

Two Series of Copper(II) Complexes Derived from Various 2-Urethanylpyridine *N*-Oxides (2-Ethoxycarbonylaminopyridine *N*-Oxides)

GÖZEN ERTEM*, JOHN C. SEVERNS and DOUGLAS X. WEST**

Department of Chemistry, Illinois State University, Normal, Ill. 61761, U.S.A.

Received August 26, 1985

Abstract

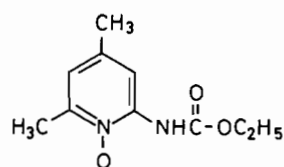
A series of new aromatic *N*-oxide ligands have been prepared by converting the 2-amino group of 2-aminopyridine *N*-oxide, 2-aminopicoline *N*-oxides and 2-amino-4,6-lutidine *N*-oxide into a urethane. Two series of copper(II) complexes have been prepared and characterized by their infrared, electronic and ESR spectra along with other physicochemical methods. One series has the stoichiometry $[\text{Cu}(\text{UOH})_4](\text{ClO}_4)_2$ and involves monodentate coordination via the *N*-oxide oxygen and the other series is prepared from copper(II) acetate and has the stoichiometry $[\text{Cu}(\text{UO})_2]$. In this latter series coordination occurs via the *N*-oxide oxygen and the deprotonated amino function.

Introduction

Our laboratory has been involved in the preparation and characterization of metal ion complexes of 2-substituted pyridine *N*-oxides. One series of copper(II) complexes that has been studied extensively involves the various 2-aminopyridine *N*-oxides such as 2-alkylaminopyridine *N*-oxides [1], 2-dialkylaminopyridine *N*-oxides [2] and 2-aminopicoline *N*-oxides [3]. Metal ion complexes of the unsubstituted 2-aminopyridine *N*-oxide have been reported by others [4, 5] as well as by this laboratory [6]. Most recently, we have prepared some copper(II) complexes of 2-alkyl- and 2-dialkylamino-6-picoline *N*-oxides [7] and the related 3-picoline *N*-oxides [8]. While most of these copper(II) complexes have involved neutral *N*-oxide ligands, these later reports have included some molecular copper(II) complexes with deprotonated ligands, and a study of molecular complexes of a number of these ligands has been communicated [9]. In contrast to the neutral *N*-oxide ligands, excepting the dialkyl-derivatives, the de-

protonated form of the ligands coordinate via the amido nitrogen as well as the *N*-oxide oxygen.

As a continuation of the alteration of the aminopyridine *N*-oxide ligand, we have prepared a series of ligands from 2-aminopyridine *N*-oxide, the various 2-aminopicoline *N*-oxides and 2-amino-4,6-lutidine *N*-oxide by converting the amino group to a urethane (Fig. 1). Although the ethoxycarbonylaminopyridine



4,6 MUOH

Fig. 1. An example of a substituted 2-urethanylpyridine *N*-oxide.

N-oxide, UOH, has been prepared previously [10], the other substances have to our knowledge not been reported. Recently, there has been a report [11] on complexes of UOH with Co(II), Ni(II) and Cu(II), but none of the complexes that these authors prepared are the same as the ones that we report on here. Their complex prepared from $\text{Cu}(\text{ClO}_4)_2$ had the formula $\text{Cu}(\text{UOH})_2(\text{ClO}_4)_2$ with coordination occurring via the *N*-oxide and carbonyl oxygens, while ours has four ligands per Cu(II) center (*vide infra*). We were interested in preparing species with four ligands per Cu(II) ion in order to compare them to the various 2-aminopyridine *N*-oxide ligands in terms of the steric effect of the ethoxycarbonyl group. Also, formation of anionic ligands occurs with ease because of the electron withdrawing effect of this group and a new series of molecular Cu(II) complexes is included in this report. There is considerable interest in molecular copper(II) complexes due to their solubility in lipids and, therefore, potential pharmaceutical use [12].

Experimental

UOH and the remaining 2-urethanylpyridine *N*-oxides described in Fig. 1 were prepared from 2-

*NATO Fellow, on leave from Medical Faculty, Istanbul University, Turkey.

**Author to whom correspondence should be addressed.

aminopyridine, the various 2-aminopicolines and 2-amino-4,6-lutidine by the method of Katritzky [10]. Modifications were necessary since not all of the ethoxycarbonylpicoline intermediates were insoluble in water. Alternatively, the ligands can be made by reaction of ethyl chloroformate with the appropriate 2-aminopicoline *N*-oxide. These *N*-oxides were prepared from the pyridines by oxidation with *m*-chloroperoxybenzoic acid in methanol [13]. The melting points and chemical shifts (ppm) for the protons of the methyl, ring methyl and methylene groups, respectively, are the following: UOH: 78 °C; 1.34t, 2.29q; 2MUOH: 208 °C; 1.32t, 2.37s, 4.25q; 4MUOH: 77 °C; 1.35t, 2.37sm, 4.32q; 5MUOH: 218 °C; 1.36t, 2.27, 4.29; 6MUOH: 174 °C; 1.37t, 2.53s, 4.30q and 4,6MUOH: >280 °C; 1.34t, 2.32s, 2.52s, 4.31q.

The perchlorate solids were isolated from a 4:1 molar ratio of ligand to Cu(ClO₄)₂ in ethanolic solution, while the molecular solids were prepared in aqueous solution using copper(II) acetate. All solids were filtered with suction and dried in a vacuum desiccator over calcium sulfate. We were unable to isolate a solid of either type with 3MUOH which gave meaningful elemental analyses. Partial elemental analyses of the isolated solids were performed by Micro-analysis, Inc. of Wilmington, Del. All instrumentation used in the characterization of these solids was the same as in our previous studies [1–8, 6–9].

Results and Discussion

The stoichiometries of the various solids isolated are shown in Table I along with their colors, partial elemental analyses and molar conductivities. All of the complexes prepared from copper(II) acetate contain only deprotonated ligands and presumably these ligands bind in a bidentate manner via the

exocyclic nitrogen and the *N*-oxide oxygen resulting in five membered chelate rings. The dark green color of most of the solids derived from the perchlorate salts suggest that they contain ligands bound via the *N*-oxide oxygen in a similar manner to the various 2-aminopyridine *N*-oxides [7, 8]. As would be expected the complexes containing the deprotonated ligands have molar conductivities consistent with their non-electrolytic behavior while the solids having perchlorate anions behave as 1:2 electrolytes in acetonitrile [14]. The latter result is consistent with the non-coordinating nature of the perchlorate anions. The most notable result shown in Table I is the blue color of Cu(6MUOH)₄(ClO₄)₂·2H₂O, which is the first 4:1 pyridine *N*-oxide complex reported that is not green.

In Table II we show the results obtained from thermal experiments for the molecular solids containing the anionic bidentate ligands. The initial event in each thermogram is an extremely sharp endotherm which is accompanied by a weight loss consistent with the loss of one ligand (L) or one ligand less an oxygen (L'). The enthalpy value for the removal of one ligand ranges from 8.6 kcal/mol to 14.1 kcal/mol and averages 11.6 kcal/mol. This is usually followed by a large exothermic peak resulting from extensive bond formation in the new substance having either one ligand or one ligand and an oxygen per metal ion. Interestingly, the two compounds having ligands with substituents in the 6-position appear to lose only a pyridine moiety rather than the complete *N*-oxide ligand.

In Table III we have compiled the IR bands associated with the ligand that are most useful in establishing its mode of coordination. For the perchlorate solids the $\nu(\text{NH})$ band is found at considerably higher energy than in the spectra of the free urethanes indicating non-coordination of the nitrogen as well as decreased involvement in hydrogen bonding.

TABLE I. Colors, Partial Elemental Analyses and Molar Conductivities (ohm⁻¹ cm² mol⁻¹) for Two Series of Copper(II) Complexes of some 2-Urethanylpiperidine *N*-oxides

Compound	Color	Calculated (%)			Found (%)			ΔM^a (ohm ⁻¹ cm ² mol ⁻¹)
		C	H	N	C	H	N	
Cu(UO) ₂	dull green	44.7	4.2	13.0	45.4	4.1	12.8	4
Cu(4MUO) ₂	dark green	47.6	4.9	12.3	47.6	4.7	12.4	4
Cu(5MUO) ₂	olive green	47.6	4.9	12.3	48.3	4.8	11.9	4
Cu(6MUO) ₂	green	47.6	4.9	12.3	47.8	4.6	12.1	3
Cu(4,6MUO) ₂	mint green	49.8	5.4	11.6	49.8	5.2	11.6	3
Cu(UOH) ₄ (ClO ₄) ₂	mint green	38.1	4.2		37.8	3.9		256
Cu(4MUOH) ₄ (ClO ₄) ₂	green	41.3	4.6		40.7	4.5		256
Cu(5MUOH) ₄ (ClO ₄) ₂	dark green	41.3	4.6		41.0	4.2		238
Cu(6MUOH) ₄ (ClO ₄) ₂ ·2H ₂ O	dark blue	39.9	4.8		39.3	4.7		264
Cu(4,6MUOH) ₄ (ClO ₄) ₂ ·2H ₂ O	dark	42.2	5.3	9.8	42.3	4.9	10.0	262

^aca. 10⁻³ M CH₃CN.

TABLE II. Thermal Decomposition Data for the Molecular Copper(II) Complexes

Compound	DSC (°C)	H (kcal/mol)	Weight loss (%)	-L or -L' (% calculated)
Cu(UO) ₂	222v,sh	+12.0	44.0	42.5
	257sh	-57.5		
Cu(4MUO) ₂	231v,sh	+12.6	41.0	42.5
	252	-51.7		
Cu(5MUO) ₂	251v,sh	+8.6	46.5	42.5
	262sh	-56.7		
Cu(6MUO) ₂	228v,sh	+14.1	36.0	39.0 (L')
	265	-11.1		
Cu(4,6MUO) ₂	212v,sh	+11.1	37.5	39.3 (L')
	234v,br	+5.3		
	258	-20.3		

TABLE III. Infrared Spectral Assignments (cm⁻¹) for some 2-Urethanylpyridine *N*-oxides and Two Series of Copper(II) Complexes

Compound	$\nu(\text{NH})$	$\nu(\text{CO})$	$\delta(\text{NH})$	$\nu(\text{NO})$	$\delta(\text{NO})$	$\nu(\text{CuO})$	$\nu(\text{CuN})$
UOH	3230s	1732s	1639m	1219m	842m		
Cu(UO) ₂		1686s		1187m	825m	437m	355m
Cu(UOH) ₄ (ClO ₄) ₂	3350m	1782s	1619m	1199m	861m	412m	
4MUOH	3265m	1722s	1629m	1205sh	843m		
Cu(4MUO) ₂		1670s		1189m	830m	423s	352m
Cu(4MUOH) ₄ (ClO ₄) ₂	3285m 3299sh	1771s	1618m	1212m	825m	423s	
6MUOH	3258w	1745s	1623m	1212m	824m		
Cu(6MUO) ₂		1700s		1200m	836m	388m	340m
Cu(6MUOH) ₄ (ClO ₄) ₂ ·2H ₂ O	3305 3265sh	1730s	1613sh	1197m	828m	400sh (Cu-OH ₂) = 345s	
4,6MUOH	3200w	1720s	1620m	1238sh	818sh		
Cu(4,6MUO) ₂		1710s		1199m	839m	380m	347m
Cu(4,6MUOH) ₄ (ClO ₄) ₂ ·2H ₂ O	3360w	1733s	1636m	1208sh	822m	422m	

Similarly, the band for $\nu(\text{CO})$ is shifted to higher energies in these complexes which indicates that the carbonyl oxygen is not bonding directly to the copper(II) centers. $\delta(\text{NH})$ is also shifted to a different position in the perchlorate solids but the shift is to both lower and higher energies indicating that loss of hydrogen bonding upon complexation is not the only factor affecting this band. Complexation of the *N*-oxide oxygen is generally accompanied by a shift to lower energy of this band with the energy in the complexes being as low as 1180 cm⁻¹ [1, 3, 6]. The magnitude of the shift is not as great for these complexes because of both the hydrogen bonding in the free ligands and the steric crowding involved with having four of these ligands about a single Cu(II) center. The $\delta(\text{NO})$ band often remains unchanged in energy upon complexation due to two opposing effects [15]. There is a general tendency in the spectra of the perchlorate solids for this band to be found a somewhat higher energy indicating that the metal ion effect is more important than

the loss of double bond character. The $\nu(\text{CuO})$ band is found in the 400 to 430 cm⁻¹ range in agreement with other 2-substituted pyridine *N*-oxides [1].

The molecular complexes have no assignable bands for $\nu(\text{NH})$ of the exocyclic nitrogen indicating its loss on complex formation. The $\nu(\text{CO})$ band is found at lower energy in these complexes due to the loss of the proton and the accompanying loss in polar character of the C-O bond. The decrease in energy is not sufficient in the spectra to indicate bonding of the carbonyl oxygen although it is possible that the urethane oxygens occupy the axial coordination position(s) of either the same or an adjacent copper(II) center. Coordination of the *N*-oxide oxygen is indicated by the lower energy of $\nu(\text{NO})$, the sporadic changes in $\delta(\text{NO})$ and the appearance of bands in the 400 cm⁻¹ region assignable to $\nu(\text{CuO})$ in this series of complexes. Coordination of the exocyclic nitrogen is suggested by the appearance of a band in the 340–365 cm⁻¹ region for this series of complexes. Therefore, the infrared spectra help to

confirm the bidentate bonding (O,*N*) of the deprotonated ligand and the monodentate bonding (O) of the neutral ligand. The non-coordination of the perchlorate anions is confirmed by the presence of a very strong band at 1080–1120 cm⁻¹ assignable to $\nu_3(\text{ClO}_4)$, a very strong, sharp band at *ca.* 625 cm⁻¹ due to $\nu_4(\text{ClO}_4)$, and a weak, sharp band at *ca.* 935 cm⁻¹ assignable to $\nu_1(\text{ClO}_4)$. The small distortion from *T_d* symmetry that is observed for this anion is probably due to its involvement in hydrogen bonding rather than direct bonding to the Cu(II) center.

The blue perchlorate solid prepared with 6MUOH, $\text{Cu}(\text{6MUOH})_4(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, has a strong band at 345 cm⁻¹ assignable to $\nu(\text{Cu}-\text{OH}_2)$ and this band is not present in any of the other spectra of the perchlorate solids including the complex prepared with 4,6MUOH which also has two water molecules per Cu(II) center. Therefore, the latter solid's two water molecules are not coordinated. In addition, a relatively sharp band is present at 3365 cm⁻¹ which is assignable to $\nu(\text{OH})$ of a coordinated water molecule. The DSC of the blue solid has an endothermic peak at 120 °C which is unique to the series and is presumably due to loss of coordinated water. All of this evidence suggests that the blue color is caused by coordination of one or more water molecules which increases the coordination number above 4.

The electronic spectral assignments for solid and solution spectra are shown in Table IV. All of the spectra show a band in the 25–27 kK region common to Cu(II) complexes of 2-substituted pyridine *N*-oxides and assignable to a O(p) → Cu(II) charge transfer band [16]. In some cases the band is obscured by more intense intraligand bands and, possibly, other charge transfer bands such as *N*(p) → Cu(II) which would be expected for the neutral complexes. An energy range for this band unfortunately has not been established for previous complexes from this laboratory [9] or by other workers [17].

The d–d bands are found at higher energy for the molecular complexes as would be expected for CuO₂-N₂ chromophores compared to CuO₄ chromophores. The appearance of a second peak or resolved shoulders on some of the d–d composite bands suggests a planar arrangement of the donor atoms about the Cu(II) center. A comparison of the energies of the d–d bands to those found for the analogous complexes formed with 2-methylaminopyridine *N*-oxide(M) (*i.e.*, Cu(M–H)₂, $\nu(\text{d}-\text{d}) = 17.86, 13.04$ kK [9] and Cu(M)₄(ClO₄)₂, $\nu(\text{d}-\text{d}) = 15.63$ kK [1]) shows the present centers to have lower energies in both cases presumably due to less planar arrangements due to the greater steric requirements of these ligands. When larger alkyl groups than a methyl group are present on the amino nitrogen (*i.e.*, ethyl, propyl and isopropyl), the energy of the main d–d band increases for the perchlorate solids presumably due to steric interference to increasing the coordination number by axial bonding of either perchlorate ions or bridging *N*-oxide oxygens from adjacent copper(II) sites [1]. However, in the analogous series of molecular solids $\nu(\text{d}-\text{d})$ reaches a maximum with the ethyl derivative and then decreases indicating that the nature of the solid and its packing arrangement play an important role in determining the stereochemistry of the copper(II) center and its resulting d–d spectrum [9]. Finally, Cu(UOH)₂(ClO₄)₂ has $\nu(\text{d}-\text{d}) = 15.38$ kK [11] compared to 14.35 for Cu(UOH)₄(ClO₄)₂ indicating that a stronger crystal field is achieved by the O, O chelating ligand. This is probably due to steric factors since the *N*-oxide oxygen would in general be the stronger donor atom.

The plasticity [18] of the copper(II) coordination sphere allows for numerous modes of distortion and the two series of compounds being studied here appear to exemplify this characteristic. For both series of solids substitution on the ring seems to increase the energy of the d–d band suggesting

TABLE IV. Electronic Spectra (kK) of Two Series of Copper(II) Complexes of 2-Urethanylpyridine *N*-oxides

Compound	Solid		Solution ^a	
	CT	d–d	CT	d–d
Cu(UO) ₂	27.27	16.84, 12.17	28.09	16.03
Cu(4MUO) ₂	25.19	16.18	27.78	16.05
Cu(5MUO) ₂	26.32	16.56	27.25	15.97
Cu(6MUO) ₂	26.11	16.39	27.25	15.90
Cu(4,6MUO) ₂	26.60	16.10	27.55	16.08
Cu(UOH) ₄ (ClO ₄) ₂	26.67	14.08	26.25	14.35
Cu(4MUOH) ₂ (ClO ₄) ₂	25.64	13.74	26.32	14.49
Cu(5MUOH) ₂ (ClO ₄) ₂	25.64	15.67, 13.89sh	26.31	14.53
Cu(6MUOH) ₂ (ClO ₄) ₂ ·2H ₂ O	27.03	16.10, 14.18sh	26.18	14.75
Cu(4,6MUOH) ₂ (ClO ₄) ₂ ·2H ₂ O	27.25	14.97	25.00	14.99

^aMolecular complexes in CHCl₃, perchlorate solids in CH₃NO₂.

TABLE V. Powder Electron Spin Resonance g -values for Two Series of Copper(II) Complexes of 2-Urethanylpyridine *N*-oxides

Compound	Temperature ^a	g_{\parallel}	g_{\perp}	g_{av} or g_{iso}	A_{\parallel} (G)
Cu(UO) ₂	RT	2.234	2.057	2.116	
	77 K	2.227	2.053	2.111	
Cu(4MUO) ₂	RT		2.055	?	
	77 K		2.056	?	
Cu(5MUO) ₂	RT	2.254	2.031	2.105	162
	77 K		2.064	?	
Cu(6MUO) ₂	RT		2.059	?	
	77 K		2.056	?	
Cu(4,6MUO) ₂	RT		2.055	?	
	77 K		2.049	?	
Cu(UOH) ₄ (ClO ₄) ₂	RT	2.270	2.062	2.131	
	77 K	2.257	2.061	2.126	
Cu(4MUOH) ₄ (ClO ₄) ₂	RT	2.272	2.066	2.135	
	77 K	2.267	2.050	2.122	
Cu(5MUOH) ₄ (ClO ₄) ₂	RT	2.242	2.061	2.121	
	77 K	2.240	2.060	2.120	
Cu(6MUOH) ₄ (ClO ₄) ₂ ·2H ₂ O	RT	2.233	2.058	2.116	
	77 K	2.216	2.055	2.109	
Cu(4,6MUOH) ₄ (ClO ₄) ₂ ·2H ₂ O	RT	2.239	2.055	2.116	176
	77 K	2.244	2.056	2.119	181

^aRT = room temperature.

reduced axial bonding due to steric hindrance. Upon dissolution in chloroform there is little change in the $d-d$ spectra except that those solids having two bands or resolved shoulders have only one broad band assignable to $d-d$ transitions. The small changes in energy appear to be due to a medium effect rather than a change in the nature of the coordination spheres of these complexes. This suggests little bonding in the axial positions of these complexes in the solid state.

The ESR parameters derived from the spectra of the powdered solids are shown in Table V. While many of the spectra of the molecular complexes appear to have broad isotropic spectra, assignment as such gives g_{iso} values which appear to be far too low compared with both those samples having anisotropic spectra and the previously studied molecular CuO_2N_2 chromophores. Our inability to observe the features associated with g_{\parallel} for most of the solids is probably due to it being obscured by the larger g_{\perp} feature rather than it being broadened beyond detection. The expected value for g_{\parallel} for CuO_2N_2 chromophores having very weak axial bonding is 2.22 [19] and a feature having this value would be difficult to detect in these spectra. When we are able to observe g_{\parallel} , its value, as well as the values of g_{av} , are higher than those of the previously studied molecular complexes [9]. The resolution of

the g_{\parallel} feature for the room temperature spectrum of $Cu(5MUO)_2$ is surprising and its values for g_{\parallel} and A_{\parallel} are considerably higher and lower, respectively, than would be expected for a CuO_2N_2 chromophore.

The perchlorate solid spectra are consistent with a $d_{x^2-y^2}$ ground state and the values in general are what we have come to expect for CuO_4 chromophores involving pyridine *N*-oxide ligands [1]. These complexes do have g_{\parallel} values that are higher than those found for the various 2-aminopyridine *N*-oxide $Cu(II)$ complexes. This indicates weaker bonding by these ligands which may be due to greater axial bonding or a tetrahedral distortion of the $Cu(II)$ center. Resolution of the g_{\parallel} feature in the spectra of the 4,6MUOH complex is more than likely due to the size of this ligand being sufficient to reduce dipolar and exchange interactions between adjacent $Cu(II)$ centers to give a 'diluted' spectrum [20]. This along with the two absorptions assignable to $d-d$ transitions in the electronic spectra of some of these compounds allows for calculation of covalency parameters [20]. For $Cu(UO)_2$: $k_{\parallel} = 0.65$, $k_{\perp} = 0.72$; for $[Cu(5MUOH)_4](ClO_4)_2$: $k_{\parallel} = 0.71$, $k_{\perp} = 0.75$; and for $[Cu(6MUOH)_4(H_2O)](ClO_4)_2$: $k_{\parallel} = 0.70$, $k_{\perp} = 0.74$. For all three of these solids the values of k_{\perp} are larger than the values for k_{\parallel} indicating that in-plane π -bonding is more important

TABLE VI. Solution (CHCl₃) ESR Parameters of the Molecular Cu(II) Complexes

Compound	298 K		77 K			
	g_{O}	A_{O} (G)	g_{\parallel}	A_{\parallel} (G)	g_{\perp}^{a}	A_{\perp}^{a} (G)
Cu(UO) ₂	2.119	68	2.226	172	2.066	16
Cu(4MUO) ₂	2.121	68	2.237	169	2.063	17.5
Cu(5MUO) ₂	2.120	67	2.232	175	2.064	13
Cu(6MUO) ₂	2.121	66	2.232	176	2.066	11
Cu(4,6MUO) ₂	2.120	67	2.232	173	2.064	14

^aCalculated from $g_{\perp} = (3g_{\text{O}} - g_{\parallel})/2$ and $A_{\perp} = (3A_{\text{O}} - A_{\parallel})/2$.

than out-of-plane π -bonding. The greater π -bonding and covalency of the Cu(UO)₂ is probably due to the chelation which forces the aromatic rings to be coplanar with the CuO₂N₂ portion of the molecule as well as the lower electronegativity of the nitrogen atoms. Since the values for the two CuO₄ chromophores are close to the 0.77 value expected for ionic bonding, it is likely that these complexes have the *N*-oxide rings twisted out of the coordinate plane which reduces their potential for involvement in π -bonding to Cu(II). A crystal structure determination of Cu(M)4(CIO4)2 (M = 2-methylaminopyridine *N*-oxide) showed that the four pyridine *N*-oxide rings were twisted out of the CuO₄ plane to give a propeller-like structure [22], which we envision for these two compounds.

In Table VI we show the CHCl₃ solution ESR parameters for the five molecular complexes. The ionic solids undergo decomposition resulting in multiple Cu(II) centers in solvents such as acetonitrile and methanol and these solutions were not studied in detail. All of the samples in Table VI give similar parameters indicating little effect on the nature of the Cu(II) center with substitution on the ring. The g_{\parallel} and A_{\parallel} values of these solutions are in reasonable agreement with 2.224 and 175 G proposed for CuO₂N₂ chromophores [23]. The only significant difference between the spectra of these compounds is the ability to resolve nitrogen super-hyperfine. As in our previous studies [8], greatest resolution of the isotropic spectra occurred at ca. -25 °C and Cu(4,6MUO)₂ provided the most highly resolved spectra at all temperatures. Example $A(\text{N})$ values for Cu(4,6MUO)₂ are the following: at 248 K: $A(\text{N}) = 12$ G; at 77 K: $A_{\parallel}(\text{N}) = 9$ G, $A_{\perp}(\text{N}) = 14$ G. The resolution of these spectra confirm planar nitrogen coordination and the five lines in the room temperature spectrum indicate that two nitrogens are coordinated.

A preliminary single crystal study has shown Cu(4MUO)₂ to have the two ligands bound in a *cis*

arrangement with some distortion from planarity [22].

References

- 1 D. X. West and J. S. Sedgwick, *J. Inorg. Nucl. Chem.*, **43**, 2307 (1981) and refs. therein.
- 2 D. X. West and W.-H. Wang, *J. Inorg. Nucl. Chem.*, **42**, 985 (1980); **43**, 1511 (1981).
- 3 D. X. West, *Inorg. Chim. Acta*, **71**, 251 (1983); *Polyhedron*, **2**, 999 (1983).
- 4 H. Sigel and H. Brintzinger, *Helv. Chim. Acta*, **46**, 701 (1963).
- 5 A. E. Landers and D. J. Phillips, *Inorg. Chim. Acta*, **74**, 43 (1983).
- 6 D. X. West, *J. Inorg. Nucl. Chem.*, **43**, 3169 (1981).
- 7 D. X. West and L. K. Goodmon, *Inorg. Chim. Acta*, in press.
- 8 D. X. West and C. A. Nipp, *Transition Met. Chem.*, **10**, 201 (1985).
- 9 D. X. West and L. M. Roberts, *Inorg. Chim. Acta*, **90**, 79 (1984).
- 10 A. R. Katritzky, *J. Chem. Soc.*, 2063 (1954).
- 11 M. Srivastava, A. K. Srivastava and R. K. Agarwal, *Pol. J. Chem.*, **53**, 393 (1984).
- 12 J. R. J. Sorenson, *J. Med. Chem.*, **19**, 135 (1976); S. W. C. Leuthauser, L. W. Oberley, T. D. Oberley, J. R. J. Sorenson and K. Ramakrishna, *J. Nat. Cancer Inst.*, **66**, 1077 (1981).
- 13 L. W. Deady, *Synth. Commun.*, **7**, 509 (1977).
- 14 W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
- 15 S. Kida, J. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).
- 16 G. Ertem and D. X. West, *Transition Met. Chem.*, **10**, 131 (1985).
- 17 M. Nonoyama, *Inorg. Chim. Acta*, **13**, 5 (1975).
- 18 J. Gazo, I. B. Bersuker, J. Gerai, M. Kabisova, J. Kohout, H. Langfelderova, M. Melnik, M. Seraton and F. Valach, *Coord. Chem. Rev.*, **19**, 253 (1976).
- 19 H. Yokoi, *Inorg. Chem.*, **17**, 538 (1978).
- 20 B. A. Sastry, S. M. Asadullah, G. Ponticelli and M. Mascesi, *J. Inorg. Nucl. Chem.*, **43**, 1521 (1981).
- 21 M. Mohan and B. D. Paramhans, *Transition Met. Chem.*, **5**, 113 (1980).
- 22 S. F. Pavkovic, private communication.
- 23 G. Formicka-Kazłowska, H. Kozłowski and B. Jeżowska-Trzbiatowska, *Inorg. Chim. Acta*, **25**, 1 (1977).