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The Crystal and Molecular Structure of Di-μ-hydroxo-bis[2-(2-ethylaminoethyl)pyridine]dicopper(II) Perchlorate

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The crystal and molecular structure of di-μ-hydroxo-bis[2-(2-ethylaminoethyl)pyridine]dicopper(II) perchlorate, $[Cu(C_9N_2H_{14})OH]_2(ClO_4)_2$, has been determined from three-dimensional single-crystal X-ray data obtained on an automatic four-circle diffractometer using Mo Kα radiation. The complex crystallizes in the space group $C_2{}^2$-$P2_1$ of the monoclinic system with cell constants $a = 9.195$ (19), $b = 19.290$ (44), $c = 7.679$ (16) Å, and $\beta = 77.00$ (7)°. The observed density is 1.64 (2) g cm^{-3}, while that calculated for two formula units in the cell is 1.652 g cm^{-3}. Independent intensities (1710) greater than twice their estimated standard deviations were used in the least-squares refinement, and the final value of the R factor (on F) is 0.042. The complex consists of pairs of copper atoms linked by two hydroxo bridges. The coordination geometry around each copper atom is roughly tetragonal pyramidal, the basal plane consisting of the two bridging oxygen atoms and the two nitrogen atoms of the 2-(2-ethylaminoethyl)pyridine (EAEP) ligand while the axial coordination site is occupied by an oxygen atom from a perchlorate anion. The average Cu–O distance in the bridge is 1.916 (12) Å and the Cu–Cu separation is 2.917 (5) Å. The average Cu–O–Cu and O–Cu–O angles in the bridge are 99.2 (3) and 80.8 (6)°, respectively. The influence of the Cu–O–Cu angle on the magnetic properties of this and similar dimers is discussed.

Introduction

A number of copper(II) hydroxo complexes with N-substituted 2-(2-aminoethyl)pyridines have been reported by Uhlig and coworkers,[1] and on the basis of electronic spectroscopy and magnetic susceptibility data these workers suggested that the complexes should be formulated as dimers of the type $[CuL(OH)]_2{}^{2+}$, where L is the substituted aminoethylpyridine. The magnetic susceptibility measurements of Uhlig and coworkers[1] suggest that there may be significant structural differences between the complexes of the mono- and disubstituted ligands, since for the methyl- and isopropyl-substituted complexes the magnetic data show large antiferromagnetic interactions with Néel temperatures of 116 and 202°, respectively, while the dimethyl- and diethyl-substituted complexes appear to obey the Curie–Weiss law above 80°K. Our recent magnetic measurements on the ethyl-substituted complex[2] tend to confirm the above findings for the monosubstituted complexes.

The crystal structures of two other complexes of the type $[CuL(OH)]_2{}^{2+}$, where L is 2,2′-bipyridine[3,4] and N,N,N',N'-tetramethylethylenediamine (tmen),[5] have been reported recently. Our low-temperature magnetic susceptibility measurements on the sulfate salt of the bipyridine (bipy) complex demonstrate that it undergoes a ferromagnetic interaction[6] with a value of $2J$, the singlet–triplet energy difference, of approximately $+48$ cm^{-1}, whereas the tmen complex has been shown[7] to undergo an antiferromagnetic interaction with $2J = -509$ cm^{-1}. Clearly this great disparity in the magnetic behavior of these complexes suggests some significant structural differences, and it is our hope that a comparison of the structural and magnetic properties of these complexes with those of the substituted aminopyridine complexes will enable us to gain an understanding of the magnetic consequences of minor structural changes in hydroxo-bridged copper(II) dimers. Hence, we felt that it was of great importance to determine the structure of the 2-(2-ethylaminoethyl)pyridine (EAEP) complex, which we report here.

Data Collection and Reduction

Violet crystals of $[Cu(EAEP)OH]_2(ClO_4)_2$ were prepared by a minor modification of the general procedure of Uhlig and coworkers,[1] and their composition was confirmed by elemental analysis. Precession and Weissenberg photography indicated that the crystals belong to the monoclinic system. The systematic absences which were observed are $0k0$ for k even, which implies that the space group is either $C_{2h}{}^2$-$P2_1/m$ or $C_2{}^2$-$P2_1$; the former space group was initially chosen, but examination of the data showed that the noncentrosymmetric choice $P2_1$ is the correct space group (*vide infra*). The cell constants, obtained by the least-squares procedure described previously[8], are $a = 9.195$ (19), $b = 19.290$ (44), $c = 7.679$ (16) Å, and $\beta = 77.00$ (7)°; these observations were made at 23° with the wavelength assumed as λ(Mo Kα_1) = 0.7093 Å. A density of 1.652 g cm^{-3} calculated for two dimeric formula units in the cell is in good agreement with the value of 1.64 (2) g cm^{-3} obtained by flotation in dichloromethane–dibromoethane solution. Hence, in the noncentrosymmetric space group $P2_1$ no crystallographic symmetry is imposed on the dimer.

Diffraction data were collected from a parallelpiped crystal with faces $(00\bar{1})$, (001), (010), $(0\bar{1}0)$, (101), and $(\bar{1}0\bar{1})$; the separations between opposite faces were: (001) and $(00\bar{1})$, 0.030 cm; (010) and $(0\bar{1}0)$, 0.008 cm; (101) and $(\bar{1}0\bar{1})$, 0.016 cm. The crystal was mounted normal to the (001) planes, and data were collected on a Picker four-circle automatic diffractomer using Mo Kα radiation in the manner previously described.[8] A single form (hkl) of the data was collected out to a value of $2\theta = 45°$, a total of 1957 independent intensities being recorded. There were very few intensities above background at values of $2\theta > 45°$.

Data processing was carried out as described by Corfield, Doedens, and Ibers,[9] using our program DATPRC.[10] The value of p in the expression[11]

$$(\sigma) = (C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2)^{1/2}$$

was chosen as 0.04. An absorption correction was applied; the absorption coefficient for these atoms and Mo Kα radiation is

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19.2 cm^{-1}, and for the present sample the transmission coefficients[12] were found to range from 0.767 to 0.887. Of the 1957 independent intensities, 1615 were greater than three times their estimated standard deviations, and 1710 exceeded twice their estimated standard deviations.

Solution and Refinement

Examination of a three-dimensional Patterson function suggested that the space group is noncentrosymmetric, and a Wilson plot verified this conclusion; the statistics from the Wilson plot are presented in Table I.

TABLE I

STATISTICS OBTAINED FROM WILSON PLOT

Quantity	Obsd	Theor (centric)	Theor (acentric)
Av $\|E\|$	0.864	0.798	0.886
Av $\|E^2 - 1\|$	0.791	0.968	0.736
% $E > 1$	36.37	32.00	37.00
% $E > 2$	2.20	5.00	1.80
% $E > 3$	0.05	0.30	0.01

The positions of the two independent copper atoms were determined from the Patterson function. Five cycles of least-squares refinement of these positions were run. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o)^2$. In all calculations of F_c the atomic scattering factors for Cu and Cl were taken from Cromer and Waber,[13] that for H was from Stewart, Davidson, and Simpson,[14] and those for C, O, and N were from the tabulation of Ibers.[15] The effects of anomalous dispersion were included in calculations of F_c,[16] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer.[17] Only the 1615 independent intensities which were greater than three times their estimated standard deviations were used in the initial refinement of the structure.

Initially, the two atoms were assigned variable isotropic thermal parameters. After five cycles of least-squares refinement, using the data before they had been corrected for absorption effects, the usual agreement factors $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ were 0.358 and 0.426, respectively.

A difference Fourier map revealed the location of all nonhydrogen atoms with the exception of one perchlorate oxygen atom, and after two cycles of isotropic least-squares calculations the values of R_1 and R_2 were 0.095 and 0.116, respectively. At this stage it was decided to refine the pyridine rings as groups,[18] the four methylene carbon atoms in the chelate rings isotropically, and all other atoms anisotropically. This decision leads to 220 variable parameters for these 1615 observations; inclusion of the 20 extra variables required to refine all nongroup atoms anisotropically, or of the extra 102 variables required to refine all atoms anisotropically, was considered unjustified because of the relatively small number of data available. The methylene carbon atoms (C(6), C(7), C(16), C(17)) were singled out for isotropic refinement since their thermal motion was expected to be relatively small, and because their parameters were expected to have little influence on the parameters of the atoms in the inner coordination spheres of the copper atoms. Two cycles of least-squares refinement on these 211 variables yielded values of R_1 and R_2 of 0.071 and 0.093, respectively. The missing perchlorate oxygen atom was located in a difference Fourier map, the absorption correction was applied (*vide supra*), and two further cycles of least-squares calculations on the 220 variables led to values of R_1 and R_2 of 0.051 and 0.064. The locations of all hydrogen atoms except the methyl and hydroxyl hydrogen atoms were calculated, assuming C–H and N–H bond lengths of 1.00 and 0.95 Å, respectively, and all of these positions were verified in a difference Fourier map; the two hydrogen atoms were located in the same difference map. All of these hydrogen atoms were included in the next least-squares calculation, the hydroxyl atoms being given the positions obtained from the Fourier map and the others being given their calculated locations; all of the hydrogen atoms were given fixed, isotropic thermal parameters of 5.0 A^2, and none of their parameters were varied. This reduced the values of R_1 and R_2 to 0.040 and 0.046.

Since $P2_1$ is a polar space group, a further least-squares calculation was run in which (hkl) was replaced by $(\bar{h}\bar{k}\bar{l})$; the resulting values of R_1 and R_2 were 0.050 and 0.060. This increase in R_2 indicates that the choice of (hkl) rather than $(\bar{h}\bar{k}\bar{l})$ is correct at any meaningful confidence level.[19] This choice was also verified by an examination of the bond lengths calculated from the two models;[20,21] the four chemically equivalent Cu–O bond lengths showed a range of form 1.90 (1) to 1.93 (1) Å for the first choice, while the range was from 1.87 (1) to 1.94 (1) Å for the second choice. It should be noted here, however, that the results obtained from examination of the Cu–N bond lengths are not as convincing since the ranges calculated for each model are very similar and because there are only two equivalent Cu–N bonds in the molecule.

In an attempt to improve the precision of the refinement, two cycles of least squares were calculated using the 1710 intensities greater than twice their estimated standard deviations. The inclusion of these extra 95 weak data led to slightly increased values of the agreement factors ($R_1 = 0.042$ and $R_2 = 0.047$) but did bring about a decrease in the estimated standard deviations of the refined parameters. A final difference Fourier synthesis showed no peak higher than 0.5 e $Å^{-3}$, and, while there were several peaks in the vicinity of the methyl carbon atoms (C(9) and C(19)), they could not be interpreted on the basis of any reasonable geometry for the methyl group. We conclude that there may be considerable disorder of the methyl hydrogen atoms.

In the last cycle of least-squares refinement, the greatest shift in any parameter was 0.7 times its estimated standard deviation, which is taken as evidence that the refinement had converged. The value of R_2 showed no dependence on sin θ or on $|F_o|$, which indicates that our choice of $p = 0.04$ is essentially correct. Examination of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is necessary. The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables II and III. A table of observed and calculated structure amplitudes is available.[22]

Description of the Structure

The structure consists of dimeric $[Cu(OH)EAEP]_2^{2+}$ ions as postulated by Uhlig and coworkers.[1] The geometry of the dimeric unit is shown in Figure 1, and the coordination around the copper atoms is shown in Figure 2. The geometry at each copper atom is best described as a slightly distorted tetragonal pyramid, with the two oxygen atoms of the bridging hydroxyl groups and the two nitrogen atoms of the EAEP ligand forming the basal plane; the fifth (axial) coordination site of each copper atom is occupied by an oxygen atom from the perchlorate anions. This achievement of tetragonal-pyramidal geometry through axial coordination to an anion (or solvent) molecule is also found in both the nitrate[4] and sulfate[3] salts of $[Cu(OH)bipy]_2^{2+}$.

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[12] In addition to various local programs for the IBM 360/75, the programs used in this analysis were modifications of Hamilton's GONO 9 absorption correction program, Ibers' NUCLS least-squares program, Busing, Levy, and Martin's ORFFE function and error program, Zalkin's FORDAP Fourier program, Johnson's ORTEP plotting program, and Doedens' RSCAN program.

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[22] This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number INORG-72-2216. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE II

POSITIONAL AND GROUP PARAMETERS FOR $[Cu(EAEP)OH]_2(ClO_4)_2$

Atom	x	y	z
Cu(1)	−0.1140 (1)	0.0	−0.2577 (2)
Cu(2)	−0.3044 (1)	0.1226 (1)	−0.2163 (2)
Cl(1)	−0.0648 (3)	0.1516 (2)	−0.6652 (4)
Cl(2)	−0.3623 (2)	0.0366 (1)	0.1887 (4)
O(1)	−0.1256 (7)	0.0914 (3)	−0.1534 (9)
O(2)	−0.2947 (7)	0.0327 (3)	−0.3176 (9)
O(3)	0.002 (1)	0.0899 (5)	−0.624 (1)
O(4)	0.045 (1)	0.1992 (7)	−0.749 (2)
O(5)	−0.148 (1)	0.1810 (5)	−0.506 (1)
O(6)	−0.161 (1)	0.1359 (7)	−0.778 (1)
O(7)	−0.467 (1)	−0.0893 (6)	0.208 (2)
O(8)	−0.428 (1)	0.030 (2)	0.156 (1)
O(9)	−0.308 (1)	−0.0297 (5)	0.344 (1)
O(10)	−0.247 (1)	−0.0523 (6)	0.042 (1)
N(1)	−0.1123 (9)	−0.0824 (4)	−0.416 (1)
N(4)	−0.3114 (9)	0.2092 (5)	−0.059 (1)
C(6)	−0.581 (1)	0.1924 (7)	0.017 (2)
C(7)	−0.455 (1)	0.2423 (7)	−0.004 (2)
C(8)	−0.185 (1)	0.2569 (6)	−0.133 (2)
C(9)	−0.157 (2)	0.3106 (6)	−0.003 (2)
C(16)	0.163 (1)	−0.0629 (6)	−0.502 (2)
C(17)	0.039 (1)	−0.1161 (7)	−0.473 (2)
C(18)	−0.230 (1)	−0.1332 (7)	−0.335 (2)
C(19)	−0.250 (2)	−0.1926 (8)	−0.466 (2)
Group	x_c[a]	y_c	z_c
Py 1	−0.6366 (5)	0.1465 (2)	−0.3141 (6)
Py 2	0.2208 (5)	−0.0205 (2)	−0.1678 (6)
Group	ϕ	θ	ρ
Py 1	−2.321 (9)	2.095 (4)	2.247 (9)
Py 2	0.812 (9)	−2.079 (4)	−2.242 (9)
Group atoms	x_d[b]	y_d	z_d
N(3)	−0.4968 (6)	0.1463 (9)	−0.2825 (9)
C(1)	−0.5183 (7)	0.1259 (7)	−0.4416 (8)
C(2)	−0.6601 (8)	0.1260 (5)	−0.4736 (7)
C(3)	−0.7825 (5)	0.147 (1)	−0.347 (1)
C(4)	−0.7549 (7)	0.1671 (7)	−0.1865 (9)
C(5)	−0.6131 (8)	0.1669 (4)	−0.1546 (7)
N(2)	0.0805 (5)	−0.0192 (9)	−0.1974 (9)
C(11)	0.1039 (7)	0.0003 (7)	−0.0385 (8)
C(12)	0.2463 (8)	−0.0011 (5)	−0.0084 (7)
C(13)	0.3674 (6)	−0.022 (1)	−0.137 (1)
C(14)	0.3378 (7)	−0.0414 (6)	−0.2970 (9)
C(15)	0.1954 (7)	−0.0400 (4)	−0.3271 (6)
H atoms	x_h[c]	y_h	z_h
HO(1)	−0.1350	0.1200	−0.0700
HO(2)	−0.2800	0.0400	−0.4550
H(61)	−0.5574	0.1538	0.0873
H(62)	−0.6741	0.2176	0.0871
H(71)	−0.4607	0.2683	0.1142
H(72)	−0.4673	0.2802	−0.0944
H(81)	−0.2024	0.2818	−0.2474
H(82)	−0.0873	0.2290	−0.1807
H(161)	0.2568	−0.0810	−0.5838
H(162)	0.1306	−0.0203	−0.5663
H(171)	0.0501	−0.1499	−0.3726
H(172)	0.0409	−0.1458	−0.5823
H(181)	−0.3278	−0.1062	−0.2994
H(182)	−0.2039	−0.1519	−0.2272
H(11)	0.0211	0.0157	0.0538
H(12)	0.2653	0.0130	0.1042
H(13)	0.4730	−0.0231	−0.1239
H(14)	0.4228	−0.0563	−0.4040
H(1)	−0.4289	0.1089	−0.5416
H(2)	−0.6700	0.1095	−0.6014
H(3)	−0.8825	0.1470	−0.3821
H(4)	−0.8401	0.1838	−0.1009
HN(1)	−0.1061	−0.0453	−0.3332
HN(4)	−0.2866	0.1878	0.0399

[a] x_c, y_c, and z_c are fractional coordinates of the group centers. The angles ϕ, θ, and ρ are in radians. [b] x_d, y_d, and z_d are the derived crystallographic positions of the group atoms. [c] The hydrogen atom positions were not refined.

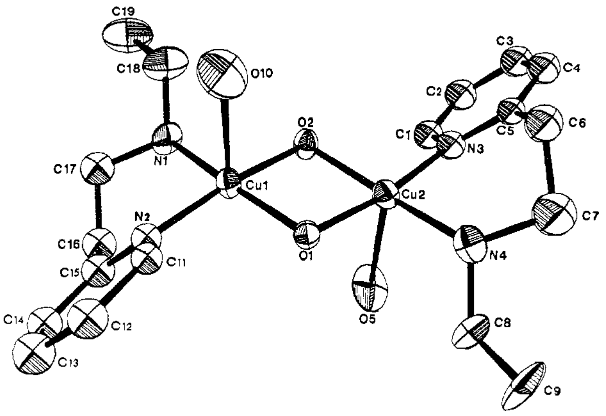

Figure 1.—View of the dimeric unit in $[Cu(OH)EAEP]_2(ClO_4)_2$. Atoms O(5) and O(10) are perchlorate oxygen atoms. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

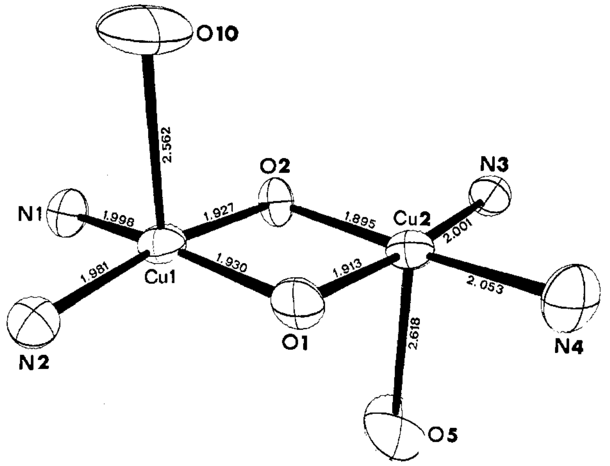

Figure 2.—View of the coordination geometry around the copper atoms in $[Cu(OH)EAEP]_2^{2+}$.

A similar situation occurs[23] in $[Cu(OH)(NH_2CH_3)_2]_2SO_4 \cdot H_2O$, but in this latter case the axial site of one of the copper atoms is occupied by a bridging oxygen atom from a neighboring dimer. In the bromide salt of the tmen complex, however, the copper atoms have four-coordinate, square-planar geometry.[5]

In both of the tetragonal pyramids in the $[Cu(OH)EAEP]_2^{2+}$ dimer the copper atom is displaced out of the basal plane formed by the two nitrogen and two oxygen atoms in the direction of the axial ligand; this feature is very common in tetragonal-pyramidal complexes.[24] In each case, however, there is a good plane through the four basal ligands, the largest deviations from the least-squares planes around Cu(1) and Cu(2) being 0.05 and 0.06 Å, respectively, while the copper atoms are 0.13 and 0.11 Å, respectively, above these planes. The six atoms N(1), N(2), N(3), N(4), O(1), and O(2) which comprise the two basal planes are nearly coplanar, the largest deviation from the least-squares plane being 0.09 Å. Alternatively, the angle between the two basal planes is very small, its value being 1.4°. This is similar to the geometry of the nitrate salt of the bipy complex[4] and of the tmen complex,[5] in which six basal ligands are coplanar, but is in

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TABLE III

THERMAL PARAMETERS OF $[Cu(EAEP)OH]_2(ClO_4)_2$

Atom	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.0087 (2)	0.0020 (1)	0.0129 (3)	0.0006 (1)	−0.0029 (2)	−0.0010 (1)
Cu(2)	0.0083 (2)	0.0021 (1)	0.0135 (2)	0.0047 (1)	−0.0028 (2)	−0.0009 (1)
Cl(1)	0.0119 (4)	0.0039 (1)	0.0130 (6)	−0.0005 (2)	−0.0016 (4)	−0.0013 (2)
Cl(2)	0.0129 (5)	0.0046 (1)	0.0138 (6)	−0.0014 (2)	−0.0037 (4)	−0.0009 (2)
O(1)	0.0091 (9)	0.0017 (2)	0.0153 (1)	0.0007 (4)	−0.005 (1)	−0.0017 (5)
O(2)	0.009 (1)	0.0024 (2)	0.016 (2)	0.0012 (4)	−0.004 (1)	−0.0015 (5)
O(3)	0.026	0.0059 (4)	0.041 (3)	0.0066 (8)	−0.017 (2)	−0.004 (1)
O(4)	0.021 (2)	0.0081 (5)	0.049 (4)	−0.0070 (8)	0.014 (2)	−0.001 (1)
O(5)	0.024 (2)	0.0040 (3)	0.013 (2)	0.0020 (6)	0.004 (1)	−0.0006 (6)
O(6)	0.003 (2)	0.0058 (5)	0.035 (3)	0.0024 (9)	−0.024 (2)	−0.003 (1)
O(7)	0.002 (2)	0.0064 (5)	0.059 (4)	−0.0050 (8)	−0.005 (2)	0.001 (1)
O(8)	0.027 (2)	0.0050 (4)	0.037 (3)	0.0046 (8)	−0.016 (2)	−0.0037 (9)
O(9)	0.048 (3)	0.0054 (4)	0.027 (2)	0.0033 (9)	−0.028 (2)	−0.0033 (9)
O(10)	0.022 (2)	0.0058 (5)	0.024 (2)	0.0021 (7)	0.011 (2)	−0.0006 (9)
N(1)	0.013 (1)	0.0019 (3)	0.020 (2)	−0.0001 (5)	−0.005 (1)	−0.0030 (6)
N(4)	0.013 (1)	0.0026 (3)	0.016 (2)	0.0011 (6)	−0.003 (1)	−0.0007 (7)
C(8)	0.020 (2)	0.0023 (4)	0.022 (3)	−0.0009 (8)	−0.004 (2)	−0.0002 (9)
C(9)	0.034 (3)	0.0021 (4)	0.042 (5)	−0.001 (1)	−0.016 (3)	−0.005 (1)
C(18)	0.019 (2)	0.0035 (5)	0.027 (3)	−0.0018 (9)	−0.004 (2)	−0.003 (1)
C(19)	0.030 (3)	0.0038 (6)	0.032 (4)	−0.003 (1)	−0.009 (3)	−0.002 (1)
C(6)	5.1 (3)					
C(7)	5.2 (3)					
C(16)	4.2 (3)					
C(17)	4.9 (3)					
N(3)	3.1 (2)					
C(1)	3.4 (2)					
C(2)	4.2 (2)					
C(3)	4.1 (2)					
C(4)	4.4 (3)					
C(5)	3.2 (2)					
N(2)	3.2 (2)					
C(11)	3.1 (2)					
C(12)	4.2 (2)					
C(13)	4.5 (3)					
C(14)	4.0 (2)					
C(15)	3.1 (2)					

[a] The form of anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

contrast to the sulfate salt of the bipy complex,[5] where the interplanar angle is 7.9°. In $[Cu(NH_2CH_3)_2OH]_2SO_4 \cdot H_2O$, the interplanar angle is 50.8°, but this molecule is not analogous to the other molecules discussed here because of its tetrameric nature.[23] There is no evidence for hydrogen bonding involving the bridging hydroxyl groups. The only short contacts to the bridges are an O(1)—H···O(6) separation of 2.95 Å and an O(2)—H···O(9) distance of 2.89 Å, with associated O—H···O angles of 147 and 130°. While the locations of the hydrogen atoms are only approximate because of the contraction of the O—H bond lengths which is a feature of X-ray experiments,[25,26] the calculated H···O separations of 2.11 and 2.22 Å are probably too long for there to be any strong interaction. More conclusive evidence is obtained from the infrared spectrum of the complex in the O—H stretching region. Hydrogen-bonded OH groups usually give rise[27] to broad bands around 3320 cm^{-1} while free OH groups lead[27] to sharp bands near 3620 cm^{-1}; the infrared spectrum of the complex (KBr disk) shows a strong, sharp band at 3580 cm^{-1} which strongly suggests that there is no hydrogen bonding to the bridging hydroxyl groups. This absence of hydrogen bonding in the EAEP complex is in contrast to the bipy nitrate[4] and tmen complexes,[5] where O—H···O and O—H···Br hydrogen bonding has been postulated. The possible influence of hydrogen bonding on the magnitude of the magnetic exchange will be discussed in a separate communication.

TABLE IV

INTERNUCLEAR DISTANCES[a] IN $[Cu(EAEP)OH]_2(ClO_4)_2$

Atoms[b]	Dist, Å	Atoms	Dist, Å
Cu(1)–Cu(2)	2.917 (5)	Cu(2)–O(1)	1.913 (7)
Cu(1)–O(1)	1.930 (8)	Cu(2)–O(2)	1.895 (7)
Cu(1)–O(2)	1.927 (8)	Cu(2)–N(3)	2.001 (8)
Cu(1)–N(1)	1.998 (10)	Cu(2)–N(4)	2.053 (10)
Cu(1)–N(2)	1.981 (8)	Cu(2)–O(5)	2.618 (9)
Cu(1)–O(10)	2.562 (10)	C(5)–C(6)	1.497 (16)
C(15)–C(16)	1.506 (16)	C(6)–C(7)	1.485 (17)
C(16)–C(17)	1.513 (16)	C(7)–N(4)	1.442 (15)
C(17)–N(1)	1.506 (15)	C(8)–N(4)	1.490 (14)
C(18)–N(1)	1.484 (14)	C(9)–C(8)	1.499 (17)
C(18)–C(19)	1.562 (18)	Cl(1)–O(3)	1.408 (10)
Cl(2)–O(7)	1.388 (10)	Cl(1)–O(4)	1.409 (11)
Cl(2)–O(8)	1.464 (10)	Cl(1)–O(5)	1.406 (9)
Cl(2)–O(9)	1.399 (9)	Cl(1)–O(6)	1.404 (9)
Cl(2)–O(10)	1.391 (9)		

[a] The pyridine rings were restricted to planar geometry with C–N = 1.340, C(1)–C(2) = C(4)–C(5) = C(11)–C(12) = C(14)–C(15) = 1.380, and C(2)–C(3) = C(3)–C(4) = C(12)–C(13) = C(13)–C(14) = 1.370 Å. [b] The numbering scheme for the atoms is shown in Figure 1.

The bond lengths and angles in the complex are given in Tables IV and V. The Cu(1)–Cu(2) separation of 2.917 (5) Å is in the range 2.78–3.00 Å found[3–5,23] in other di-μ-hydroxo-copper(II) complexes but is significantly longer than the Cu–Cu bond lengths of

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TABLE V

INTERNUCLEAR ANGLES IN $[Cu(EAEP)OH]_2(ClO_4)_2$

Atoms	Angles, deg	Atoms	Angles, deg
Cu(1)–O(1)–Cu(2)	98.8 (3)	N(3)–Cu(2)–N(4)	93.0 (5)
Cu(1)–O(2)–Cu(2)	99.5 (4)	N(3)–Cu(2)–O(1)	174.8 (5)
O(1)–Cu(1)–O(2)	80.2 (3)	N(3)–Cu(2)–O(2)	93.8 (5)
O(1)–Cu(2)–O(2)	81.5 (3)	N(3)–Cu(2)–O(5)	91.8 (4)
N(1)–Cu(1)–N(2)	96.3 (5)	N(4)–Cu(2)–O(1)	91.3 (4)
N(1)–Cu(1)–O(1)	166.2 (4)	N(4)–Cu(2)–O(2)	168.0 (4)
N(1)–Cu(1)–O(2)	90.3 (4)	N(4)–Cu(2)–O(5)	95.2 (3)
N(1)–Cu(1)–O(10)	99.8 (4)	O(1)–Cu(2)–O(5)	90.7 (3)
N(2)–Cu(1)–O(1)	92.4 (5)	O(2)–Cu(2)–O(5)	94.5 (3)
N(2)–Cu(1)–O(2)	171.6 (5)	Cu(2)–N(4)–C(7)	115.9 (3)
N(2)–Cu(1)–O(10)	89.5 (4)	Cu(2)–N(4)–C(8)	111.1 (3)
O(1)–Cu(1)–O(10)	90.9 (3)	C(7)–N(4)–C(8)	114.9 (9)
O(2)–Cu(1)–O(10)	94.6 (3)	N(4)–C(7)–C(6)	112.7 (11)
Cu(1)–N(1)–C(17)	113.7 (4)	C(5)–C(6)–C(7)	114.7 (10)
Cu(1)–N(1)–C(18)	111.6 (4)	N(4)–C(8)–C(9)	114.3 (11)
C(17)–N(1)–C(18)	111.8 (9)	O(4)–Cl(1)–O(6)	110.1 (8)
N(1)–C(17)–C(16)	111.5 (10)	O(5)–Cl(1)–O(6)	109.0 (7)
C(15)–C(16)–C(17)	111.4 (11)	O(7)–Cl(2)–O(8)	110.8 (7)
N(1)–C(18)–C(19)	113.5 (10)	O(7)–Cl(2)–O(9)	110.7 (8)
O(3)–Cl(1)–O(4)	110.2 (8)	O(7)–Cl(2)–O(10)	108.2 (8)
O(3)–Cl(1)–O(5)	109.3 (6)	O(8)–Cl(2)–O(9)	107.7 (6)
O(3)–Cl(1)–O(6)	109.0 (7)	O(8)–Cl(2)–O(10)	108.6 (7)
O(4)–Cl(1)–O(5)	109.2 (7)	O(9)–Cl(2)–C(10)	110.8 (8)

2.63–2.65 Å found in copper acetate monohydrate[28] and monopyridine copper acetate.[29,30] The average bridging Cu–O distance of 1.916 (12) Å is similar to the values of 1.902, 1.922, and 1.94 Å in the tmen,[5] bipy nitrate,[4] and bipy sulfate[3] complexes, respectively. Similarly, the average O–Cu–O and Cu–O–Cu angles of 80.8 (6) and 99.2 (3)° are in the expected range. The Cu(1)–N(2) and Cu(2)–N(3) distances of 1.981 (8) and 2.001 (8) Å, respectively, are comparable with the values of 1.98 (1) and 2.02 (1) Å in dichlorobis(2-methylpyridine)copper(II),[31] 1.980 (6) and 1.985 (6) Å in dibromobis(2-methylpyridine)copper(II),[32] 2.021 (5) Å in dibromo(2-(2-aminoethyl)pyridine)copper(II),[33] and other reported values.[34–37] The Cu(2)–N(4) distance of 2.053 (10) Å is significantly longer than the Cu(1)–N(1) distance of 1.998 (10) Å, and we are unable to offer any satisfactory explanation for this except to note that the standard deviations calculated from the inverse matrix are frequently optimistic. These Cu–N distances are similar to the values of 1.971 (2) and 1.984 (2) Å in carbonatodiamminecopper(II),[38] 2.012 (9) and 2.017 (9) Å in selenatotetraamminecopper(II),[39] 2.031 and 2.032 (6) Å in sulfatotetraamminecopper(II),[39] 1.989 (6) Å in dibromo(2-(2-aminoethyl)pyridine)copper(II),[33] and in other copper(II) amines. The geometry of the exocyclic moieties of EAEP ligands is normal, while the pyridine rings were constrained to planar geometry in the refinement.

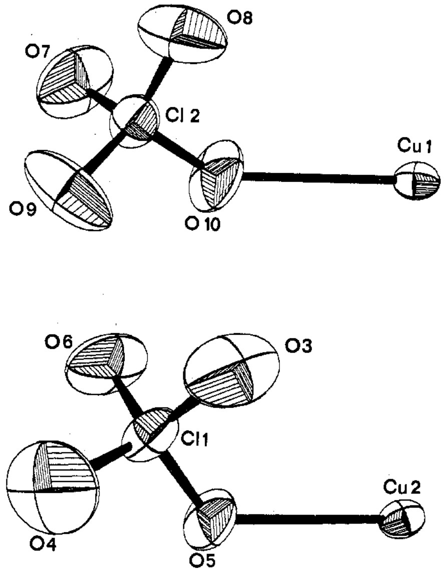

Figure 3.—View of the perchlorate anions in $[Cu(OH)EAEP]_2(ClO_4)_2$, showing their coordination to the copper atoms.

The geometries of the perchlorate ions are shown in Figure 3. Both perchlorates are roughly tetrahedral, with no O–Cl–O angle in the first perchlorate group deviating from tetrahedral geometry by more than 0.7° and none in the second group by more than 1.8°. Seven of the eight Cl–O distances fall in the range 1.388 (10) to 1.409 (11) Å, the average deviation from the mean value of 1.401 Å being 0.007 Å; the eighth value of 1.464 (10) Å is significantly larger than this mean value. An examination of Figure 3 shows no apparent difference between the oxygen atom O(8) and the other oxygen atoms, and there is no evidence of any interaction involving this oxygen atom and any other atom in the cell.

Magnetic Properties.—The magnetic susceptibility data and electron paramagnetic resonance spectrum of the complex have been reported previously.[2] The susceptibility data can be fitted to the Van Vleck equation[40] for pairs of exchange-coupled copper(II) ions, yielding a value for $2J$, the singlet–triplet splitting, of $-130.4\ cm^{-1}$. An examination of the structural and magnetic properties of the bipy,[41] EAEP, and tmen complexes of the type $[Cu(OH)L]_2^{2+}$, which are summarized in Table VI, reveals a monotonic decrease in the value of $2J$ as the Cu–O–Cu bridging angle increases. If the principal path for the magnetic interaction is through the bridging ligands, as seems reasonable in view of the relatively large Cu–Cu separations, this observation is consistent with the principle of

TABLE VI

MAGNETIC AND STRUCTURAL PROPERTIES OF $[CuL(OH)]_2^{2+}$

L	$2J$, cm^{-1}	CuO–Cu, deg
bipy	$+48^a$	97^b
EAEP	-130.4^c	$99.2\ (3)^d$
tmen	-509^e	$104.1\ (2)^f$

[a] Reference 6. [b] Reference 3. [c] Reference 2. [d] Present work. [e] Reference 7. [f] Reference 5.

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(41) Data for the bipy complex are for the sulfate salt since magnetic data are not available for the nitrate salt.

super-exchange.[42] If the orbitals used by the bridging oxygen atoms are pure p orbitals, the bond angle is expected to be 90° and the ground state is predicted to be a triplet (*i.e.*, $2J > 0$); if the orbitals are purely s, the ground state is predicted to be a singlet (*i.e.*, $2J < 0$). Hence, since an increased value of the bridging angle implies greater s character in the bridging orbitals, we would expect a decrease in $2J$ as the bridging angle is increased from 90°. For the three cases which have been studied in detail, this trend is observed.

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The Crystal and Molecular Structure of Tris(octamethylmethylenediphosphonic diamide)copper(II) Perchlorate[1a]

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Tris(octamethylmethylenediphosphonic diamide)copper(II) perchlorate, $Cu\{[(CH_3)_2N]_2P(O)CH_2P(O)[N(CH_3)_2]_2\}_3(ClO_4)_2$, crystallizes in the orthorhombic space group $Pna2_1$, with four molecules in the unit cell. The unit cell dimensions are a = 19.196 (4), b = 12.131 (2), and c = 22.868 (4) Å. Intensity data were collected with a four-circle computer-controlled diffractometer. Reflections were measured with the θ–2θ scan technique. All 62 nonhydrogen atoms were refined anisotropically and the 78 hydrogen atoms were included as fixed atoms. Refinement by full-matrix least squares using 6305 reflections gave a final R factor of 0.046. The CuO_6 group is a slightly distorted octahedron with each chelate ring in a boat conformation. The bend in one of the chelate rings is opposite that of the other two. Average bond distances and bond angles with rms deviations for the chelate rings are as follows: Cu–O, 2.085 Å (range 2.023–2.134 Å); P–O, 1.483 (5) Å; P–C(P), 1.798 (13) Å; O–Cu–O, 89.9 (12)°; Cu–O–P, 132.1 (14)°; O–P–C, 110.5 (6)°; P–C–P, 115.3 (15)°.

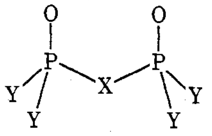
Introduction

During the past several years a number of six-coordinate Cu(II) complexes have been found to have higher symmetry than that allowed by the Jahn–Teller theorem. These include tris(octamethylpyrophosphoramide)copper(II) perchlorate, referred to as CuOMPA,[2] tris(ethylenediamine)copper(II) sulfate,[3] and potassium lead hexanitrocuprate(II).[4,5] The site symmetry of Cu(II) is 32 (D_3) in the first two and $m3$ (T_h) in the last one. Another example is $[Cu(H_2O)_6]SiF_6$ which crystallizes in space group $R\bar{3}$ with four molecules per unit cell. One of the cations is at a $\bar{3}$ (C_{3i}) symmetry site while the other three are at $\bar{1}$ (C_i) sites.[6]

CuOMPA was the first of a series of tris chelates of Cu(II) with organophosphorus bidentate ligands to be prepared in this laboratory. Members of this series (shown with their abbreviations in Table I) have similar physical and chemical properties.

The crystal structures of CuOMPA, previously reported,[2] and CuNIPA are isomorphous, based on a comparison of precession photographs.[7] This observation supports the conclusion that Cu(II) also has 32 (D_3) site symmetry in CuNIPA and has prompted us to investigate the structures of two additional systems, CuPCP and CuIPCP, which crystallize in lower symmetry space groups. The present report is a description of the structural results for CuPCP.

TABLE I
STRUCTURE OF LIGANDS



X	Y	Ligand	Abbreviation for tris chelate of $Cu(ClO_4)_2$	Ref
O	$N(CH_3)_2$	Octamethylpyrophosphoramide (OMPA)	CuOMPA	2
NCH_3	$N(CH_3)_2$	Nonamethylimidodiphosphoramide (NIPA)	CuNIPA	7, 8
CH_2	$N(CH_3)_2$	Octamethylmethylenediphosphonic diamide (PCP)	CuPCP	*a*
CH_2	$OCH(CH_3)_2$	Tetraisopropylmethylenediphosphonate (IPCP)	CuIPCP	7

[a] K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, **8**, 1775 (1969).

Collection and Reduction of Data

Caution! Although the toxicity of PCP is not known, it should be handled with care because of its similarity to OMPA, a toxic anticholinesterase agent.

Crystals of CuPCP, $Cu\{[(CH_3)_2N]_2P(O)CH_2P(O)[N(CH_3)_2]_2\}_3(ClO_4)_2$, were obtained by evaporating an acetone solution of

[1] (a) Abstracted in part from the Ph.D. thesis of P. T. Miller, Vanderbilt University, Aug 1971. (b) Department of Chemistry. (c) Department of Physics.

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