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Crystal and Molecular Structure of Bis[*N*-(picolinoyl)-3-amino-1-propoxidoaquocopper(II)] Dihydrate. A Copper(II) Dimer Containing a Bent Four-Membered Ring

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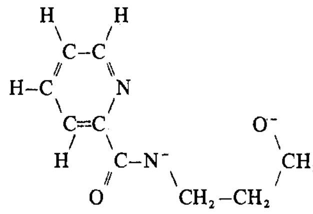
The crystal structure of the compound $CuC_9H_{14}N_2O_4$, $CuL{\cdot}2H_2O$ (where L represents the dianion of the amide formed by the condensation of picolinic acid and 3-aminopropanol), has been studied by X-ray diffraction. The structure consists of dimeric units, $[CuL(H_2O)]_2$, and waters of crystallization that are linked by weak hydrogen bonding into an infinite, nearly planar network. The dimeric unit has twofold symmetry and contains a bent Cu_2O_2 ring (dihedral angle of 15.8 (4)° between the O-Cu-O planes). The coordination of the copper(II) is a distorted tetragonal pyramid with the weakly coordinated water (Cu-O = 2.394 (6) Å) in the apical position. The pyridine nitrogen (2.010 (5) Å), amide nitrogen (1.919 (5) Å), and alkoxide oxygen (1.951 (4) Å) of one ligand and the alkoxide oxygen of the second ligand occupy the basal coordination positions. The magnetic susceptibility data that were previously reported for this compound are discussed in terms of exchange coupling within the Cu_2O_2 ring of the dimer and through the hydrogen-bonding network. Crystal data for $[CuL(H_2O)]_2{\cdot}2H_2O$ are as follows: space group $C2/c$, $a = 20.328$ (7) Å, $b = 7.317$ (3) Å, $c = 16.862$ (3) Å, $\beta = 119.58$ (2)°, $Z = 4$, $\rho_{obsd} = 1.69$ g cm^{-3}, $\rho_{calcd} = 1.67$ g cm^{-3}. Final residual factors for the 1279 reflections above 3σ are $R = 0.043$ and $R_w = 0.031$.

Introduction

Recently, the preparation and properties of two copper(II) complexes containing the dianion of *N*-(picolinoyl)-3-amino-1-propanol (hereafter referred to as L), I, were reported.[1,2]



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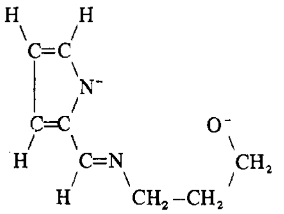

II

An anhydrous material with empirical formula CuL was isolated and found to exhibit antiferromagnetic behavior. The magnetic susceptibility observed for this compound at temperatures above 150°K agreed well with the Bleaney and Bowers equation[3] for a binuclear formulation ($2J = -555$ cm^{-1}, $g = 2.14$, $N\alpha = 60 \times 10^{-6}$ emu). The geometry of the ligand L is very similar to that of the Schiff base, II, obtained by the condensation of pyrrole-2-carboxaldehyde and 3-amino-1-propanol and the copper complexes of both ligands show similar magnetic behavior. Thus, it is probable that the structures of the two complexes are similar and that $[CuL]_2$ also contains planar, four-coordinate copper ions bridged by the alkoxide groups into a planar, four-membered Cu_2O_2 ring.[4]

A blue hydrated compound, $CuL{\cdot}2H_2O$, was isolated as an intermediate in the preparation of CuL and, although its magnetic susceptibility was considerably higher than that of CuL at all temperatures, the hydrate also exhibited antiferromagnetic behavior; however, attempts to describe the temperature variation of the magnetic susceptibility of the hydrate in terms of a binuclear formulation were unsuccessful. The best agreement with the experimental values was obtained with a tetrameric ring formulation ($2J = -128$ cm^{-1}, $g = 2.08$) but even that formulation did not agree perfectly and the possibility of two or more kinds of magnetic interactions was suggested.

Because of the weaker magnetic coupling (higher susceptibility) and the lack of agreement of the magnetic properties with any assumed structure, a crystal structure analysis of the hydrated compound was undertaken. In this paper we report the results of that analysis.

Experimental Section

Preparation. The method of Ojima[1] was used to synthesize $CuL{\cdot}2H_2O$. Large blue diamond-shaped platelets, adequate for X-ray structural analysis, were obtained by recrystallization from water. The crystals gradually change to dark green on heating above 150° and melt at 260-262°. *Anal.* Calcd for $CuC_9H_{14}N_2O_4$: C, 38.92; H, 5.08; N, 10.09. Found: C, 38.73; H, 5.17; N, 10.19.

Magnetic Susceptibility. The magnetic susceptibility was determined by the Faraday method using $HgCo(NCS)_4$ as calibrant. Diamagnetic corrections were applied using tabulated values.[5] The experimental moments (BM) per gram-atom of copper (temperature in °K in parentheses) are 1.48 (298), 1.38 (195), and 0.70 (77) assuming a TIP correction of 60×10^{-6} cgsu/g-atom of copper. The corresponding values calculated from the previously reported data[2] are 1.45, 1.31, and 0.70 BM.

Collection and Reduction of the Intensity Data. A blue platelet was mounted on a glass fiber parallel to the h, 0, $2h$ row of the reciprocal lattice. Precession photographs of the $h0l$, $h1l$, $h2l$, and $hk2h$ levels revealed lattice symmetry $2/m$. The systematic absences, hkl ($h + k = 2n + 1$) and $h0l$ ($l = 2n + 1$), were consistent with either monoclinic space group Cc (No. 9) or $C2/c$ (No. 15).[6] Successful refinement of the structure in $C2/c$ verified the assumption of the centrosymmetric space group, $C2/c$.

The crystal was transferred to a Picker automated diffractometer and 16 reflections were centered manually and used to refine cell parameters by a least-squares procedure. In both the cell refinement and the actual data collection, Zr-filtered molybdenum Kα radiation (λ 0.70926 Å) was used. The cell parameters are $a = 20.328$ (7) Å, $b = 7.317$ (3) Å, $c = 16.862$ (3) Å, and $\beta = 119.58$ (2)°.[7] The experimental density, 1.69 (2) g cm^{-3}, was determined by flotation in a carbon tetrachloride-ethylene bromide mixture and agrees well with the calculated density, 1.67 g cm^{-3}, assuming four dinuclear units per cell. Thus, a dimeric formulation in space group $C2/c$ would require the molecule to occupy a special position and to possess either an inversion center or a twofold axis.

Intensity data were collected in the manner previously reported.[8]

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(7) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

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Table I. Individual Atomic and Thermal Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.03056 (3)	0.21512 (9)	0.18686 (4)	0.00146 (2)	0.01497 (13)	0.00193 (2)	0.00024 (6)	0.00090 (2)	0.00051 (7)
N1	−0.0112 (3)	0.2408 (8)	0.576 (3)	0.0021 (1)	0.0126 (14)	0.0023 (2)	0.0004 (3)	0.0011 (1)	−0.0002 (4)
N2	0.1242 (2)	0.1518 (6)	0.1808 (3)	0.0021 (2)	0.0154 (11)	0.0029 (2)	0.0006 (3)	0.0014 (2)	−0.0006 (4)
O1	−0.0663 (2)	0.1870 (7)	0.1834 (2)	0.0018 (1)	0.0167 (11)	0.0020 (2)	0.0002 (3)	0.0010 (1)	−0.0007 (3)
O2	0.0245 (2)	0.2675 (7)	−0.0516 (3)	0.0031 (2)	0.0193 (12)	0.0029 (2)	0.0014 (4)	0.0017 (1)	0.0007 (4)
O3	0.0650 (3)	0.5315 (7)	0.2066 (3)	0.0034 (1)	0.0190 (14)	0.0028 (2)	0.0007 (4)	0.0014 (1)	0.0007 (4)
O4	−0.0928 (3)	0.8150 (9)	0.1567 (3)	0.0039 (2)	0.0172 (11)	0.0045 (3)	0.0002 (5)	0.0029 (2)	0.0003 (5)
C1	−0.1290 (3)	0.2741 (13)	0.1137 (4)	0.0032 (2)	0.0443 (24)	0.0034 (3)	0.0065 (7)	0.0019 (2)	0.0024 (7)
C2A	−0.1439 (5)	0.2294 (21)	0.0214 (6)	0.0014 (3)	0.0136 (23)	0.0018 (4)	−0.0011 (9)	0.0002 (3)	−0.0017 (10)
C2B	−0.1298 (8)	0.3606 (28)	0.0454 (8)	0.0023 (5)	0.0270 (38)	0.0028 (6)	0.0022 (12)	0.0006 (4)	0.0037 (13)
C3	−0.0897 (2)	0.2874 (10)	−0.0076 (3)	0.0017 (2)	0.0185 (12)	0.0024 (2)	0.0006 (5)	0.0006 (2)	0.0008 (5)
C4	0.0373 (2)	0.2381 (7)	0.0281 (3)	0.0020 (1)	0.0119 (13)	0.0023 (2)	0.0006 (4)	0.0013 (1)	−0.0003 (4)
C5	0.1165 (3)	0.1942 (9)	0.1002 (3)	0.0023 (2)	0.0128 (12)	0.0026 (2)	0.0002 (4)	0.0013 (2)	0.0002 (5)
C6	0.1766 (3)	0.1908 (9)	0.0836 (3)	0.0026 (2)	0.0149 (13)	0.0037 (2)	0.0006 (4)	0.0020 (2)	0.0006 (5)
C7	0.2464 (3)	0.1454 (9)	0.1529 (4)	0.0021 (2)	0.0198 (15)	0.0055 (3)	0.0005 (4)	0.0023 (2)	−0.0010 (5)
C8	0.2544 (3)	0.0930 (9)	0.2355 (4)	0.0022 (2)	0.0218 (16)	0.0043 (4)	0.0015 (5)	0.0017 (2)	0.0004 (5)
C9	0.1918 (3)	0.0978 (9)	0.2469 (4)	0.0029 (2)	0.0143 (14)	0.0035 (3)	0.0016 (4)	0.0018 (2)	0.0008 (4)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H1C1	−0.172	0.237	0.117	4.4	HC6	0.164 (3)	0.229 (8)	0.022 (4)	2.9
H2C1	−0.122	0.402	0.123	4.4	HC7	0.286 (4)	0.139 (9)	0.142 (4)	3.9
H1C2A	−0.190	0.291	−0.019	3.0	HC8	0.300 (3)	0.058 (7)	0.283 (4)	3.5
H2C2A	−0.149	0.105	0.014	3.0	HC9	0.194 (3)	0.081 (7)	0.302 (4)	3.0
H1C2B	−0.106	0.480	0.070	3.0	H1O3	0.058 (4)	0.569 (10)	0.174 (5)	3.3
H2C2B	−0.181	0.384	0.002	3.0	H2O3	0.070 (4)	0.602 (9)	0.244 (5)	3.3
H1C3	−0.097 (3)	0.415 (8)	0.035 (4)	3.0	H1O4	−0.084 (4)	0.907 (9)	0.174 (5)	3.5
H2C3	−0.105 (3)	0.212 (9)	−0.068 (4)	3.0	H2O4	−0.078 (4)	0.775 (10)	0.134 (5)	3.5

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$. Atom multiplier of C2A 0.52 (1); atom multiplier of C2B 0.48 (1).

A takeoff angle of 1.6° was used. Three approximately orthogonal reflections (040, $\bar{4}08$, 400) and null reflection (050) were monitored after every 150 reflections and showed no systematic variation in intensity. The corrected intensities were assigned standard deviations according to the formula[9]

$$\sigma(I) = [\mathrm{CT} + 4.5 + (t_c/t_b)^2(\mathrm{bgd1} + \mathrm{bgd2} + 9.0) + (pI)^2]^{1/2}$$

where p, the "ignorance factor," was assigned a value of 0.02 and the values 4.5 and 9.0 account for uncertainties in the number of counts due to truncation of the last digit by the scalar. From a total of approximately 4000 reflections collected in a full quadrant of reciprocal space, 1369 unique reflections were accepted as statistically above background on the basis that $\sigma(I)/I < 0.33$. Lorentz and polarization corrections were applied in the usual way.

Solution and Refinement of the Structure. Computations were carried out on the Univac 1108 computer. Programs employed include Carter's cell parameter and diffractometer setting angle program, Zalkin's FORDAP Fourier summation program, Iber's NUCLS modification of the Busing–Martin–Levy ORFLS full-matrix least-squares program, the Martin–Busing–Levy ORFFE function and error program, Johnson's ORTEP plotting program, Stewart's ABSORB absorption correction program from the X-Ray 72 system, and various locally written programs. In the structure factor calculations, the scattering factors were taken from Cromer and Waber's tabulation[10] for all atoms except hydrogen; Stewart's hydrogen atom scattering factors were used.[11] The scattering factor for copper was corrected for the real and imaginary anomalous dispersion components, using the dispersion factors tabulated by Cromer.[12] The agreement factors are defined in the usual way as $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$. In all least-squares refinements, the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic coordinates for copper, two oxygen atoms, and two nitrogen atoms were deduced from a three-dimensional Patterson synthesis and refined to give the initial residuals, $R = 0.33$ and $R_w = 0.41$. The remaining atoms were located by means of Fourier syntheses and least-squares refinements. A refinement using a weighting scheme based on counting statistics ($w = 4I/\sigma^2(I)$) and isotropic temperature factors for all nonhydrogen atoms converged with $R = 0.109$ and $R_w = 0.139$. Anisotropic thermal parameters were introduced and further refinement reduced R to 0.090 and R_w to 0.092. The 12 principal faces of the crystal were identified as the following (distance in millimeters from the center of the crystal to the face is given in parentheses): {111} (0.11), {100} (0.05), and {001} (0.18). Absorption corrections, calculated by the gaussian quadrature method, were applied; corrections on F^2 ranged from 1.22 to 1.43. Refinement with the absorption-corrected data set, after deletion of several reflections which had erroneous scans due to instrumental malfunctions, reduced R to 0.062 and R_w to 0.051. The 14 hydrogen atoms were located as the principal features on an electron density map; in subsequent refinements, the hydrogen coordinates were varied but the hydrogen thermal parameters were fixed at the values of the corresponding carbon atoms prior to conversion to the anisotropic form. These refinements converged to give $R = 0.056$ and $R_w = 0.044$.

Examination of thermal ellipsoids for propyl carbon atoms C1 and C2 gave strong indications of either disorder or severe libration approximately normal to the coordination plane (approximately normal to the b axis). A difference electron density map revealed two distinct maxima separated by *ca.* 0.6 Å about the refined C2 position and a slightly elongated streak of electron density about C1. Thus, in further refinements two partial atoms, C2A and C2B, were refined with occupancies α and $1 - \alpha$ rather than a single atom of occupancy 1.0. Nearly equal occupancy factors, 0.52 and 0.48, were obtained for C2A and C2B, respectively. The refinements converged to final values of $R = 0.043$ and $R_w = 0.033$. Because of the success of the refinement and the normalcy of the thermal parameters for the other atoms, it is considered unlikely that the problem with C2 and C1 is due to ambiguity in the space group determination (*i.e.*, *Cc vs. C2/c*) rather than to a genuine twofold static disorder. In the final cycle of refinement, the maximum parameter shift was 0.1σ(y coordinate for H1O3). The major feature on a final difference Fourier map was a peak of 0.48 e Å^{-3} *ca.* 2 Å from O3; this compares to values of *ca.* 5.0 and 0.8 e Å^{-3} for typical carbon and hydrogen atoms in this structure. Final atomic parameters are listed in Table I; final observed and calculated structure factors are available.

Description of the Structure

The structure of CuL·2H$_2$O is best represented by the formula [CuL(H$_2$O)]$_2$·2H$_2$O. The dimeric molecular units, with crystallographic twofold symmetry, and the waters of crystallization are linked by weak hydrogen bonding into an infinite two-dimensional network. The structure of the dimeric unit is illustrated in Figure 1 and the crystal packing is

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(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

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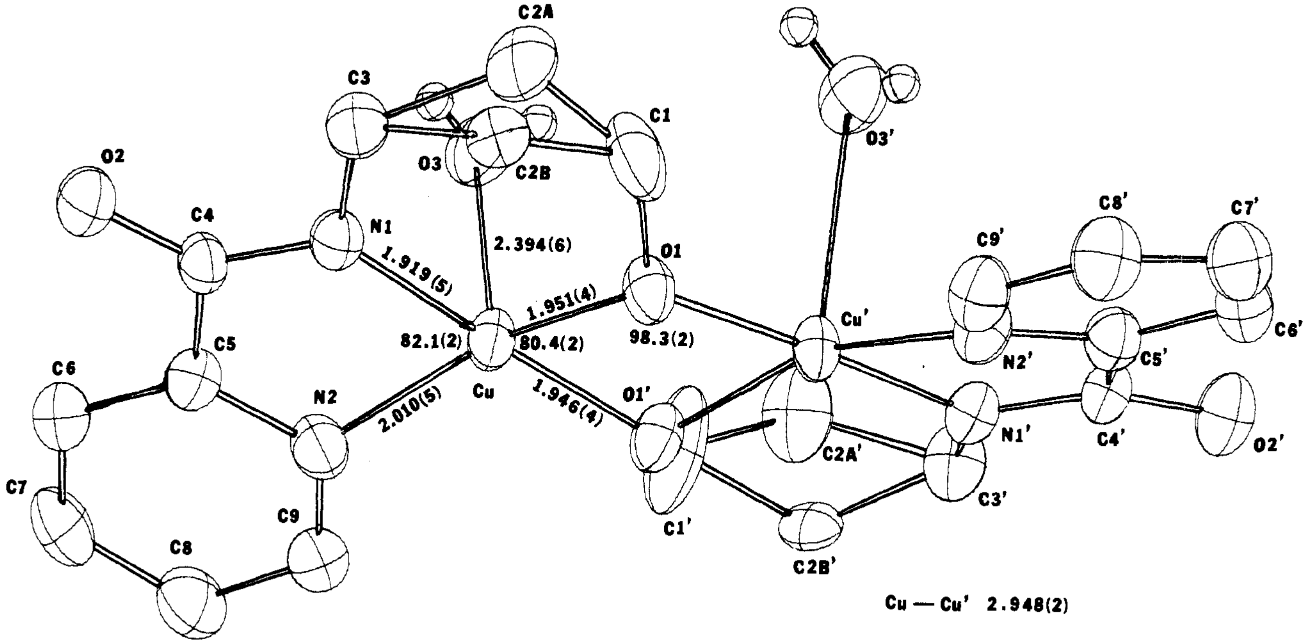


Figure 1. Molecular structure of $[CuL(H_2O)]_2 \cdot 2H_2O$.

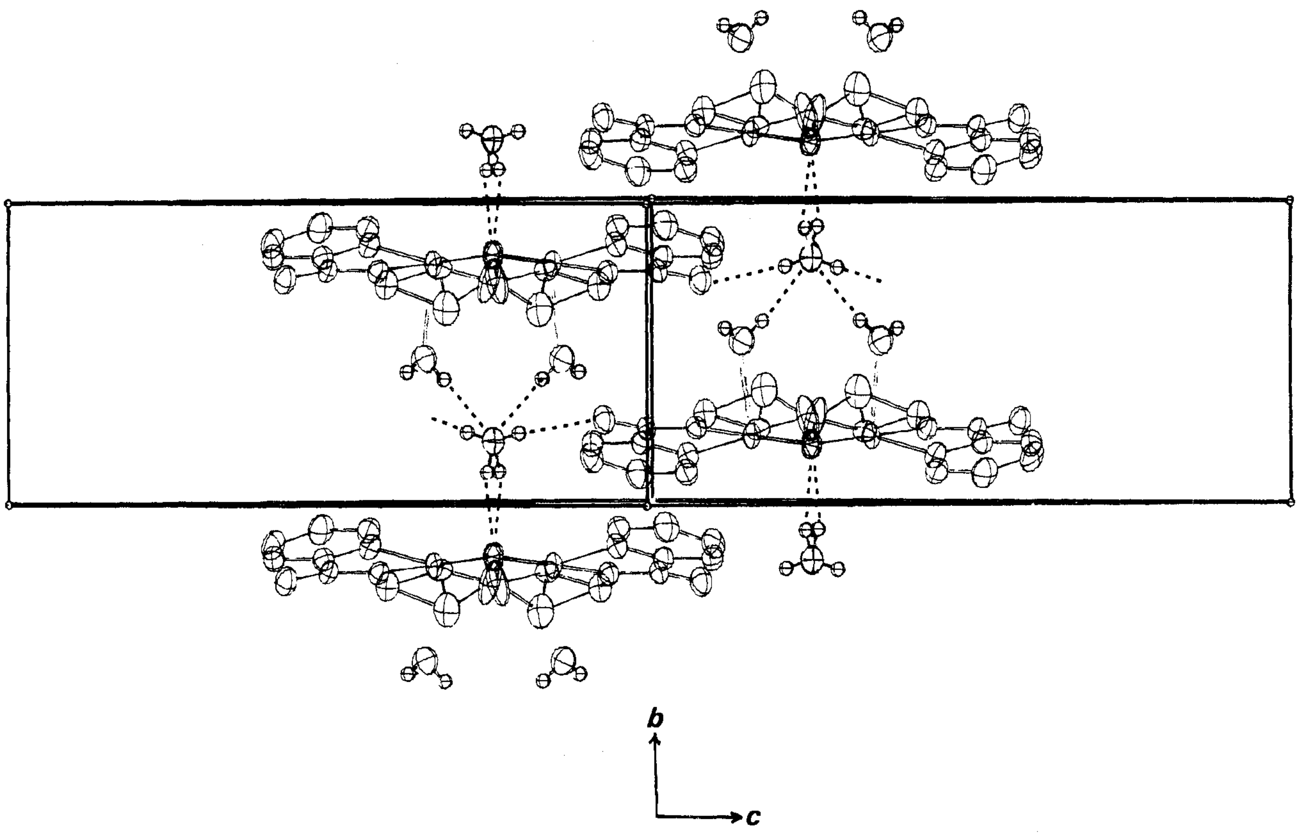


Figure 2. Perspective view of the crystal packing. The structure is approximately projected onto the (101) plane, resulting in overlap of O4 and O4' (related by the twofold operation).

illustrated in Figure 2; selected intramolecular distances and angles are presented in Table II.

Each copper atom has a distorted tetragonal-pyramidal geometry with coordination by two nitrogen atoms (a pyridyl and an amide nitrogen, both from the same ligand) and two oxygen atoms (alkoxide oxygens from the two ligands of the dimer) in the basal plane and by a water molecule in the axial position. The distortion of the tetragonal pyramid is indicated by the fact that the basal donor atoms are not planar, Table III, but deviate by as much as 0.19 Å from their least-squares plane. The nature of the distortion is indicated by the dihedral angle between the N1-Cu-N2 plane and the O1-Cu-O1' plane, 19.8 (2)°, and by the nature of the displacements from the least-squares plane; Cu, N1, and O1' are displaced (0.16, 0.11, and 0.19 Å, respectively) in the direction of the axial water molecule and N2 and O1 are displaced (both by 0.18 Å) to the opposite side of the plane to give a distortion toward a trigonal-bipyramidal arrangement. As usual in the case of

Table II

A. Selected Intramolecular Distances[a]

Atoms	Dist, Å	Atoms	Dist, Å
Cu-N1	1.919 (5)	C2A-C3	1.471 (11)
Cu-N2	2.010 (5)	C2B-C3	1.571 (16)
Cu-O1	1.951 (4)	C4-C5	1.497 (7)
Cu-O3	2.394 (6)	C5-C6	1.381 (7)
N1-C3	1.463 (7)	C6-C7	1.361 (8)
N1-C4	1.306 (7)	C7-C8	1.375 (8)
N2-C5	1.326 (6)	C8-C9	1.378 (7)
N2-C9	1.333 (7)	O1-O4	2.840 (7)
O1-C1	1.391 (7)	O4‴-O2″	2.788 (7)
O2-C4	1.254 (6)	Cu-Cu′	2.948 (2)
O3-O4	2.890 (7)	Cu-O1′	1.946 (4)
C1-C2A	1.468 (11)	O4‴-O1	2.840 (7)
C1-C2B	1.307 (15)		

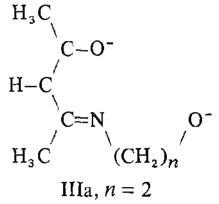
B. Selected Bond Angles

Atoms	Angles, deg	Atoms	Angles, deg
N1-Cu-N2	82.1 (2)	Cu-O1-Cu′	98.3 (2)
N1-Cu-O1	95.9 (2)	Cu-O3-O4	135.2 (2)
N1-Cu-O3	89.9 (2)	O1-C1-C2A	114.7 (6)
N2-Cu-O1′	101.3 (2)	O1-C1-C2B	125.1 (8)
N2-Cu-O3	90.6 (2)	C1-C2A-C3	119.4 (8)
O1-Cu-O1′	80.4 (2)	C1-C2B-C3	123.5 (13)
O1-Cu-O3	109.1 (2)	C2-C3-N1	113.7 (5)
O1′-Cu-O3	91.4 (2)	N1-C4-O2	127.5 (5)
N1-Cu-O1′	176.3 (2)	N1-C4-C5	113.9 (4)
N2-Cu-O1	101.3 (2)	O2-C4-C5	118.6 (4)
Cu-N1-C3	125.6 (4)	N2-C5-C4	114.7 (4)
Cu-N1-C4	116.0 (3)	N2-C5-C6	122.3 (5)
C3-N1-C4	117.8 (4)	C4-C5-C6	122.9 (4)
Cu-N2-C5	111.3 (3)	C5-C6-C7	118.9 (5)
Cu-N2-C9	129.6 (4)	C6-C7-C8	119.3 (5)
C5-N2-C9	118.5 (5)	C7-C8-C9	118.6 (6)
Cu-O1-C1	117.8 (4)	C8-C9-N2	122.3 (5)

[a] X and X′ are related by the twofold operation; X and X″ are related by the inversion operation; X and X‴ are related by a "*b*" translation.

copper(II) complexes, the axial Cu-O distance (2.394 (6) Å) is considerably longer than the Cu-O distances in the basal plane (1.951 (4) and 1.946 (4) Å).

An interesting feature of the molecular structure is the geometry of the four-membered Cu_2O_2 ring. Unlike oxygen-bridged copper(II) dimers which crystallize with the dimer on an inversion center[4,13,14] and thus have a planar Cu_2O_2 ring, in $[CuL(H_2O)]_2\cdot 2H_2O$ the dimer has twofold symmetry and the four-membered ring is bent to give a dihedral angle of 15.9 (4)° between the O1-Cu-O1′ and the O1-Cu′-O1′ planes. The extent of bending is slightly greater than that observed in the tetrameric complex,[13] $[Cu(EIA)]_4$, of copper(II) and the tridentate ligand IIIa, in which the dihedral angle is *ca.* 12° but is considerably less than that of the corresponding nickel complex,[15] $[Ni(EIA)]_2$, in which the dihedral angle is



IIIa, *n* = 2
b, *n* = 3

Table III. Equations of Least-Squares Planes[a,b] and Distances (Å) of Atoms from These Planes

(a) Equation of the Plane of the Coordination Sphere (O1, N1, N2, O1′)

$0.0645X + 0.9889Y + 0.1337Z = 1.7031$

Cu	0.160	C1	0.273	C5	−0.003
N1	0.107	C2A	−0.201	C6	0.028
N2	−0.184	C2B	0.800	C7	−0.110
O1	−0.176	C3	0.248	C8	−0.361
O1′	0.188	C4	0.109	C9	−0.392
O2	0.191				

(b) Equation of the Plane of the Five-membered Chelate Ring and Amide Oxygen (Cu, N1, N2, C4, C5, O2)

$0.1531X + 0.9667Y + 0.2049Z = 1.8555$

Cu	0.085	N2	−0.082	C4	−0.006
N1	−0.087	O2	0.023	C5	0.054

(c) Equation of the Plane of Pyridine Ring (C5, C6, C7, C8, C9, N2)

$0.0633X + 0.9518Y + 0.3002Z = 1.8974$

Cu	0.364	C7	0.025	N2	0.020
C5	−0.007	C8	−0.010	C9	−0.013
C6	−0.017				

[a] Direction cosines of the plane refer to the orthogonal axis system *a, b, c**. [b] All atoms weighted at unity.

39°. The effect of this bending on the copper-copper distance, the Cu-O-Cu angle, and the O-Cu-O angle can be seen by comparing these parameters for the bent rings in $[CuL(H_2O)]_2$ and in $[Cu(EIA)]_4$ with those for the planar ring[13] in $[Cu(PIA)]_2$ (where PIA represents the ligand IIIb). The Cu-Cu distance is 2.948 (3) Å in $[CuL(H_2O)]_2$, 3.006 (8) Å in $[Cu(EIA)]_4$, and 3.026 (6) Å in $[Cu(PIA)]_2$; the Cu-O-Cu angles for the same three compounds are 98.3 (2), 97.8 (8), and 106.4 (6)° and the corresponding O-Cu-O angles are 80.4 (2), 81.4 (8), and 73.6 (6)°. The effect of bending is, thus, to decrease the copper-copper distance, decrease the angle at oxygen, and increase the angle at copper.

Bond distances and bond angles of the ligand are listed in Table II and are reasonable in comparison to corresponding values in other structures. The C-H distance ranges from 0.91 (6) to 1.06 (6) Å, with an average value of 0.96 Å, and bond angles involving hydrogens indicate reasonable geometries about the carbons.

The hydrogen bonding in the structure is relatively weak and involves the uncoordinated water molecule (O4), which serves as a proton donor to the alkoxide oxygen (O4‴-O1, 2.840 (7) Å; H1O4‴-O4, 0.79 (6) Å; H1O4‴-O1, 2.08 (7) Å; O4-H2O4‴-O2″, 168 (9)°) and as a proton acceptor from the coordinated water (O4-O3, 2.890 (7) Å; H1O3-O3, 0.57 (7) Å; H1O3-O4, 2.11 (7) Å; O3-H1O3-O4; 174 (6)°). Dimers are connected into chains in the *c* direction by the O4-O2″ interaction and these chains are connected into sheets in the *b* direction by the uncoordinated waters bridging between the O3 atoms of one chain and the O1 atoms of another chain.

Discussion

The crystal structure analysis of $CuL\cdot 2H_2O$ has revealed dimeric units of $[CuL(H_2O)]_2$ and waters of crystallization linked by weak hydrogen bonding into an infinite planar network. The dimeric unit has twofold symmetry and a bent Cu_2O_2 ring with a dihedral angle of 15.8 (4)° between the O-Cu-O planes. The coordination of the copper(II) is a slightly distorted tetragonal pyramid with the weakly coordinated water molecule (Cu-O, 2.394 (6) Å) in the axial position.

Our measurement of the room-temperature magnetic susceptibility of this compound approximately agrees with that reported by Inoue, *et al.*[2] The values at 298, 195, and 77°K

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(Inoue's values in parentheses) are 1.48 (1.45), 1.38 (1.31), and 0.70 (0.70) BM/g-atom of copper, respectively. The moment at room temperature is considerably below the spin-only value for copper(II) but is well above the moment found for the strongly coupled planar dimers (μ_{eff} = *ca.* 0.5 BM). The observed value is indicative of weak antiferromagnetic coupling and, as the previous workers found, the variation of the magnetic susceptibility with temperature follows neither the theoretical prediction for isolated dinuclear units[3] nor the theoretical prediction for higher polymeric units.[16] Since the structure analysis has indicated dinuclear units, the discrepancy probably results from interactions between clusters.

Significant antiferromagnetic exchange has been found in copper(I) dimers having Cu–O· · ·H· · ·O–Cu[17] and Cu–C≡N· · ·H· · ·N≡C–Cu[18] hydrogen-bonded bridges. Weak antiferromagnetic behavior has long been observed in hydrated salts such as $MCl_2 \cdot 2H_2O$ (M = Fe, Co, Cu) and $MCl_2 \cdot 6H_2O$ (M = Co, Ni), with $2J$ values as great as -25 cm^{-1}.[19]

The principal antiferromagnetic coupling is undoubtedly related to superexchange within the four-membered Cu_2O_2 ring. The nonplanar nature of the ring should diminish markedly the importance of a potential π pathway[13] for superexchange. This structure, thus, provides additional evidence for superexchange through a σ pathway. The weak coupling in the present compound and the small Cu-O-Cu angle are also in line with recent geometric correlations for hydroxy-bridged complexes[20] and chloro-bridged complexes.[21]

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Supplementary Material Available. Observed and calculated structure factors (in electrons) for $CuC_9H_{14}N_2O_4$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2067.

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Cyclomer Complexes. Crystal Structure of a 2:1 Pentahydrate Complex of 1,4,7,10-Tetraoxacyclododecane with Sodium Chloride $[Na^+(C_8H_{16}O_4)_2][Cl^- \cdot 5H_2O]$

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The crystal structure of $NaCl \cdot 2C_8H_{16}O_4 \cdot 5H_2O$, where $C_8H_{16}O_4$ is 1,4,7,10-tetraoxacyclododecane, has been determined by a single-crystal X-ray diffraction study. The complex crystallizes in space group *Pcca* with lattice parameters $a = 22.122 \pm 0.012$, $b = 9.544 \pm 0.004$, and $c = 12.082 \pm 0.006$ Å ($Z = 4$). The intensities of 2203 reflections were measured on a Picker automatic diffractometer (Cu Kα radiation) and the structure was solved by iterative application of Sayre's equation. All but water hydrogens were located by difference synthesis. Full-matrix least-squares refinement of atom positions, hydrogen isotropic thermal parameters, and anisotropic thermal parameters for all other atoms converged at a final $R_1 = 7.6\%$ for 1948 reflections above background. The sodium ion forms an eight-coordinate sandwich complex of approximate D_4 symmetry with two polyether rings, each of which obeys approximate C_4 symmetry. The oxygen atoms are arranged at the corners of a square antiprism with Na–O distances ranging from 2.473 to 2.517 Å. The Na^+ cation is in no way associated with either the chloride ion or the water molecules. The latter form rings consisting of six waters joined by hydrogen bonds which are linked by a spiro oxygen that is hydrogen bonded to four other oxygens to form infinite chains along *c*. The chloride ions are located between these chains and appear to be hydrogen bonded to four water molecules.

Introduction

Cyclomers of alkylene oxides are readily prepared[1] and constitute a remarkably versatile series of new ligands. The unique properties of these compounds and the unexpected and novel geometries of their complexes appear to be associated with their conformational flexibility and the presence of lone-pair electrons on the oxygen atoms. One of the most promising members of this series is 1,4,7,10-tetraoxacyclododecane, the cyclic tetramer of ethylene oxide. This report describes the structure of an unusual eight-coordinate crystalline complex formed by this heterocycle, where the sodium cation lies sandwiched between eight oxygen atoms at the vertices of a square antiprism. This structural type seems to be of general significance since complexes formed by NaCl, KCl, RbCl, NaBr, KBr, and NaI have been shown to be isomorphous by X-ray powder diffraction.[2]

Although the affinity of ethers for alkali ions in solution is well-known[3] and a few crystalline complexes of linear

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