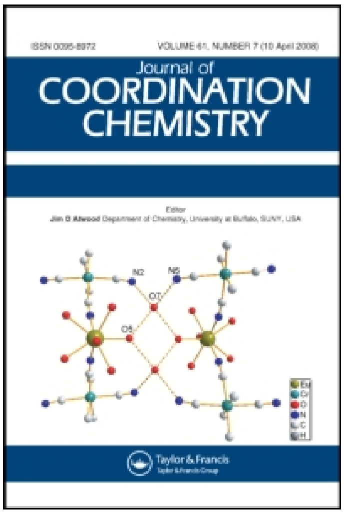

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THE CRYSTAL AND MOLECULAR STRUCTURE OF DI-μ-(PYRIDINE-1-OXIDE)-BIS(DIBROMOCOPPER(II)), $[(C_5H_5NO)CuBr_2]_2$

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The crystal structure of di-μ-(pyridine-1-oxide)-bis(dibromocopper(II)), $[(C_5H_5NO)CuBr_2]_2$, has been determined by single crystal X-ray diffraction techniques. Counter methods were used to collect 759 non-zero reflections. The complex crystallizes in the monoclinic space group $P2_1/c$ with 2 dimeric molecules per unit cell. The cell dimensions are $a = 10.977(5)$, $b = 10.007(5)$, $c = 7.88(1)$ Å and $\beta = 110° 30' (10)$. The observed and calculated densities are 2.601 and 2.608, g. cm^{-3}, respectively. The structure was refined by least-squares methods to a conventional R factor of .072. The oxygen-bridged dimer has a center of symmetry which requires the two Cu(II) ions and the two bridging oxygen atoms to lie in a plane. Each Cu(II) ion is five coordinate and the geometry is best described as a square-based pyramid. Two bridging oxygen atoms and two bromine atoms form the square base while the apical site is occupied by a bromine from an adjacent dimer. The Cu—O distances are 1.965(9) and 1.994(6) Å, the basal Cu—Br distances are both 2.332(2) Å and the intermolecular Cu—Br distance is 3.130(3) Å. The complex is not isostructural with the chloride complex, and there is little distortion of the square-basal geometry due to steric interactions. The $d_{x^2-y^2}$ orbitals in the bromide complex are able to overlap to a greater extent than in the chloride complex, and the magnetic moment is reduced. The nephelauxetic effect need not be introduced to rationalize the differences in magnetic behavior.

INTRODUCTION

The 1 : 1 complexes of aromatic N-oxides and $CuCl_2$ exist as oxygen-bridged dimers, and magnetic exchange results in reduced magnetic moments. The magnetic properties have been characterized by magnetic susceptibility or resonance techniques, but the detailed mechanism of the superexchange process has not been elucidated.

The crystal structure of di-μ-(pyridine-1-oxide)-bis(dichlorocopper(II)), $[(C_5H_5NO)CuCl_2]_2$, has been reported.[1-3] The geometry around the copper(II) ion can be described as a highly distorted square-based pyramid with the two bridging oxygen atoms and the two chlorine atoms forming the base. The apical position is occupied by a chlorine atom from an adjacent dimer. The room temperature magnetic moment of the chloride complex is 0.63 B.M.[4] while that of the bromide complex is 0.29 B.M.[5-7] This reduction in moment has been attributed to the nephelauxetic properties of the bromine atom;[8] however, other factors may be responsible for this difference. One theory of superexchange considers the expansion of the magnetic metal ion orbitals through interaction with the ligand orbitals of appropriate symmetry. The expanded orbitals of the two metal ions overlap (delocalization) and an antiferromagnetic interaction occurs. Ferromagnetic interactions may occur if orthogonal orbitals are involved. The magnitude of the superexchange should be sensitive to the orientation of ligand and magnetic orbitals, and geometric and electronic factors which reduce the magnetic orbital overlap should reduce the magnitude of the exchange. A review of this subject has been presented by R. L. Martin.[9] To investigate the factors influencing magnetic exchange, we have determined the structure of di-μ-(pyridine-1-oxide)-bis(dibromocopper(II)), $[(C_5H_5NO)CuBr_2]_2$.

EXPERIMENTAL

Di-μ-(pyridine-1-oxide)-bis(dibromocopper(II)) was prepared by mixing ethanol solutions of pyridine-1-oxide and copper(II) bromide in a 1 : 1 molar ratio. The dark brown precipitate was dissolved in an excess of ethanol and slow evaporation yielded dark brown block shaped crystals suitable for X-ray analysis.

A single crystal was selected and ground to a sphere in a Nonius crystal grinder. The spherical crystal, 0.13 mm in diameter, was used in the collection of all intensity data. Preliminary X-ray photographs had indicated the crystal was monoclinic, and the ground sphere was oriented with the *c* axis coincident with the rotation axis. The unit cell parameters were determined at room temperature from precession and Weissenberg photographs which were calibrated by superimposed NaCl powder lines, $a = 5.6402$ Å. The photographs were obtained using zirconium-filtered MoKα radiation.

CRYSTAL DATA

$[(C_5H_5NO)CuBr_2]_2$ Mol. Wt. = 636.9

$a = 10.977(5)$, $b = 10.007(5)$, $c = 7.88(1)$ Å,

$\beta = 110°30'(10)$

Systematic absences: $h0l$, $l = 2n + 1$; 0k0, $k = 2n + 1$. (Observed on precession and Weissenberg photographs and three-dimensional counter-collected data.)

Space group: $P2_1/c$.

$Z = 2$, $V = 811.0$ Å^3 $\mu = 131.187$ cm^{-1} (MKoα)

$D_{obs.} = 2.601$ g. cm^{-3}, $D_{calc.} = 2.608$ g. cm^{-3}

The errors in the cell edges are the average deviations calculated from measurements of several high angle reflections or layer lines. The error in the angle is the average deviation calculated from several measurements of the same angle. The density was measured by the flotation technique using a mixture of bromoform and chloroform. The bromide complex is not isostructural with the chloride complex.

Three-dimensional intensity data were collected through the 7th level (*hk*0 to *hk*7) with a Philips PAILRED diffractometer using equi-inclination Weissenberg geometry and a continuous ω-scan technique. The scan range varied from 3° for *hkO* to 4.8° for *hk*7. A scan speed of 1° per minute and background counts of 20 seconds were taken at the extremes of the scan range. MoKα radiation ($\lambda = 0.71069$ Å) and a silicon monochromator crystal (d(111) = 3.1355 Å) were used to collect the room temperature counter data. A total of 1312 reflections were measured and 759 were considered to have an observed intensity. An intensity was designated as observed if it was greater than twice the calculated standard deviation for the reflection. The intensities of several standard reflections were monitored during the data collection period, and the data were corrected for small variations in these intensities.[10] The reference reflections were used to scale the levels together, and the scaling was checked several times during the refinement.

The raw data were reduced to structure factors and standard Lorentz and polarization corrections were applied.[11] Absorption corrections were made for a spherical crystal.[12] Standard deviations for the structure factors were assigned on the basis of counting statistics. Included in the standard deviation is a term for instrument instability which was chosen as 3% of the magnitude of the observed raw intensity. The standard deviation is given by

$$\sigma^2(I) = S + t^2B + [0.03\,(S - tB)]$$

where S = total scan count, B = total background count and t = ratio of time for scan to that for background.

The *hkO* and $\bar{h}kO$ reflections were averaged and a Wilson plot was used to put all data on an approximate absolute scale and to obtain an overall temperature factor. The scattering factors[13] of copper and bromine were corrected for the real and complex part of the anomalous dispersion.

STRUCTURE DETERMINATION

The structure was solved using Patterson and Fourier techniques. The positions of the copper and two bromine atoms were determined from a three-dimensional Patterson map in which the origin peak had been removed. Two cycles of refinement with 529 of the most intense reflections gave a conventional *R*-value of 0.25, where $R = \Sigma\big||F_0| - |F_c|\big|/\Sigma|F_0|$. A subsequent Fourier map yielded the positions of all non-hydrogen atoms. Three cycles of isotropic refinement, with all non-hydrogen atoms included, lowered the *R*-value to 0.112 with a weighted *R* of 0.107, where $R(\text{wtd}) = \Sigma w\big||F_0| - |F_c|\big|/\Sigma w|F_0|$. Three cycles of refinement with the copper, oxygen and bromine atoms assigned anisotropic thermal parameters gave $R = .064$ and $R(\text{wtd}) = .059$. Hydrogen atoms were located in a difference Fourier; however, their positional parameters were calculated by assuming the atoms were in the plane of the pyridine ring and at a distance of 1.08 Å from the carbon atoms. Inclusion of the hydrogen atoms lowered *R* to .051 which is significant at the $\alpha = .005$ level.[14] The

TABLE I

Atomic and thermal parameters for di-μ-(pyridine-1-oxide)-bis(dibromocopper(II)), $[(C_5H_5NO)CuBr_2]_2$

Atom	X[a]	Y	Z	B or B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	.0920(1)	−.0778(2)	−.0899(2)	2.30(2)	2.84(2)	3.70(4)	.29(4)	−.23(5)	−1.62(6)
Br(1)	.0377(1)	−.1829(1)	−.3708(2)	3.23(2)	3.72(2)	3.77(4)	.94(4)	.12(4)	−2.45(6)
Br(2)	.3180(1)	−.0901(2)	−.0017(2)	2.46(2)	5.21(3)	4.40(4)	.49(4)	.42(5)	−.77(5)
O	.0902(6)	.0300(9)	.1175(9)	2.36(15)					
N	.1965(8)	.0580(12)	.2703(12)	2.94(26)					
C(1)	.2377(11)	−.0364(18)	.3982(19)	4.19(37)					
C(2)	.3430(12)	−.0027(19)	.5511(19)	4.84(45)					
C(3)	.4030(12)	.1231(17)	.5626(17)	4.11(38)					
C(4)	.3564(11)	.2173(19)	.4244(17)	4.40(36)					
C(5)	.2498(12)	.1806(18)	.2730(18)	4.47(42)					
H(1)[c]	.2106	.2484	.1603	2.0					
H(2)	.4008	.3147	.4342	2.0					
H(3)	.4867	.1470	.6804	2.0					
H(4)	.3789	−.0731	.6614	2.0					
H(5)	.1916	−.1332	.3831	2.0					

[a] Numbers in parentheses are estimated standard deviations of the last significant digit.

[b] Anisotropic thermal parameters have the form

$$\exp\left[-.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^{b*} + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

[c] Hydrogen atom parameters were used to calculate structure factors but they were not refined.

neutron determined distance was used since we are interested in intermolecular interactions. The final R for all 759 observed reflections was .072 with R(wtd) = .056. The weighted sum of the squares of the residuals was the function minimized in the least-squares refinement, and an individual weighting scheme $w = 1/\sigma(Fo)^2$ was used. A final three-dimensional Fourier map was calculated and the largest residual peak was 0.89 $\bar{e}/Å^3$. On the same scale carbon had a weight of 3.97 $\bar{e}/Å^3$.

All shifts of the positional parameters during the final cycle of full-matrix refinement were much less than the estimated standard deviations of the parameters. The largest relative change was 0.1 standard deviations for a carbon atom. The estimated standard deviation of the parameters were calculated from the inverse of the normal-equations matrix of the last least-squares cycle. The final positional and thermal parameters are given in Table I. A listing of the final observed and calculated structure factors may be obtained from the editor. The uniform bond lengths and bond angles, together with the reasonable thermal parameters, indicates the data collection procedure was reliable. The function $Qs = \Sigma(|F_0|-|F_c|)/\sigma(F_0)$ was plotted for incremental ranges of F_0, $\sin\theta/\lambda$, h, k, l and the counter angle. No systematic errors were indicated.

DISCUSSION

Projections of the unit cell contents along the a and b axes are shown in Figures 1 and 2. The oxygen-bridged dimer contains a center of symmetry and the copper and oxygen atoms must be coplanar. Bond distances and bond angles are given in Table II.

A unit-weighted least-squares plane fitted to the pyridine ring gives the equation $(-.820x + .369y + .438z - .076 = 0)$. The average deviation of the six atoms from the plane is .006 Å, with the largest deviation being .009 Å. The C—C bond distances, which average 1.399 Å, are within one standard deviation of the expected value of 1.395 Å. The N—C distances of 1.335 and 1.339 Å are normal. The dihedral angle between the normal to the copper-oxygen bridging plane and the normal to the pyridine ring plane is 83° while that in the corresponding chloride complex is 70°.[2] The larger intermolecular separation affects steric interactions of the rings.

The geometries about the copper ions in the chloride and bromide complexes appear to be quite similar; however, there are significant differences which lead to differences in the magnitudes of the magnetic exchange. The coordination about the copper ions in these two complexes is shown in

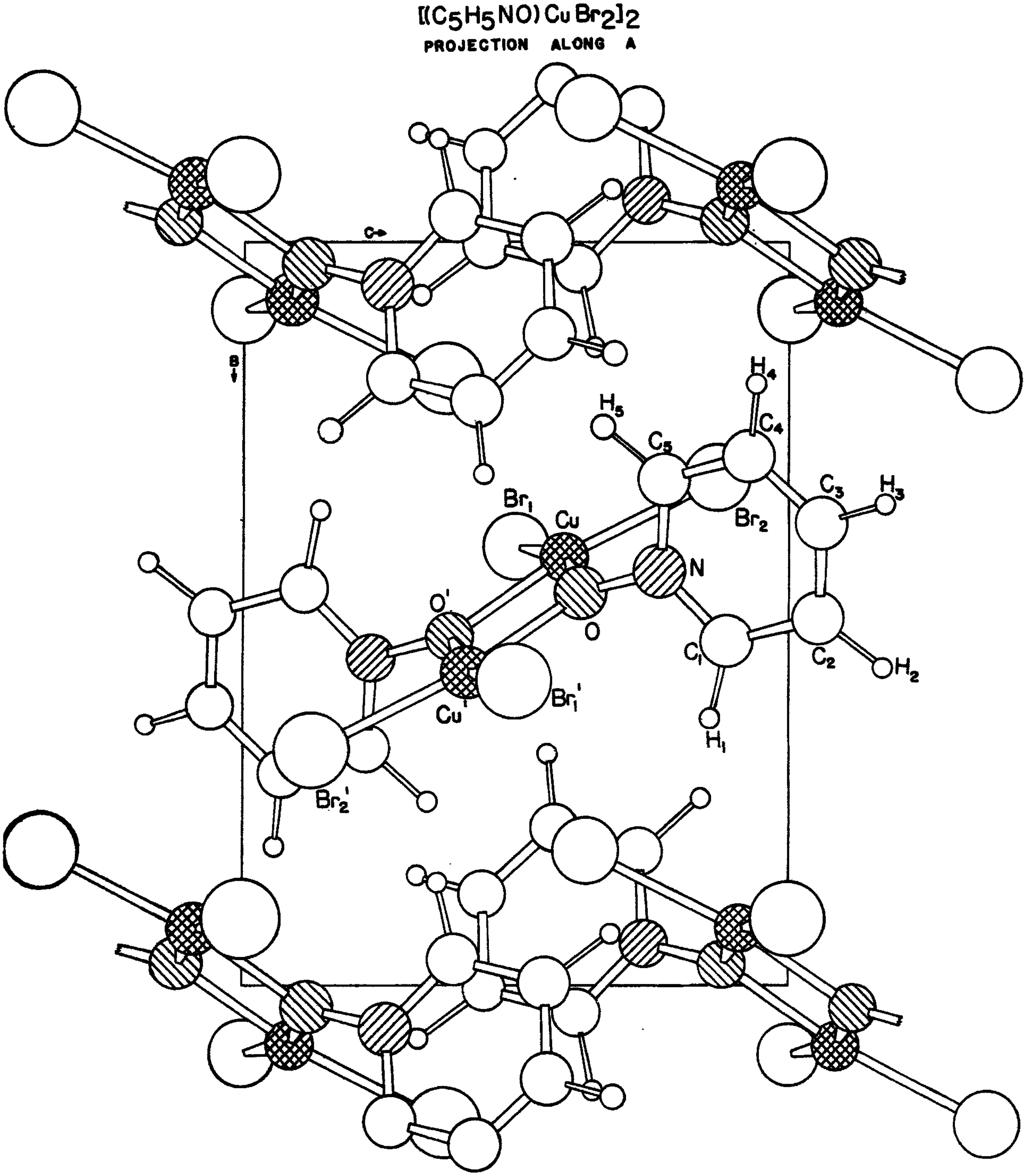

FIGURE 1 Projection of the structure of $[(C_5H_5NO)CuBr_2]_2$ onto the *bc* plane.

TABLE II

Interatomic distances and bond angles for di-μ-(pyridine-1-oxide)-bis(dibromocopper(II)), $[(C_5H_5NO)CuBr_2]_2$[a]

Cu—Br(1)	2.333(2)	N—C(5)	1.355(21)
Cu—Br(2)	2.332(2)	C(1)—C(5)	1.388(24)
Cu—Br(1)″	3.130(3)	C(2)—C(3)	1.409(24)
Cu—O	1.965(9)	C(3)—C(4)	1.396(24)
Cu—O′	1.994(6)	C(4)—C(5)	1.397(23)
O—N	1.381(14)	O—O′	2.269(10)
N—C(1)	1.339(22)	Cu—Cu′	3.244(2)
Br(2)CuBr(1)	98.7(1)	Cu′ON	123.8(7)
OCuO′	69.9(3)	ONC(1)	118.2(1.2)
CuOCu′	110.1(4)	ONC(5)	115.2(1.2)
Br(1)CuBr(1)″	98.3(1)	O′ON	174.6(8.2)
Br(2)CuBr(1)″	100.6(1)	NC(1)C(2)	116.2(1.5)
OCuBr(1)″	84.4(3)	C(1)C(2)C(3)	120.0(1.7)
OCuBr(2)	95.8(2)	C(2)C(3)C(4)	121.2(1.5)
O′CuBr(1)	95.2(3)	C(3)C(4)C(5)	117.2(1.6)
O′CuBr(1)″	82.3(3)	C(4)C(5)N	118.6(1.5)
CuON	125.9(6)	C(5)NC(1)	126.6(1.4)

[a] Numbers in parentheses are estimated standard deviations of the last significant digit.

Figure 3. The Cu—O—Cu angles of 108° and 110° and the O—Cu—O angles of 72° and 70° are similar. The Cu—Cu separations of 3.245 and 3.244 Å are the same. The Cu—O bond lengths of 1.965(9) and 1.994(6) Å in the bromide complex are slightly shorter than the Cu—O bond lengths of 1.979(11) and 2.036(11) Å in the chloride complex, and this is consistent with the magnetic properties. Although the 2.036(11) Å distance apparently is statistically different from the two distances in the bromide complex, these differences should be used with some discrimination. The basal plane of the chloride complex is more distorted than that of the bromide complex. One chlorine atom lies .38 Å above the plane defined by the copper and oxygen atoms while the other lies 1.2 Å below. The two bromine atoms lie 0.18 Å and 0.16 Å below this plane.

Although the apical bromine does not lie directly above the Cu(II) ion, the angles between the *trans* atoms in the base are 183° and 182° compared to 211° and 171° for the chloride complex. The two

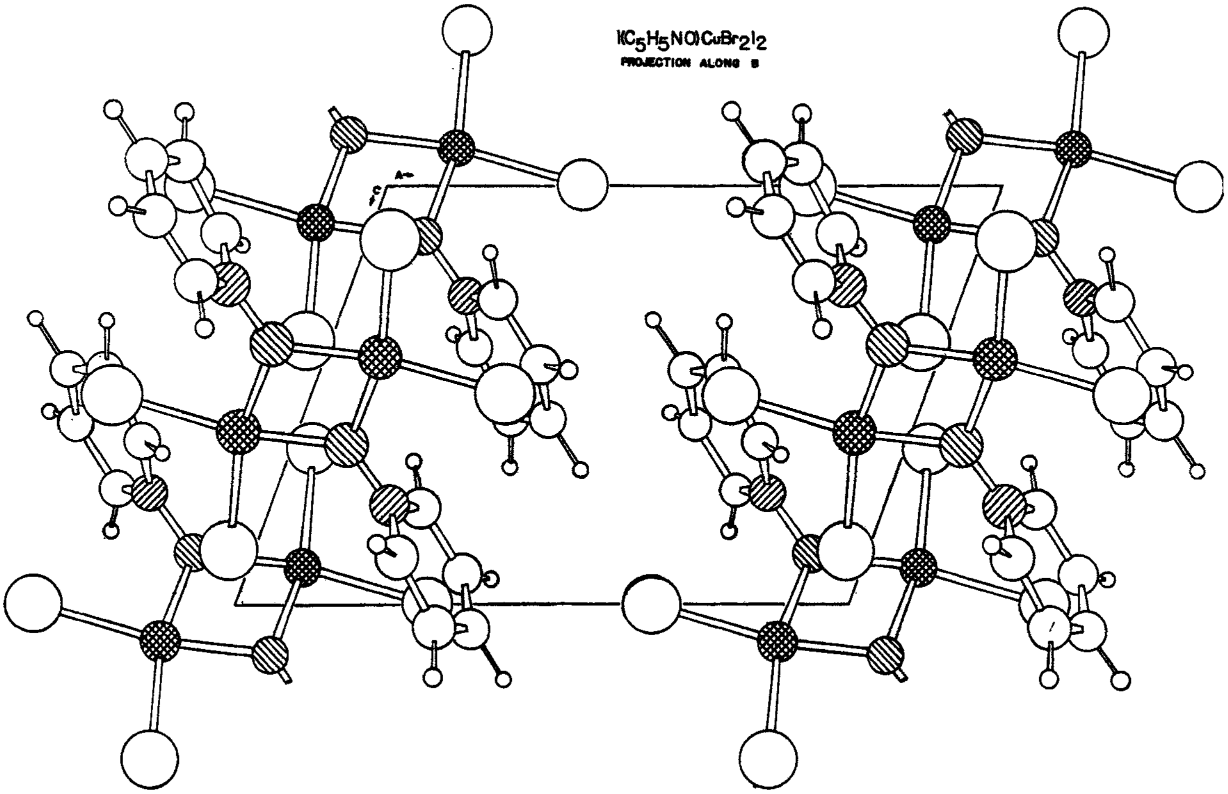

FIGURE 2 Projection of the structure of $[(C_5H_5NO)CuBr_2]_2$ onto the *ac* plane.

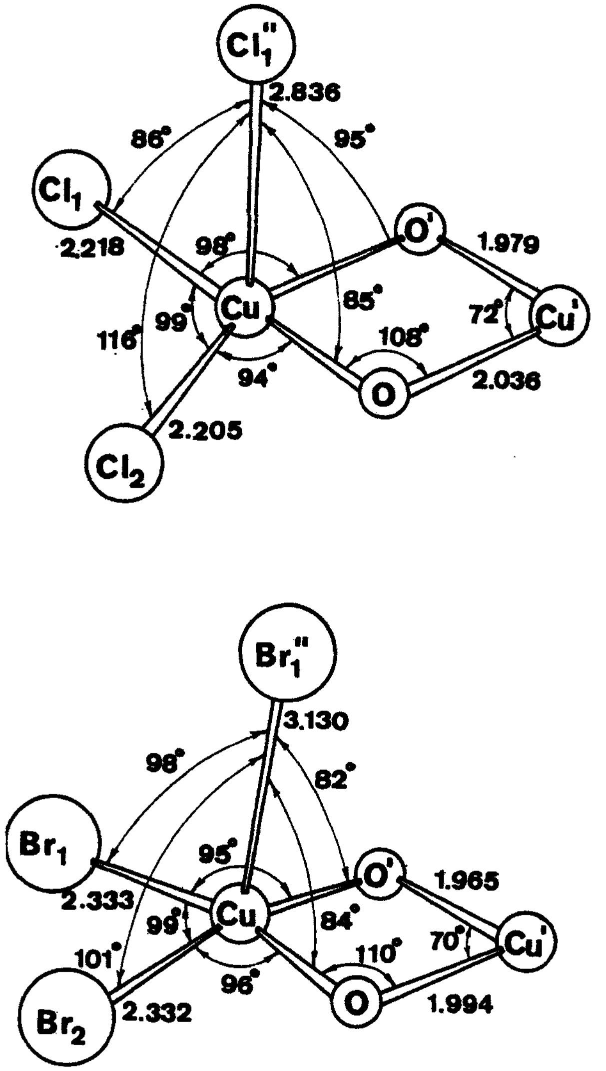

FIGURE 3 Coordination around the Cu(II) ion in the $[(C_5H_5NO)CuBr_2]_2$ and $[(C_5H_5NO)CuCl_2]_2$ complexes.

Cu—Cl bonds, 2.218(5) and 2.206(5) Å, are about .12 Å shorter than the Cu—Br bonds, 2.333(2) Å and 2.332(2) Å. This is approximately the difference in the ionic radii of the two halogens. The intermolecular Cu—Cl distance of 2.836(5) is 0.29 Å shorter than the Cu—Br distance of 3.130(3) Å. The difference is approximately twice as great as the difference in ionic radii. The major distortion in the chloride complex is associated with a steric interaction between the ortho pyridine hydrogen of one dimer and the basal chlorine atom Cl(2) of another. Crystal packing prevents the pyridine ring from rotating to relieve this interaction, and the chlorine atom is forced out of the basal plane. Even with this distortion the H(5)''—Cl(2) interaction distance is only 2.5 Å. Also the short Cu—Cl(1)'' intermolecular distance requires chlorine atom Cl(1) to be bent from the basal plane in order to minimize other intermolecular interactions. The longer Cu—Br(1)'' intermolecular distance reduces intermolecular steric interactions. The greater intermolecular separation allows the pyridine ring to rotate and the H(5)''–Br(2) separation of 2.8 Å can be achieved without distorting the basal plane.

The weaker interaction at the apical site and only a slight distortion of the square basal geometry are consistent with a greater overlap of the magnetic orbitals in the bromide complex. A greater overlap of the magnetic orbitals would lead to a reduced magnetic moment and probably a small decrease in the Cu—O bond lengths. The relationship between apical substitution, the length of Cu—O bonds and the magnitude of the exchange interaction are consistent with other studies in this series. Geometric factors can account for the differences in the magnetic properties of the chloride and bromide complexes, and the nephelauxetic effect need not be invoked.

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REFERENCES AND NOTES

1. R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.* **8**, 694 (1969).
2. R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.* **6**, 951 (1967).
3. H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.* **42**, 504 (1965).
4. W. H. Watson, *Inorg. Chem.* **8**, 879 (1969).
5. J. V. Quagliano, J. Fujita, G. Frans, O. J. Phillips, J. A. Walmsley, and S. V. Tyree, *J. Am. Chem. Soc.* **83**, 3770 (1961).
6. C. M. Harris, E. Kokot, S. L. Lenzer, and T. N. Lockyer, *Chem. Ind.* (London), 651 (1962).
7. M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.* **64**, 99 (1964).
8. M. Kato, Y. Muto, and H. B. Jonassen, *Bull. Chem. Soc. Japan* **40**, 1738 (1967).
9. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharp, *New Pathways in Inorganic Chemistry* (Cambridge University Press, 1968), Chapter 9, pp. 175–231.
10. A difference of 5–10% frequently is observed following a power failure.

11. A listing of computer programs may be found in the Ph.D. Dissertation, N. R. Stemple, Texas Christian University, 1970.
12. *International Tables for X-ray Crystallography*, Vol. II (Kynoch Press, Birmingham, England, 1959).
13. *International Tables for X-ray Crystallography*, Vol. III (Kynoch Press, Birmingham, England, 1959).
14. W. C. Hamilton, *Acta Cryst.* **18**, 502 (1965).