

by rotating two tetrahedral ligands by 45° around an axis bisecting them and passing through the copper atom. This distortion does not appear to be due to steric factors and might result from an interaction between the copper ion and the π system of the ligands and the copper ion.

The 3-picoline N-oxide yellow form converts to the green form at 100 – 110° . It is proposed that the yellow form is distorted square-planar or distorted tetrahedral and the green form is approximately *trans*-square-planar. It is possible that diffuse reflectance spectra can be used to confirm some of these assignments.¹⁶

The zinc and copper β -diketone complexes were not in general easily characterized. The $(\text{TFA})_2\text{Zn}$ complex,

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mp 168° , was a trimer in solution and the unit cell contained 4 trimeric units. The structure may be similar to that of bis(acetylacetonato)nickel(II).¹⁷ A second white complex, mp 186 – 187° , was obtained during some of the preparations. The second complex was monomeric in solution and the analytical data are consistent with the formulation of a dihydrate.

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Refinement of the Crystal Structure of Di- μ -(pyridine oxide)-bis(dichlorocopper(II))

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The crystal and molecular structure of di- μ -(pyridine oxide)-bis(dichlorocopper(II)) has been refined using three-dimensional single-crystal X-ray data. The crystals are monoclinic, $P2_1/b$, with unit cell dimensions $a = 5.844 \pm 0.005$ Å, $b = 10.049 \pm 0.005$ Å, $c = 13.643 \pm 0.005$ Å, and $\gamma = 104^\circ 52' \pm 10'$. Two dimeric molecules are found per unit cell. The ligands about the copper ion are best described as forming a distorted square-planar configuration, and π bonding is postulated to be important in the superexchange mechanism.

Introduction

A number of complexes between transition metals and pyridine N-oxide, $\text{C}_5\text{H}_5\text{NO}$, and its derivatives have been prepared and characterized.^{1–4} The abnormally low magnetic moments of most 1:1 complexes of copper(II) halides^{4,5} have led to the prediction of a dimeric or polymeric oxygen-bridged structure. It was suggested that the low magnetic moment could be accounted for by a superexchange mechanism operating through the bridging oxygen atoms of the N-oxide ligands.^{6,7}

The crystal structure of $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$ was determined by two-dimensional, single-crystal X-ray diffraction techniques and indicated an oxygen-bridged dimer.⁴ We have collected three-dimensional X-ray data and have refined the positional and thermal parameters using a full-matrix, least-squares procedure. We wish to report the details of the refined structure.

(1) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

(2) R. L. Carlin, *ibid.*, **83**, 3773 (1961).

(3) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

(4) H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965). Space group $P2_1/b$ was used to be consistent with previous workers.

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Experimental Section

Pyridine N-oxide was obtained from K & K Chemical Laboratories and copper(II) chloride from the Allied Chemical Co. Both were used without further purification.

Di- μ -(pyridine oxide)-bis(dichlorocopper(II)), $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$, was prepared by the method of Quagliano, *et al.*¹ Green, needle-shaped crystals suitable for X-ray study were recrystallized from an ethanol solution. A single crystal, $0.87 \times 0.17 \times 0.13$ mm, was used in the collection of all data.

Crystals of $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$ are monoclinic belonging to space group $P2_1/b$ with unit cell dimensions⁴ $a = 5.844 \pm 0.005$ Å, $b = 10.049 \pm 0.005$ Å, $c = 13.643 \pm 0.005$ Å, and $\gamma = 104^\circ 52' \pm 10'$. There are two dimeric molecules per unit cell.

Three-dimensional intensity data were collected at room temperature by the multiple-film (three films), equinclination Weissenberg technique. Reflections $0kl$ – $6kl$ were recorded using filtered molybdenum radiation, $\text{Mo K}\alpha = 0.71069$ Å. A total of 1144 nonzero reflections were recorded and were visually estimated by comparison with a calibration strip. The data were corrected for absorption using Bond's values⁸ with $\mu R = 0.30$. Precession data were used initially to place all data on a common scale. Scale factors were later refined during the least-squares calculations.

Structure

The atomic positions and isotropic temperature factors of Schafer, *et al.*,⁴ were used as the starting parameters in a full-matrix, least-squares refinement.⁹ The

(8) "International Tables for X-ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

(9) Program written by Y. Okaya, IBM Watson Research Laboratories.

TABLE II

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS^a

Atom	X	Y	Z	B, A ²	B ₁₁ ^b	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cu	0.2672 (2)	0.0950 (1)	0.0161 (1)	2.73	2.40	0.93	0.28	0.66	0.11	0.20
Cl(1)	0.3604 (5)	0.2764 (2)	0.1131 (2)	3.55	3.44	0.80	0.49	1.11	-0.30	-0.37
Cl(2)	0.5871 (5)	0.1398 (2)	-0.0782 (2)	3.18	2.76	0.94	0.38	0.98	0.47	0.30
O	-0.0327 (12)	0.0098 (6)	0.0850 (5)	3.10	2.77	1.37	0.19	1.44	0.19	-0.33
N	-0.0764 (15)	0.0389 (6)	0.1783 (5)	2.70	2.94	0.94	0.20	0.78	0.17	-0.10
C(1)	0.0256 (20)	-0.0164 (8)	0.2503 (8)	3.26	3.43	1.05	0.31	1.84	-0.10	0.02
C(2)	-0.0210 (27)	0.0116 (7)	0.3471 (8)	4.32	6.51	0.80	0.33	1.75	-0.04	-0.01
C(3)	-0.1714 (25)	0.0907 (9)	0.3684 (8)	4.39	5.00	1.29	0.40	1.89	0.45	-0.18
C(4)	-0.2780 (25)	0.1471 (9)	0.2915 (9)	4.35	4.74	1.13	0.47	1.33	0.42	-0.44
C(5)	-0.2206 (19)	0.1212 (9)	0.1944 (7)	3.19	2.64	1.18	0.35	1.20	0.15	-0.41

^a Standard deviations of last significant figures are given in parentheses. ^b Anisotropic temperature factors $\times 10^3$.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)^a

Cu-Cl(1)	2.206 (5)	C(4)-C(5)	1.407 (27)	Cl(2)'-N	3.354 (14)	Cl(2)'-Cu-O	94.4 (6)
Cu-Cl(2)	2.217 (5)	C(5)-N	1.341 (21)	Cl(2)''-C(5)	3.331 (18)	O-N-C(5)	118.2 (2.5)
Cu-O	1.979 (11)	Cu-Cu'	3.245 (4)	Cl(1)-Cu-Cl(2)	99.4 (3)	C(1)-N-C(5)	123.5 (3.2)
Cu-O'	2.036 (11)	O-O'	2.366 (22)	Cu-O-Cu'	107.8 (6)	N-C(1)-C(2)	118.7 (3.1)
N-C(1)	1.341 (22)	Cl(1)-O	3.074 (12)	O-Cu-O'	72.2 (1.0)	C(1)-C(2)-C(3)	120.7 (3.7)
O-N	1.346 (17)	Cl(1)-N	3.143 (14)	Cl(1)-Cu-O	97.6 (6)	C(2)-C(3)-C(4)	119.6 (3.8)
C(1)-C(2)	1.392 (27)	Cl(1)-C(1)	3.611 (18)	Cu-O-N	123.5 (1.6)	C(3)-C(4)-C(5)	118.3 (3.4)
C(2)-C(3)	1.359 (30)	Cl(1)-C(5)	3.532 (18)	Cu'-O-N	127.8 (1.7)	C(4)-C(5)-N	119.0 (3.1)
C(3)-C(4)	1.412 (30)	Cl(2)''-O	3.204 (11)	O-N-C(1)	118.2 (2.6)	O-O'-N	171.6 (2.0)

^a Standard deviations of last significant figures are given in parentheses.

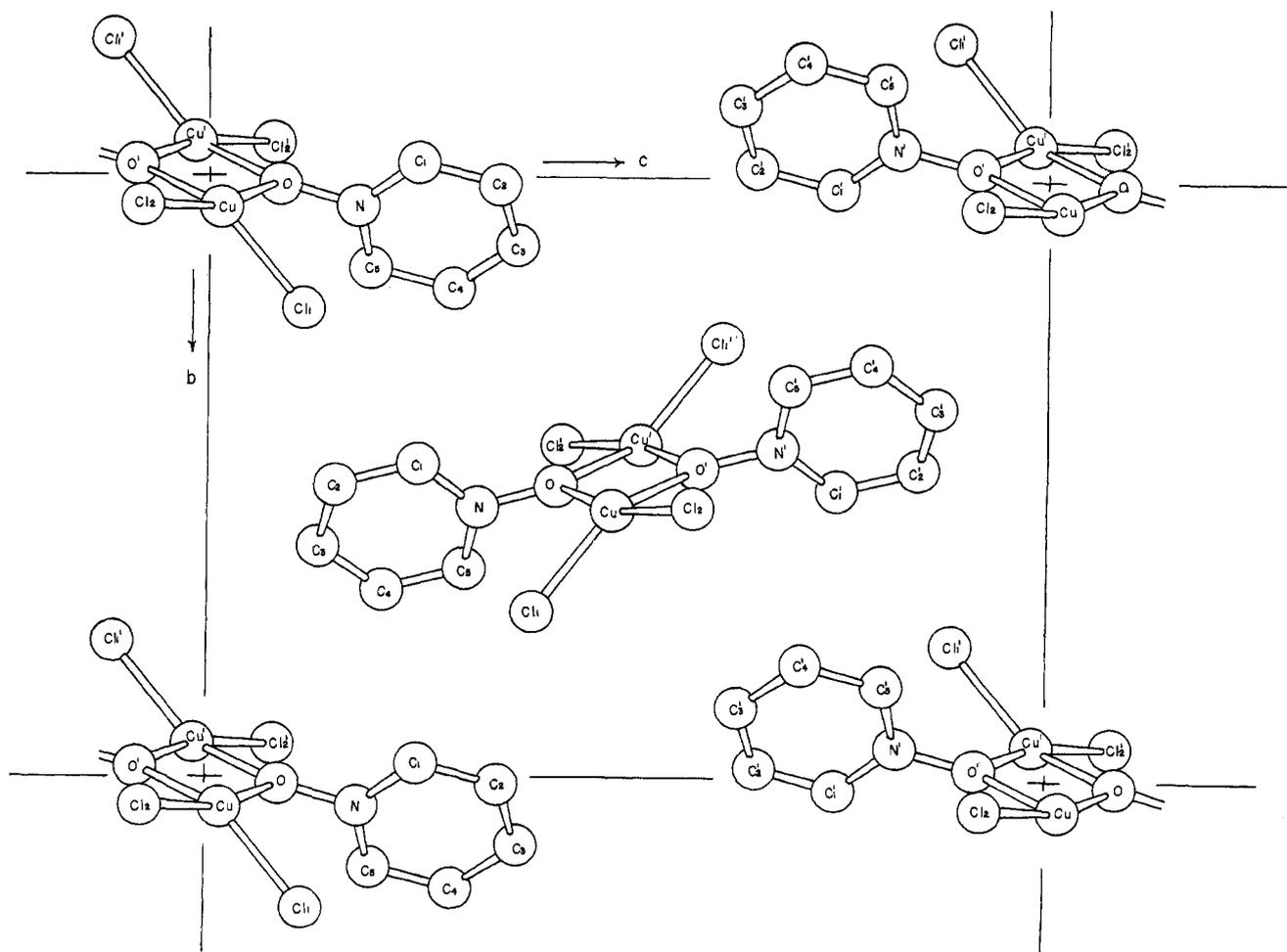


Figure 1.—A projection of $[(C_5H_5NO)CuCl_2]_2$ along the a axis.

per-oxygen plane and the normal to either pyridine ring is 70.0° . Both rings are aligned in the same direction relative to the copper-oxygen plane, making them nearly coplanar. The nitrogen-oxygen bond makes an angle of 1.6° with the pyridine ring leaving the oxygen 0.04 Å above the plane of the ring. The nitrogen atom in the pyridine ring is 0.02 Å above the plane of the ring.

The coordination around the copper ions can be most accurately described in terms of a distorted square-planar geometry. One Cu-Cl bond makes an angle of 9.9° with the Cu-O plane leaving the chlorine 0.38 Å above the plane. The other chlorine atom makes an angle of 32.6° with this plane leaving the chlorine atom 1.2 Å below it. The O-Cu-O angle is 72.2° while the Cu-O-Cu angle is 107.8° . In the copper-oxygen plane, the two oxygen atoms are within 2.37 Å of each other, causing the copper atoms to be separated by a distance of 3.25 Å.

There are no significant intermolecular interactions which could account for the bending of the chlorine atom out of the copper-oxygen plane. The distances between Cl(1) in one molecule and C(2), C(3), and C(4) of an adjacent molecule are 3.82, 3.62, and 4.00 Å. There are no additional atoms of closer approach although the predicted positions of some of the hydrogen atoms fall within this range. The second chlorine atom Cl(2) is most closely associated with C(2)', C(3)', and C(4)' of an adjacent molecule at distances of 3.90, 3.84, and 3.61 Å, respectively. The closest approach to a copper ion is from C(3) of an adjacent molecule at a distance of 3.91 Å. The shortest intermolecular distance is 3.44 Å between C(1) and C(4).

The N-O bond length of 1.35 Å is somewhat longer than that reported by Schafer, *et al.*,⁴ 1.24 Å, but agrees quite well with that found in pyridine N-oxide hydrochloride,¹⁰ 1.38 Å. The average C-N distance, 1.34 Å, and the average C-C distance, 1.39 Å, are normal.

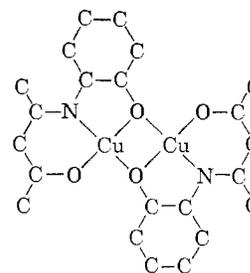
The Cu-Cu separation in the pyridine N-oxide complex of 3.25 Å is greater than the separation in most bridged copper complexes with low magnetic moments such as copper acetate monohydrate, 2.64 Å,^{11a} and diacetato(pyridine)copper(II),^{11b} 2.63 Å. There are some instances of bridged copper structures with low magnetic susceptibilities where the Cu-Cu separation may be as large as 3.0 Å;¹² however, a separation of 3.25 Å is usually associated with a normal magnetic moment such as in copper(II) benzoate trihydrate,¹³ 3.15 Å. It is interesting to speculate on this and several other interesting features of the structure.

The following questions arise when a description of the structure is given: Why is the pyridine N-oxide ring twisted 70° relative to the copper-oxygen plane, and why is one chlorine atom bent away from this plane by 32.6° ? Why are the two oxygen atoms

only 2.37 Å apart while the copper atoms are separated by 3.25 Å? What bonding scheme can account for the small value of the magnetic moment?

Two general bonding schemes have been employed to explain the magnetic exchange mechanism. One scheme involves an exchange mechanism acting through the σ -bonding system. For this to be significant, a strong covalent bond would be required. The observed Cu-O bond distances, 1.98 and 2.04 Å, are slightly longer than bond distances found in a number of complexes with normal magnetic moments where π bonding is not possible. We suggest that the σ path should make only a minor contribution to the exchange mechanism.

The second scheme for describing the low magnetic susceptibility involves a π -bonding mechanism¹⁴ Here the electron-exchange demagnetization is said to follow the path $3d(\text{Cu}(1))-2p(\text{O})-3d(\text{Cu}(2))$. This mechanism is probably more important in the case of $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$ than the σ path. A comparison might be made with the structure and properties of acetylacetonemono(*o*-hydroxyanil)copper(II).¹² The copper-oxygen bridge in this compound is very similar



to the copper-oxygen bridge in $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$; that is, the copper-oxygen bond lengths are of the same order (1.97, 2.02, 1.91, and 1.99 Å compared with 1.97 and 2.04 Å) and the copper-copper distance is similar, 3.0 Å. The observed magnetic moment ($\mu = 1.37 \text{ BM}^g$) is abnormally low but it is still much higher than that of $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$ ($\mu = 0.85 \text{ BM}^g$). The reason for this increased interaction might be accounted for in the following manner. The chlorine atom is bent 32° from the copper-oxygen plane to permit a π bond to be formed between the pyridine N-oxide ligand and the copper ion allowing the odd electron to be delocalized. The very short O-O separation, 2.37 Å, could be due to a π interaction between the coplanar pyridine rings through the two oxygens as suggested by Schafer, *et al.*⁴ Another scheme for superexchange could therefore be a $3d(\text{Cu}(1))-2p(\text{O}(1))-2p(\text{O}(2))-3d(\text{Cu}(2))$ path. This is consistent with the variation in Cu-O bond distances, 1.98 ± 0.01 and 2.04 ± 0.01 Å.

The distorted structure might be explained in terms of steric effects rather than additional bond formation. The minimum steric interaction would occur when the pyridine rings are rotated 90° with respect to the copper-oxygen plane. The observed angle of 70°

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might be due to packing considerations and one might assume that one chlorine atom is bent 32° from the plane because of an interaction with the pyridine ring. A consideration of contact distances does not show the chlorine atom to be significantly closer when it is placed in the copper-oxygen plane than when it is bent out of the plane. We do not believe that a steric interaction would be sufficiently strong to give the resulting distorted structure. Some careful theoretical

considerations will have to be employed to see if the proposed mechanism is possible.

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The Crystal Structure of Tris(2-dimethylaminoethyl)aminocobalt(II) Bromide

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The crystal structure of $\text{Co}(\text{Me}_6\text{tren})\text{Br}_2$ [$\text{Me}_6\text{tren} = \text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_3$] has been determined by three-dimensional X-ray analysis and refined to a final R factor of 8.0%. Crystals of the compound are cubic, space group $\text{P}2_13$, $a = 12.088 \pm 0.004$ Å, with four formula units per unit cell. The structure consists of $\text{Co}(\text{Me}_6\text{tren})\text{Br}^+$ and Br^- ions arranged in a distorted NaCl lattice. The $\text{Co}(\text{Me}_6\text{tren})\text{Br}^+$ ion has a trigonal bipyramidal structure with symmetry C_3 . The symmetry of the complex ion is essentially determined by the shape of the ligand molecule. The series of complexes $\text{M}^{\text{II}}(\text{Me}_6\text{tren})\text{Br}_2$ with $\text{M}^{\text{II}} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu},$ and Zn are all isomorphous.

Introduction

Although several five-coordinated cobalt(II) complexes have been described by X-ray analysis,¹⁻⁶ the factors determining the stereochemistry of these complexes are not well understood. From the results it appears that, among the other factors, the geometry of the ligand molecule plays an important role in determining the stereochemistry of the complex.

Ciampolini and Nardi⁷ have reported the preparation and the physicochemical properties of a series of high-spin complex compounds with general formula $\text{M}^{\text{II}}(\text{Me}_6\text{tren})\text{X}_2$, where $\text{M}^{\text{II}} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu},$ and Zn and $\text{Me}_6\text{tren} = \text{tris}(2\text{-dimethylaminoethyl})\text{amine}, \text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_3$, and $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3,$ and ClO_4 .

On the basis of magnetic, spectral, and conductivity measurements, these complexes have been formulated as $[\text{M}(\text{Me}_6\text{tren})\text{X}]\text{X}$, and a trigonal bipyramidal structure has been proposed for the $[\text{M}(\text{Me}_6\text{tren})\text{X}]^+$ ion.

All the complexes with the same anion are isomorphous, as shown by the similarity of their X-ray powder patterns. The bromides crystallize in well-formed tetrahedra with dimensions particularly suitable for X-ray investigation. We report here the three-

dimensional X-ray analysis of the complex $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$.

Experimental Section

Data Collection.—Crystals of the complex suitable for the structural analysis were kindly supplied by Dr. Ciampolini. Cell dimensions were determined from a Weissenberg photograph using Fe $\text{K}\alpha$ radiation (λ 1.9373 Å), with the NaCl rotation pattern superimposed on the film for calibration ($a = 5.6273$ Å). Six 2θ values were measured and treated by least squares. The results are: $a = 12.088 \pm 0.004$ Å, $d_0 = 1.688$ g/cm³, $Z = 4$, $\mu = 139.0$ cm⁻¹, space group $\text{P}2_13$.

The crystal chosen for the collection of the intensities was a truncated tetrahedron with the edge of about 0.25 mm.

Doubly integrated Weissenberg photographs $h\bar{k}0$ through $hk6$ were taken on a Nonius camera, with the multiple-film, equi-inclination technique. The intensities of the reflections were measured on a Nonius microdensitometer, the intensity being assumed proportional to the density of the spots. The various levels were scaled by means of common reflections. We examined 390 independent reflections, about 95% of the total number in the Fe sphere of reflection; we found 53 too weak to be measured.

Intensities were corrected for Lorentz and polarization effects and for spot elongation on upper levels according to Phillips.⁸

Later, during the determination of the structure, inspection of the observed and calculated structure factors at $R = 12.1\%$ showed the existence of strong secondary extinction effects. This was confirmed by a plot of $\ln(I_o/I_e)$ against I_o for the strongest reflections, but an attempt to correct all of the reflections on the basis of the plot did not give satisfactory results. It was decided then to continue the refinement, omitting those reflections which appeared to be affected most heavily by extinction. These reflections are 210, 220, 121, 231, 331, 431, 241, 351, 171, 222, and 262.

The atomic scattering factors were taken from the Dirac-

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