectra often show a resolved shoulder [3–5]. Observation of this low energy shoulder is often cited as an indication of an essentially square planar Cu(II) complex [22]. Therefore, substitution at the six position as well as on the amine nitrogen does provide steric hindrance to axial interaction and promotes the formation of more planar complexes. A similar discussion could be made based on the values listed for $g_\parallel$ of the solid state ESR spectra shown in Table V.

[Cu(6MM)$_3$(NO$_3$)]NO$_3$

Although we have often isolated a solid of stoichiometry [CuL$_4$](NO$_3$)$_2$ with related ligands in previous studies [2–10], we have to date been unable to achieve a nitrate solid with four 6MM ligands per copper ion. This suggests that the greater steric requirements of the 6MM ligand allow the weakly coordinating nitrate ion to compete favorably for the fourth coordination site. Therefore, with only very weakly coordinating anions such as BF$_4^-$ and ClO$_4^-$ can we expect to isolate CuL$_4$ complexes with ligands having these steric requirements. In addition, we have on occasion isolated a solid having the stoichiometry [CuL$_2$(NO$_3$)$_2$], such as the dimeric [Cu(IP)$_2$(NO$_3$)$_2$] [9], but this stoichiometry has also proven elusive with the 6MM ligand.

In the formula heading this section we show one of the nitrates as coordinated and the other as ionic. Our proposal is based on the following information: a Λ_M consistent with a 1:1 electrolytic behavior [14], three bands at 1793, 1779 and 1763 cm^{-1} in the $\nu_1 + \nu_4$ region of the solid's infrared spectrum, and a strong band at 307 cm^{-1} assignable to ν(CuO) of a coordinated nitrato ligand [23, 24]. The $\nu_1 + \nu_4$ spectral region is often cited as being diagnostic for the mode of coordination of nitrato ligands [25]. Since the band at 1763 cm^{-1} is approximately twice as intense as the two higher energy bands, it is probably due to the ionic nitrate ion. Therefore, the remaining bands can be assigned to the coordinated nitrate group and the energy difference of 14 cm^{-1} is consistent with monodentate coordination since the splitting falls within the 5–25 cm^{-1} range [25]. The lower value of ν(d–d) for $[Cu(6MM)_3(NO_3)]NO_3$, as well as its higher value for $g_{\|}$, is consistent with NO_3^- having a lower CFSE than 6MM. The decreased ability of the nitrate ion to involve itself in back π-bonding is probably the cause for its weaker bonding. The decrease in $g_{\|}$ upon cooling the solid to liquid nitrogen temperature suggests that this complex, as well as the tetrafluoroborate solid discussed earlier, flattens an apparent tetrahedral distortion. Finally, the presence of a shoulder on the ν(CuO) band in the spectrum of this complex is expected by virtue of the fact that one of the N-oxide ligands must be *trans* to the nitrato ligand.

$[Cu(6MM)Cl_2]_n$

Normally, we have been able to isolate a species with the stoichiometry CuL_2Cl_2 in our studies of ligands [2–10]. However, repeated attempts with this ligand to isolate a substance of the stoichiometry $Cu(6MM)_2Cl_2$ to date have been unsuccessful. Both M and 6MA yielded compounds of the above stoichiometry with the former giving a dimer with two N-oxide bridging ligands [26] and the latter a tetrahedrally distorted monomer [27]. Since 6MA is apparently incapable of bridging to form the dimer, it seems logical that the more sterically demanding 6MM would also be incapable of serving as a bridging ligand in a dimer involving 5-coordinate Cu(II) centers [26]. Evidently the steric requirements of this ligand also do not allow it to form a four coordinate monomer such as was found for 6MA [27].

This solid requires a polymeric structure in order to achieve Cu(II)'s 'minimum' coordination number of four since its infrared spectrum shows no indication of amine coordination based on the energy of ν(NH). Therefore, bridging between copper(II) sites in this solid could involve either the oxygen of 6MM or chloro ligands. The infrared results of Table II show two bands assignable to ν(Cu–Cl). The band at 329 cm^{-1} is assignable to a terminal chlorine of a 4-coordinate Cu(II) [28], but the second band at 309 cm^{-1} seems too high in energy to be assigned to a bridging chloride even for a 4-coordinate species. If the species involves planar 4-coordinate Cu(II) sites and the bridging ligands are the N-oxides, then one would expect to find two ν(Cu–Cl) bands since the chloro ligands would have to be *cis* to each other. Since $Cu(6MA)_2Cl_2$ approximates D_{2d} symmetry and has a ν(d–d) band maximum at 11,430 cm^{-1}, the substantially higher energy for ν(d–d) for $Cu(6MM)Cl_2$ shown in Table III lends support to a more planar structure and the resolution of two terminal ν(Cu–Cl) bands. The resolution of a powder ESR spectrum due to a monomer for this substance suggests very weak exchange coupling between copper(II) centers if this species is a dimeric or polymeric material.

$Cu_2(6MM)_3Br_4$

The formula of this solid, which is the only one that we have been able to isolate with $CuBr_2$, suggests that it might be a mixture of $Cu(6MM)_2Br_2$ and $Cu(6MM)Br_2$. However, it should be noted that formation of $Cu(6MM)_2Br_2$ (*i.e.*, either monomer or dimer) may be surprising in view of our inability to isolate a species of this stoichiometry with $CuCl_2$. Of interest is the fact that all of the previous solids isolated with this type of ligand and $CuBr_2$ have been various shades of brown except for $Cu(6MA)_2Br_2$ which was also violet [5]. Based on the structure of $Cu(6MA)_2Cl_2$ being a D_{2d} monomer [27], we suggested a D_{2d} structure for $Cu(6MA)_2Br_2$ [5]. Since the tetrahedral $CuBr_4^{2-}$ is also a deep violet, it would appear that mixed ligand complexes, which have at least two bromides per metal ion and a violet color, may also approach D_{2d} symmetry. Therefore, we suggest that this substance is made up of polymeric (or dimeric) host, $Cu(6MM)Br_2$, for the monomeric $Cu(6MM)_2Br_2$ and the latter species because of its D_{2d} stereochemistry imparts the violet color.

Consistent with the proposed D_{2d} structure is the presence of ν(NH) at an energy too high for a coordinated amine group. Compared to the other solids of this study its broadness and relatively low energy suggest different environments for the amine functions as well as considerable hydrogen bonding. A band at 253 cm^{-1} is consistent with the presence of terminal copper–bromide bonds, while the band at 225 cm^{-1} is probably due to a bridging bromide. The observance of a single, broad ν(d–d) band provides little information concerning our proposal of the mixture of two complex species. The presence of more than one band in the 20,000 cm^{-1} region of the spectrum allows assignment of at least one of them to a Br → Cu(II) charge transfer band.

Very often copper(II) complexes having bromide ligands yield only a broad isotopic line when their powder ESR spectra are recorded [29]. Although the spectrum is dominated by the broad isotropic line, we do see extra features on both of its low and high field sides. For example, at low field there are two broad features, which may represent two of the four g features of a diluted Cu(II) spectrum with a coupling constant of *ca.* 100 G which is consistent with a monomeric copper(II) species with D_{2d} symmetry [30]. On the high field side there are sharp features of weak intensity separated by approximately 40 G. These features could be due either to coupling of bromide ligands or to a dimeric copper(II) species. We conclude that this violet solid probably involves a mixture of monomeric and polymeric copper(II) species.

[Cu(6MM-H)$_2$]

As indicated previously, we have recently reported eight molecular Cu(II) complexes including the closely related [Cu(A-H)$_2$], [Cu(M-H)$_2$] and [Cu(6MA-H)$_2$] [12]. All of these solids were olive to tan in color, non-electrolytes and soluble in nonpolar solvents such as $CHCl_3$. In comparison to the other solids of this study [Cu(6MM-H)$_2$] has the strongest bonding via the N-oxide oxygen, since it shows the lowest and highest energies for ν(NO) and ν(CuO), respectively. The separation of the two d–d bands in the electronic spectrum is an indication of an essentially square planar complex [22]. A preliminary report of the single crystal X-ray study for the related [Cu(E-H)$_2$] shows it to be rigorously square planar [18]. [Cu(E-H)$_2$] had bands at 18,250 and 13,550 cm^{-1} [12] and these energies are comparable to those shown in Table III for [Cu(6MM-H)$_2$].

While many of these molecular solids have broad isotropic ESR spectra suggesting considerable interaction between the Cu(II) sites, [Cu(6MM-H)$_2$] possesses a resolved spectrum with its g-values indicating it to have very strong planar bonding. A $g_\parallel$ value of 2.143 is considerably lower than the 2.22 value proposed for CuO_2N_2 chromophores [31].

In $CHCl_3$ solution the familiar four line spectrum of a rotating Cu(II) species is present with $g_o = 2.098$ and $A_o = 62$ G. Note that g_{av} from the powder spectrum of the solid corresponds closely to g_o indicating no change of species upon dissolution. Although we were unable to detect any nitrogen superhyperfine lines at room temperature, cooling to *ca.* –30 °C narrows the two highest field lines of the spectrum. On both of these features resolution of five lines separated by 8 G indicates coordination of two nitrogen atoms. The frozen $CHCl_3$ solution, like the previously studied molecular complexes [12], shows a typical $d_{x^2-y^2}$ spectrum with a resolved $g_\parallel = 2.169$, $g_\perp = 2.046$ ($g_{av} = 2.087$) and $A_\parallel = 183$ G. Using $A_o = A_\parallel + 2A_\perp/3$ we calculate $A_\perp$ to be 1 G. This suggests a change in the nature of the complex on freezing, as does the non-agreement of g_o and g_{av}. The related Cu(3MA-H)$_2$ showed formation of a substantial concentration of a dimeric species upon freezing, and although no dimeric features are observable in the frozen solution spectrum of Cu(6MM-H)$_2$, increased interaction between Cu(II) centers is consistent with the changes in the ESR parameters. Finally, on the highest field parallel feature of the frozen solution spectrum, five superhyperfine lines of relative intensity 1:2:3:2:1 and with an A = 10 G are resolved which again shows coordination of the two nitrogens.

In Table VI we have listed spectral data for the related molecular complexes including Cu(E-H)$_2$ which has had its crystal structure solved [19]. The trends in the various parameters appear to indicate that stronger copper–oxygen coordination, but weaker copper–nitrogen coordination occurs for [Cu(6MM-H)$_2$]. This results in somewhat stronger bonding for this substance since both of its ν(d–d) bands are at the highest energy for any of the nine molecular complexes studied to date [5, 12]. Also, the chloroform solution of [Cu(6MM-H)2] has the lowest value for g_o.

The orbital reduction parameters $k_\parallel = 0.54$ and $k_\perp = 0.87$ have been calculated as reported previously [12] using equations based on the work of Figgis [32]. These values are the lowest and highest, respectively, for this series of compounds [12]. Since pure σ-bonding would yield a value of *ca.* 0.77 for k and k, considerable π-bonding occurs in this complex and with $k_\parallel < k_\perp$, the π-bonding is substantially more in-plane than out-of-plane [33]. In addition, we have calculated the covalency parameter $\alpha^2 = 0.749$ from $\alpha^2 = A_\parallel/0.036 + (g_\parallel - 2.002) + 3/7(g_\perp - 2.002) + 0.04$ [34]. As would be expected from the spectral data discussed above, the value of α^2 is higher than for any of the other molecular complexes of pyridine N-oxides previously studied [12]. This indicates that while the in-plane π-bonding is stronger, the σ-bonding must be significantly weaker since α^2 has the highest value for [Cu(6MM-H)$_2$].

[Cu(6MDM)$_2$](BF$_4$)$_2$

This violet solid contains two bidentate 6MDM ligands which are probably bonded in a *trans* arrange-

TABLE VI. A Spectral Comparison of Molecular Cu(II) Complexes with Deprotonated 2-Aminopyridine N-oxide and Related Ligands.

Compound	ν(NO)	ν(CuO)	ν(CuN)	ν(d–d)	A_o	g_o
Cu(A-H)$_2$	1190	420	346	17,860; 13,120	58	2.105
Cu(6MA-H)$_2$	1180	403	342	17,730; 13,120	57	2.106
Cu(M-H)$_2$	1191	440	356	17,860; 13,040	62	2.103
Cu(E-H)$_2$	1189	407	356	18,520; 13,300	63	2.102
Cu(6MM-H)$_2$	1183	435	328	18,830; 13,550	62	2.098

ment similar to the violet $[Cu(DM)_2](ClO_4)_2$ (*i.e.*, DM = 2-dimethylaminopyridine N-oxide) found by X-ray crystallography [35]. This previously studied perchlorate solid [36] was shown to have a significant interaction between the copper(II) center and the two perchlorate ions [37] which is best described by Hathaway's term 'semi-coordination' [38]. As was noted earlier we isolated a violet solid presumed to be $[Cu(6MDM)_2](ClO_4)_2$, but because of its explosive nature, we were unable to obtain an elemental analysis. However, its infrared spectrum, as was found for $[Cu(DM)_2](ClO_4)_2$ [37], shows a broadened and split $\nu_3(ClO_4)$ band centered at 1115 cm^{-1}, a strong band at 611 cm^{-1} and another reasonably strong absorption at 659 cm^{-1} possibly due to a split $\nu_4(ClO_4)$ mode and a sharp band of medium intensity at 941 cm^{-1} due to $\nu_1(ClO_4)$. All of these factors suggest semi-coordination of the perchlorate ions in this 6MDM complex as well. While infrared data confirms distortion from tetrahedral symmetry, but not necessarily coordination of the perchlorate ions, there is another factor which does suggest semi-coordination. In previously studied series of related complexes the energy of the d–d envelope was always higher for the tetrafluoroborate solid than the corresponding perchlorate solid, and this suggests greater interaction with the copper(II) center by the latter anion. For $[Cu(6MDM)_2](ClO_4)_2$ ν(d–d) is at 18,180 cm^{-1} with a shoulder at 15,150 cm^{-1} and both of these bands are significantly lower in energy than the analogous bands for $[Cu(6MDM)_2](BF_4)_2$ shown in Table III. In addition to suggesting a reasonably strong interaction for the perchlorate anions, these data suggest weak, if any, interaction for the tetrafluoroborate anions. Therefore, the broad multiplet centered at 1073 cm^{-1} due to $\nu_3(BF_4)$ and the strong band with shoulders at 529 cm^{-1} assignable to $\nu_4(BF_4)$ indicate a significant distortion from T_d symmetry and are probably due to steric factors rather than semi-coordination of the BF_4^- ions. Other bands, which would be present in the spectrum of a tetrafluoroborate ion significantly distorted from T_d symmetry [39], would be found at *ca.* 760 cm^{-1} (ν_1) and *ca.* 350 cm^{-1} (ν_2) and for this solid are probably obscured by ρ(CH) and ν(CuN), respectively. However, it should be noted that compared to the corresponding DM and DE complexes, this tetrafluoroborate solid shows a much greater distortion of its anion from T_d symmetry.

The DM solid had a single, broad ν(d–d) band at 18,420 cm^{-1} while the rose colored solid derived from $Cu(BF_4)_2$ with DE had d–d transitions at 21,550 and 18,050 cm^{-1} [10]. The violet 6MDM solid with its main d–d band at 18,520 cm^{-1} and a shoulder at 15,870 cm^{-1} is more similar to the DM solid, although resolution of the shoulder indicates a more planar Cu(II) center [22]. Like many of the CuO_2N_2 chromophores involving 2-aminopyridine N-oxides, as well as 2-picolinamine N-oxides [40], it is difficult to accurately assign the lowest field g-value because of its nearness to the other g-value(s). From Table IV we can see that this solid has a slightly rhombic ESR spectrum which again could be due to the presence of the methyl group in the 6-position. Calculation [12] of $k_\parallel = 0.71$ and $k_\perp = 0.83$ (g_2 and g_3 were averaged to determine $g_\perp$) indicates that the small amount of π-bonding is in-plane [32].

$[Cu(6MDM)_2(NO_3)_2]$

With DM we isolated a bright green $[Cu(DM)(NO_3)_2]$ solid and a green $Cu_2(DM)_3(NO_3)_4$ solid, but with DE only the blue $[Cu(DE)(NO_3)_2]$ [10]. However, despite repeated attempts, we have surprisingly not been able to isolate a solid of the stoichiometry $[Cu(6MDM)(NO_3)_2]$, but instead, have isolated the substance listed above with two ligands per copper(II). Although the conductivity measurement suggests a 1:1 electrolyte [14], the infrared spectrum suggests both nitrate ions to be coordinated. The $\nu_1 + \nu_4$ region has bands at 1782 and 1770 cm^{-1}, a broad band at 1015 cm^{-1} due in part to $\nu_1(NO_3)$ and an extremely strong band at 317 cm^{-1} assignable to ν(Cu–O) of a nitrato ligand [23, 24]. The presence of two bands in the 1700–1800 cm^{-1} region of the spectrum separated by 12 cm^{-1} is indicative of two monodentate nitrato ligands [25].

This complex with its weakly coordinated nitrato ligands is more closely related to the previously discussed perchlorate and tetrafluoroborate solids of 6MDM, than it is to nitrate solids of other dialkylaminopyridine N-oxides [10]. The considerably lower energy for ν(d–d) bands of this nitrate solid in comparison to $[Cu(6MDM)_2](BF_4)_2$ indicates a much stronger interaction by the nitrate ions than the tetrafluoroborate ions, as well as the previously mentioned perchlorate ions of the explosive solid. A 5-coordinate copper(II) center with square pyramidal symmetry, which would be consistent with the molar conductivity result and with the appearance of the low energy shoulder on the d–d band, cannot be ruled out. Also, the ESR spectrum of the solid powder appears to be intermediate beween a $d_{x^2-y^2}$ and a d_{z^2} ground state (Fig. 2), and this spectrum is probably due to the alignment of the Cu(II) centers within the crystal [40]. Of interest is that the blue $[Cu(DE)(NO_3)_2]$ had a 'reversed' ESR spectrum with $g_\parallel = 2.049$ and $g_\perp = 2.177$ [10].

$[Cu(DM)Cl_2]$

There appears to be little similarity between this yellow-green substance and the previously studied blue $[Cu(DM)Cl_2]$ solid [10]. For example, the ν(Cu–O), ν(Cu–N) and ν(Cu–Cl) bands for $[Cu(DM)Cl_2]$ were all about 20 cm^{-1} lower in energy

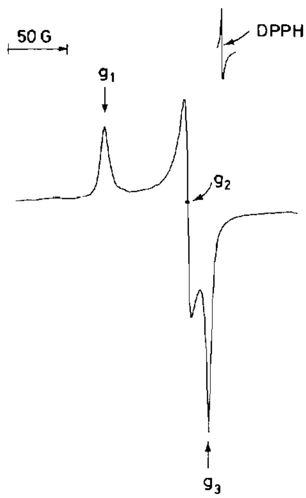

Fig. 2. Powder ESR spectrum of $[Cu(6MDM)_2(NO_3)_2]$ recorded at 77 K.

than the analogous bands for the present compound; a second band in the d–d spectrum was present at 17,240 cm^{-1} and $g_{\|} = 2.223$ compared to the 2.279 shown for $Cu(6MDM)Cl_2$ in Table IV. All of these factors suggest that the present 4-coordinate compound is more distorted toward a tetrahedral arrangement of the ligands. This distortion would be consistent with the greater steric requirements of the 6MDM ligand and its 6-methyl substituent.

$[Cu(6MDM)Br_2]$

This compound and the brownish-green $Cu(DM)Br_2$ have a relationship similar to the two chloro compounds described above. That is, a variation exists in the spectral properties that indicates a more tetrahedral arrangement of the ligands for the 6MDM compound. For this compound there is a change from a rhombic ESR spectrum at room temperature to an axial spectrum at 77 K indicating a more regular tetrahedral stereochemistry at the lower temperature. This change is accompanied by a decrease in g_{av} (similar to that for $Cu(6MDM)Cl_2$) which is due to flattening of the tetrahedron. This is accompanied by a color change from orange to yellow at the lower temperature.

In conclusion, similar bonding exists for both 6MM and 6MDM to the copper centers in the various complexes as is found for previous 2-alkyl- and 2-dialkylaminopyridine N-oxide ligands having less steric requirements. However, the steric factor of the 6-methyl group significantly affected the stereochemistry of virtually every solid isolated in this study and, in a number of instances, altered the stoichiometry of the species isolated. This alteration in stoichiometry occurs in complexes where the anion of the copper(II) salt employed in the preparation acts as a ligand. This variation in coordination sphere encourages us to continue our studies of metal complexes containing 2-substituted pyridine N-oxide ligands.

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