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## Structural Characterization of Di- $\mu$ -hydroxo-bis( $N,N,N',N'$ -tetraethylethylenediamine)dicopper(II) Perchlorate, [Cu(teen)OH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>

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The crystal and molecular structure of di- $\mu$ -hydroxo-bis( $N,N,N',N'$ -tetraethylethylenediamine)dicopper(II) perchlorate, [Cu{(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}OH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, has been determined from three-dimensional X-ray data collected by counter methods. The complex crystallizes in the space group  $P2_1/c$  of the monoclinic system with two molecules in a cell of dimensions  $a = 7.557$  (5) Å,  $b = 16.025$  (17) Å,  $c = 14.014$  (9) Å, and  $\beta = 103.56$  (3)°. The observed and calculated densities are 1.43 and 1.417 g cm<sup>-3</sup>, respectively. Least-squares refinement of the structure has yielded a final value of the conventional  $R$  factor (on  $F$ ) of 0.042 for 1524 independent reflections having  $F^2 > 3\sigma(F^2)$ . The cation is dimeric, with the two copper atoms linked by two hydroxo bridges. The coordination geometry around each copper atom is roughly square planar, the plane consisting of the two bridging oxygen atoms and the two nitrogen atoms of the  $N,N,N',N'$ -tetraethylethylenediamine (teen) ligand. The average Cu-O distance in the bridge is 1.903 (4) Å and the Cu-Cu separation is 2.978 (2) Å. The Cu-O-Cu and O-Cu-O angles in the bridge are 103.0 (2) and 77.0 (2)°, respectively. The observed bridging geometry lends strong support to the hypothesis that the magnitude of the magnetic interaction in dimers of this type is dominated by the bridging geometry.

### Introduction

During the past several years, there has been increased interest in the correlation between the structures of magnetically condensed systems and their magnetic properties.<sup>1</sup> Recent work on dimeric systems of the type [CuL(OH)]<sub>2</sub><sup>2+</sup>, where L is a bidentate ligand, has suggested a linear correlation between the bridging Cu-O-Cu angle ( $\phi$ ) and the triplet-singlet splitting ( $2J$ ) for these systems.<sup>2,3</sup>

The preparation and magnetic properties of the title compound, [Cu(teen)OH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, have been reported by Hatfield, *et al.*<sup>4</sup> These workers, who examined the magnetic susceptibility of the complex in the temperature range 77–388°K, deduced that there was a strong antiferromagnetic interaction between the two metal centers, with a value of  $2J$  (the triplet-singlet splitting) of  $-410$  cm<sup>-1</sup>. The existence of this independent datum offered, we felt, a unique opportunity to test the hypothetical relationship between  $J$  and the Cu-O-Cu bridging angle  $\phi$  alluded to above. On the basis of the available data for systems of this type, a linear  $\phi$  vs.  $J$  plot would predict a  $\phi$  angle of 102.9° for this known  $J$  value.<sup>3</sup> Hence, in order to test the validity of our hypothesis and to investigate further the structural properties of copper(II) dimers, we have undertaken a complete three-dimensional analysis of the crystal structure of [Cu(teen)OH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>.

### Experimental Section

Violet, needle-shaped crystals were prepared and generously donated by Professor J. R. Wasson. The crystal used for data collection showed no signs of decomposition.

On the basis of Weissenberg and precession photographs the crystals were assigned to the monoclinic system. The observed systematic absences are  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd, which suggests that the space group is  $P2_1/c$  ( $C_{2h}^5$ ). The lattice constants, obtained by the least-squares method of Busing and Levy,<sup>5</sup> are  $a = 7.557$  (5) Å,  $b = 16.025$  (17) Å,  $c = 14.014$  (9) Å, and  $\beta = 103.56$  (3)°. A density of 1.417 g cm<sup>-3</sup> calculated for two dimeric formula units in the cell agrees well with the value of 1.43 (2) g cm<sup>-3</sup> obtained by flotation in chloroform-methylene chloride solution. Hence, the dimer is con-

strained to lie on a crystallographic inversion center. The cell constants and observed density obtained here are markedly different from those reported by Nasanen, *et al.*,<sup>6</sup> who prepared their material from methanol while our material was made in aqueous medium; we can only conclude that Nasanen, *et al.*, obtained a different isomer of this complex. Since Hatfield, *et al.*, also prepared their material from aqueous solution, we are confident that our complex is the same as that used in the magnetic study.

A needle-shaped crystal with faces (100), ( $\bar{1}00$ ), (011), ( $0\bar{1}\bar{1}$ ), ( $0\bar{1}1$ ), and ( $01\bar{1}$ ) was chosen for data collection. The distance between the (100) and ( $\bar{1}00$ ) faces was 0.703 mm, the distance between the (011) and ( $0\bar{1}\bar{1}$ ) faces was 0.104 mm, and that between the ( $0\bar{1}1$ ) and ( $01\bar{1}$ ) faces was 0.118 mm. The crystal was mounted on a glass fiber roughly parallel to the (011) face and in this orientation intensity data were collected. The mosaicity of the crystal was examined by means of the narrow-source, open-counter  $\omega$ -scan technique and was judged to be acceptable.

Twelve reflections, accurately centered through a narrow vertical slit at a takeoff angle of 1.0°, formed the basis for the least-squares refinement of cell parameters and orientation. The logic of Busing and Levy<sup>5</sup> was used for the refinement in the PDP-8/L computer.

Intensity data were collected at a takeoff angle of 1.0°; at this angle the peak intensity for a typical strong reflection was about 95% of the maximum value as a function of takeoff angle. The counter aperture was 5.0 mm high by 5.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the  $\theta$ - $2\theta$  scan technique at a scan rate of 0.5°/min. To allow for the presence of both  $K\alpha_1$  and  $K\alpha_2$  radiations, the scan range for each reflection was from 0.8° below the calculated  $K\alpha_1$  peak position to 0.8° above the calculated  $K\alpha_2$  position. Stationary-counter, stationary-crystal background counts of 20 sec were taken at the end of each scan. The data were collected at 17° on a Picker four-circle automatic diffractometer equipped with a graphite monochromator and using Mo  $K\alpha$  radiation.

A unique data set having  $2\theta < 48^\circ$  was obtained. A total of 2563 independent intensities was recorded. The intensities of three standard reflections were measured after every 100 reflections. After approximately 700 reflections, the standards began to decline. This was accounted for by the application of a correction for linear decline. There were very few data above background at values of  $2\theta > 48^\circ$ .

Data processing was carried out as described by Corfield, *et al.*<sup>7</sup> After correction for background the intensities were assigned standard deviations according to the formula  $\sigma(I) = [C + 0.25(t_a/t_b)^2 \cdot (B_H + B_L) + (pI)^2]^{1/2}$  and the value of  $p$  was selected as 0.05. This term is used to prevent extremely high weight being given to very large reflections.<sup>8</sup> The values of  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarization effects and for absorption. The absorption

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coefficient for this compound for Mo  $K\alpha$  radiation is  $10.94 \text{ cm}^{-1}$ , and for the sample chosen the transmission coefficients ranged from 0.79 to 0.91. Of the 2563 independent reflections only 1524 were greater than 3 times their estimated standard deviations; only these were used in the refinement of the structure.

### Solution and Refinement of Structure

All least-squares refinements in this analysis were carried out on  $F$ , the function minimized being  $\sum w(|F_o| - |F_c|)^2$ ; the weights  $w$  were taken as  $4F_o^2/\sigma^2(F_o)^2$ . In all calculations of  $F_c$  the atomic scattering factors for Cu, Cl, and N were taken from Cromer and Waber,<sup>9</sup> those for C and O were from the tabulations of Ibers,<sup>10</sup> and that for H was from Stewart, Davidson, and Simpson.<sup>11</sup> The effects of anomalous dispersion were included in calculations of  $F_c$ ,<sup>12</sup> the values of  $\Delta f'$  and  $\Delta f''$  being taken from the tabulations of Cromer.<sup>13</sup>

The position of the Cu atom was determined from a three-dimensional Patterson function,<sup>14</sup> and four cycles of least-squares refinement on this position were run using a fixed isotropic thermal parameter. The usual agreement factors  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_2$  (or weighted  $R$  factor)  $= (\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2)^{1/2}$  were 0.470 and 0.549, respectively. The Cl atom, five O atoms, two N atoms, and ten C atoms were located in subsequent difference Fourier maps, and least-squares refinement of these atoms with isotropic thermal parameters yielded values of 0.081 and 0.122 for  $R_1$  and  $R_2$ , respectively. Two cycles of least-squares refinement with anisotropic thermal parameters reduced  $R_1$  and  $R_2$  to 0.061 and 0.089.

At this stage, the data were corrected for the decline in the intensities of the standards (*vide supra*) and the absorption correction was applied. A difference Fourier map revealed the positions of 19 of the 25 hydrogen atoms. A least-squares calculation including these atoms led to values of  $R_1$  and  $R_2$  of 0.048 and 0.060; because of the limited number of data available, it was not possible to refine these hydrogen parameters. The remaining hydrogen atoms were then successfully located, and further refinement led to values of  $R_1$  and  $R_2$  of 0.042 and 0.049.

The value of  $R_2$  showed some dependence on  $\sin \theta$ , and so the weighting scheme was modified by dividing the weights  $w$  for reflections with  $2\theta < 10^\circ$  by 2.62 and those for data with  $10^\circ \leq 2\theta < 20^\circ$  by 1.90. We have observed in every case in which we have used our graphite monochromator and Mo radiation that a similar correction has been necessary.<sup>15</sup> The final values of  $F_o$  and  $F_c$  suggested to us that no correction for secondary extinction was necessary, and none was applied. The final values of  $R_1$  and  $R_2$  were 0.042 and 0.048. In the final cycle of least-squares refinement, no parameter underwent a shift in excess of 10% of its estimated standard deviation, which is taken as evidence that the refinement had converged.

A final difference Fourier synthesis showed no peak higher than  $0.8 \text{ e \AA}^{-3}$ . Most of the residual electron density was in the vicinity of the bridging oxygen, and its spatial distribution might be accounted for in terms of unpaired electron density localized on that atom; in view of the limited number of data available and our consequent inability to refine the hydrogen atom parameters, however, it is not possible to assign this electron density with any degree of certainty.

The positional and thermal parameters derived from the final least-squares cycle are given in Tables I and II. A compilation of observed and calculated structure amplitudes is available.<sup>16</sup>

### Description of the Structure

The structure consists of dimeric, four-coordinate  $[\text{Cu}(\text{teen})\text{OH}]_2^{2+}$  cations and discrete  $\text{ClO}_4^-$  anions. This geometry at the copper centers is in marked contrast to that of other perchlorates of this general type which we have examined,<sup>2,3,15,17</sup> in which the perchlorate anion was in-

Table I. Positional Parameters for  $[\text{Cu}(\text{teen})\text{OH}]_2(\text{ClO}_4)_2$

Atom	x	y	z
Cu	0.03334 (10)	0.06867 (4)	0.07359 (5)
Cl	-0.3856 (2)	0.3105 (1)	0.2509 (1)
O(1)	0.0570 (6)	0.4508 (2)	0.4372 (3)
O(2)	-0.1959 (7)	0.3313 (3)	0.2722 (4)
O(3)	-0.4786 (9)	0.3402 (4)	0.1595 (4)
O(4)	-0.4616 (10)	0.3491 (5)	0.3201 (5)
O(5)	-0.3989 (8)	0.2240 (3)	0.2548 (5)
N(1)	0.0433 (7)	0.1941 (3)	0.0694 (4)
N(2)	0.0952 (7)	0.0772 (3)	0.2218 (3)
C(1)	0.0593 (10)	0.1669 (4)	0.2418 (4)
C(2)	0.1275 (10)	0.2227 (4)	0.1709 (4)
C(3)	-0.0249 (12)	0.0215 (4)	0.2646 (5)
C(4)	-0.2226 (13)	0.0227 (5)	0.2118 (7)
C(5)	0.2931 (9)	0.0544 (4)	0.2588 (5)
C(6)	0.3659 (13)	0.0571 (6)	0.3674 (5)
C(7)	-0.1487 (11)	0.2262 (4)	0.0350 (5)
C(8)	-0.1685 (18)	0.3222 (4)	0.0143 (6)
C(9)	0.3269 (4)	0.1708 (6)	0.0131 (7)
C(10)	0.1565 (12)	0.2201 (4)	-0.0010 (5)
HB <sup>a</sup>	-0.1350	0.4310	0.3930
H(11)	0.1216	0.1787	0.3028
H(12)	-0.1019	0.1655	0.2332
H(21)	0.2707	0.2140	0.1870
H(22)	0.0980	0.2813	0.1740
H(31)	-0.0185	0.0331	0.3405
H(32)	-0.0103	0.4600	0.2404
H(41)	-0.2411	0.0126	0.1422
H(42)	-0.2798	0.0764	0.2180
H(43)	-0.2951	-0.0262	-0.2442
H(51)	0.3643	0.1014	0.2241
H(52)	0.3150	-0.0059	0.2326
H(61)	0.3579	0.1127	0.3954
H(62)	0.4631	0.0330	0.3847
H(63)	0.3096	0.0320	0.4090
H(71)	-0.2008	0.1989	0.0886
H(72)	-0.2097	0.3051	0.4762
H(81)	-0.1598	0.2706	0.0186
H(82)	-0.1366	0.3398	0.0572
H(83)	-0.1279	0.1552	0.4762
H(101)	0.0659	0.2916	0.4260
H(102)	0.1845	0.2844	0.0091
H(91)	0.3266	0.1286	-0.0050
H(92)	0.3526	0.3206	0.4695
H(93)	0.3800	0.1481	0.0652

<sup>a</sup> Hydrogen atom parameters were not varied. The numbering scheme for hydrogen atoms indicates to which carbon atom the hydrogen is bound; e.g., H(71) and H(72) are bonded to C(7), H(102) is bonded to C(10), etc.

variably coordinated to the metal; moreover, the oxy anions in the related complexes  $[\text{Cu}(\text{bipy})\text{OH}]_2(\text{NO}_3)_2$  and  $[\text{Cu}(\text{bipy})\text{OH}]_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$  (bipy = 2,2'-bipyridine) are coordinated to the copper atoms.<sup>18,19</sup> The geometry around the copper is slightly distorted from planarity, with N(1) and one oxygen atom 0.14 and 0.16 Å, respectively, above the best least-squares plane while N(2) and the symmetry-related oxygen atom were 0.13 and 0.16 Å below it; the copper atom, however, lies in the plane. The bridging Cu-O-Cu-O unit, of course, is constrained to planarity by the inversion center. The geometry, therefore, is very similar to that found<sup>20</sup> in the related species  $[\text{Cu}(\text{tmen})\text{OH}]_2\text{Br}_2$  (tmen = *N,N,N',N'*-tetramethylethylenediamine). A view of the cation is given in Figure 1.

The bond lengths and angles in the complex are given in Tables III and IV. The Cu-Cu' separation of 2.978 (2) Å is in the range observed for other di- $\mu$ -hydroxo-copper(II) com-

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Table II. Thermal Parameters for  $[\text{Cu}(\text{teen})\text{OH}]_2(\text{ClO}_4)_2$ 

Atom	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	0.01232 (16)	0.00270 (3)	0.00384 (4)	0.00020 (7)	0.00129 (6)	-0.00024 (3)
Cl	0.0153 (4)	0.0041 (1)	0.0064 (1)	-0.0006 (1)	0.0017 (2)	-0.0008 (1)
O(1)	0.0202 (11)	0.0029 (2)	0.0037 (2)	-0.0015 (4)	-0.0013 (4)	-0.0001 (2)
O(2)	0.0150 (12)	0.0050 (2)	0.0108 (4)	-0.0025 (4)	0.0024 (6)	-0.0022 (3)
O(3)	0.0312 (17)	0.0086 (3)	0.0082 (4)	-0.0034 (7)	-0.0022 (7)	0.0020 (3)
O(4)	0.0372 (20)	0.0129 (5)	0.0104 (5)	0.0082 (8)	0.0096 (9)	-0.0016 (4)
O(5)	0.0220 (15)	0.0038 (2)	0.0197 (7)	-0.0024 (5)	-0.0014 (8)	0.0010 (3)
N(1)	0.0138 (11)	0.0031 (2)	0.0044 (3)	-0.0003 (5)	0.0020 (5)	0.0001 (2)
N(2)	0.0152 (11)	0.0028 (2)	0.0042 (3)	0.0001 (4)	0.0022 (4)	-0.0005 (2)
C(1)	0.0199 (17)	0.0033 (3)	0.0037 (4)	0.0004 (6)	0.0020 (6)	-0.0005 (3)
C(2)	0.0184 (17)	0.0027 (3)	0.0046 (4)	-0.0004 (6)	0.0014 (6)	-0.0009 (3)
C(3)	0.0250 (21)	0.0038 (3)	0.0057 (4)	0.0001 (7)	0.0052 (8)	0.0004 (3)
C(4)	0.0237 (22)	0.0050 (4)	0.0114 (7)	-0.0023 (8)	0.0091 (11)	-0.0004 (4)
C(5)	0.0153 (15)	0.0036 (3)	0.0053 (4)	0.0014 (6)	-0.0002 (6)	-0.0008 (3)
C(6)	0.0304 (23)	0.0080 (5)	0.0057 (5)	0.0044 (9)	-0.0025 (8)	0.0000 (4)
C(7)	0.0233 (20)	0.0031 (3)	0.0060 (5)	0.0022 (6)	0.0006 (8)	0.0009 (3)
C(8)	0.0659 (41)	0.0029 (3)	0.0089 (6)	0.0051 (9)	0.0061 (13)	0.0013 (3)
C(9)	0.0310 (26)	0.0091 (6)	0.0090 (6)	-0.0035 (11)	0.0116 (11)	-0.0013 (5)
C(10)	0.0241 (21)	0.0045 (3)	0.0065 (5)	-0.0030 (7)	0.0061 (8)	-0.0004 (3)

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

Table III. Intramolecular Distances in  $[\text{Cu}(\text{teen})\text{OH}]_2(\text{ClO}_4)_2$ 

Atoms	Dist, Å	Atoms	Dist, Å	Atoms	Dist, Å
Cu-O(1)	1.899 (4)	N(1)-C(10)	1.508 (9)	C(7)-C(8)	1.567 (9)
Cu-O(1')	1.907 (4)	N(2)-C(1)	1.500 (7)	C(9)-C(10)	1.485 (13)
Cu-N(1)	2.103 (5)	N(2)-C(3)	1.495 (9)	Cl-O(2)	1.434 (5)
Cu-N(2)	2.024 (4)	N(2)-C(5)	1.508 (8)	Cl-O(3)	1.392 (5)
Cu-Cu'	2.978 (2)	C(1)-C(2)	1.514 (9)	Cl-O(4)	1.383 (7)
N(1)-C(2)	1.488 (7)	C(3)-C(4)	1.504 (12)	Cl-O(5)	1.392 (5)
N(1)-C(7)	1.508 (9)	C(5)-C(6)	1.492 (9)		

Table IV. Bond Angles in  $[\text{Cu}(\text{teen})\text{OH}]_2(\text{ClO}_4)_2$ 

Atoms	Angle, deg	Atoms	Angle, deg
Cu-O(1)-Cu	103.0 (2)	Cu-N(1)-C(10)	109.0 (4)
O(1)-Cu-O(1')	77.0 (2)	Cu-N(1)-C(7)	108.0 (4)
O(1)-Cu-N(1)	98.1 (2)	C(7)-N(1)-C(10)	110.4 (5)
O(1)-Cu-N(2)	98.3 (2)	C(1)-N(2)-C(5)	112.1 (5)
N(1)-Cu-N(2)	87.8 (2)	Cu-N(2)-C(3)	110.8 (4)
Cu-N(1)-C(2)	106.8 (3)	Cu-N(2)-C(5)	108.0 (4)
N(1)-C(2)-C(1)	108.1 (5)	C(3)-N(2)-C(5)	111.3 (5)
C(2)-C(1)-N(2)	109.8 (5)	C(1)-N(2)-C(3)	110.1 (5)
C(1)-N(2)-Cu	104.3 (3)	O(2)-Cl-O(3)	112.1 (4)
N(1)-C(10)-C(9)	111.9 (6)	O(2)-Cl-O(4)	108.0 (4)
N(1)-C(7)-C(8)	115.9 (7)	O(2)-Cl-O(5)	107.5 (3)
N(2)-C(3)-C(4)	114.9 (6)	O(3)-Cl-O(4)	106.8 (5)
N(2)-C(5)-C(6)	116.2 (6)	O(3)-Cl-O(5)	110.5 (4)
C(2)-N(1)-C(7)	111.4 (5)	O(4)-Cl-O(5)	111.9 (5)
C(2)-N(1)-C(10)	111.0 (5)		

plexes<sup>2,17-21</sup> and is much longer than the range of 2.61-2.65 Å observed for complexes in which direct copper-copper bonding is postulated.<sup>22-24</sup> The Cu-N distances of 2.013 (5) and 2.024 (5) Å are normal.<sup>2,3,15,17-20</sup> The Cu-O bridges are symmetric, and the Cu-O distances of 1.899 (4) and 1.907 (4) Å are again very similar to the value of 1.902 (3) Å in the tmen complex.<sup>20</sup> The geometry of the substituted ethylenediamine rings is normal,<sup>25-30</sup> in the present complex,

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(26) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 597 (1972).

(27) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842, 1362 (1968); K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

(28) J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, **9**, 2397 (1970).

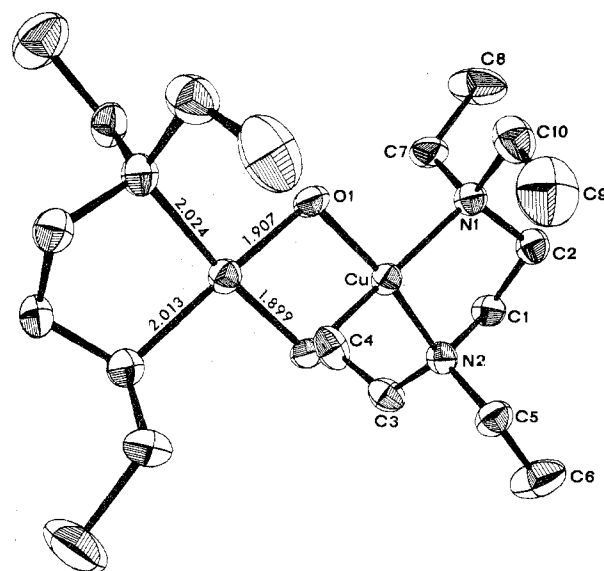


Figure 1. View of the  $[\text{Cu}(\text{teen})\text{OH}]_2^{2+}$  cation; atoms C(9)' and C(10)' (which are related to C(9) and C(10) by the inversion center) and all hydrogen atoms have been omitted for clarity. The  $\lambda$  ring is on the right in the dimer shown.

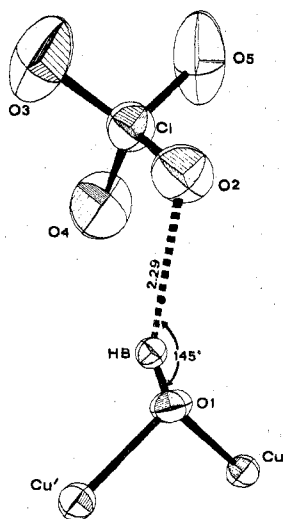
each dimer contains one  $\delta$  and one  $\lambda$  conformer,<sup>31</sup> whereas in the tmen complex both rings in any given dimer have the same conformation.<sup>20</sup>

As was noted above, the perchlorate anion is not coordinated to the metal. There may be, however, a hydrogen-bonding interaction between the anion and the bridging hydroxyl group. The  $\text{O}(2) \cdots \text{O}(1)$  separation of 3.00 Å is greater than twice the van der Waals radius of oxygen as reported by

(29) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1468 (1971).

(30) Mazhar-Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970).

(31) The notation used is from *Inorg. Chem.*, **9**, 1 (1970).



**Figure 2.** The approach of the perchlorate ion to the Cu-OH-Cu bridge in  $[\text{Cu}(\text{teen})\text{OH}]_2(\text{ClO}_4)_2$ . The probable O-H...O hydrogen bond is represented by the dashed bond.

Pauling<sup>32</sup> (2.80 Å) but slightly less than that of Bondi (3.04 Å).<sup>33</sup> Moreover, the O(2)···HB separation of 2.30 Å is less than the sum of the reported van der Waals radii of H and O, and Hamilton and Ibers<sup>34</sup> have noted that the existence of two O-H separations which are less than this sum is a sufficient condition for hydrogen bonding, even if the O···O distance exceeds the van der Waals radius sum. The O(1)-HB···O(2) angle of 145° is in the range normally observed for weak hydrogen bonds.<sup>28</sup> Further support for this con-

(32) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(33) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(34) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 16.

clusion is found in an examination of the geometry of the perchlorate group (Tables III and IV). The three Cl-O distances not involving O(2) are 1.383 (7), 1.392 (5), and 1.392 (5) Å, with an average value of 1.389 (5) Å; the Cl-O(2) distance of 1.434 (5) Å is significantly longer than these three, as would be expected if O(2) were involved in hydrogen bonding to the bridge. A view of the perchlorate anion and its probable interaction with the bridge is shown in Figure 2.

The Cu-O-Cu bridging angle,  $\phi$ , is 103.0 (2)°. The best unweighted least-squares line through the five available values of  $\phi$  and  $2J$  for di- $\mu$ -hydroxo-copper(II) dimers has an intercept of 7730  $\text{cm}^{-1}$  and a slope of  $-79.1 \text{ cm}^{-1} \text{ deg}^{-1}$ . Using the published<sup>4</sup> value for  $2J$  of  $-410 \text{ cm}^{-1}$ , the predicted value of  $\phi$  is 102.9 (1)°, which is in remarkable agreement with the observed angle. Evidently, therefore, the present structural data strongly support the hypothesis that, over the angular range  $95^\circ \leq \phi \leq 105^\circ$ , there is a linear relationship between  $\phi$  and  $J$ . In the light of this observation, it should now be possible to predict  $J$  from  $\phi$  or *vice versa* for this class of complexes.

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**Registry No.**  $[\text{Cu}(\text{teen})\text{OH}]_2(\text{ClO}_4)_2$ , 51259-55-3.

**Supplementary Material Available.** A listing of structure factor amplitudes 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1654.

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## Structure of Tetrafluoroboratotris(triphenylphosphine)copper(I), $\text{Cu}(\text{BF}_4)(\text{P}(\text{C}_6\text{H}_5)_3)_3$ . An Example of a Copper(I) Complex Containing a Weakly Coordinated Tetrafluoroborate Anion

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The structure of tetrafluoroboratotris(triphenylphosphine)copper(I),  $\text{Cu}(\text{BF}_4)(\text{P}(\text{C}_6\text{H}_5)_3)_3$ , has been determined from three-dimensional X-ray data collected by counter techniques. The material crystallizes in space group  $C_3^1-P3$  of the trigonal system with three crystallographically independent molecules of the complex in the unit cell, each possessing imposed  $C_3$  symmetry. Crystal data are  $a = 18.749$  (3) Å,  $c = 11.588$  (2) Å,  $V = 3527.8$  Å<sup>3</sup>,  $\rho_{\text{measd}} = 1.34$  (2) g/cm<sup>3</sup>, and  $\rho_{\text{calcd}} = 1.32$  g/cm<sup>3</sup>. The structure has been refined by a full-matrix least-squares procedure to a conventional  $R$  index of 0.050 for 2615 observations having  $F_o^2 > 3\sigma(F_o^2)$ . The absolute configuration has been assigned on the basis of statistical and experimental tests as *RSS*. The structural results reveal a molecular complex with the  $\text{BF}_4^-$  anion weakly coordinated to the copper atom through one of its terminal fluorine atoms. The coordination geometry about the copper atom may be described as trigonally distorted tetrahedral. The three independent molecules are roughly equivalent and the structure is discussed in terms of an averaged molecule. Averaged distances and angles of interest are as follows: Cu-P, 2.298 Å; Cu-F (coordinated), 2.31 Å; B-F (coordinated), 1.39 Å; B-F (terminal), 1.35 Å; P-Cu-P, 115.6°; P-Cu-F (coordinated), 102.2°. The infrared and Raman spectra of the complex have been recorded and the frequencies of the Cu-F stretch and the various modes of the  $\text{BF}_4^-$  group have been assigned. The nature of the Cu-FBF<sub>3</sub> interaction is discussed.

### Introduction

Monodentate tertiary phosphine complexes of Cu(I) with a variety of monoanions exhibit a diversity of stoichiometries and structural types. Complexes with metal to phos-

phine ratios of 1:1, 1:2, 1:3, 1:4, and 2:3 have thus far been noted. The structural types represented by these stoichiometries involve Cu(I) in two-, three-, and four-coordinate environments with four-coordination predominant. The