the C(6) hydrogen to O(1) distances of 2.46, 2.64, and 2.77 Å in the three complexes.

The geometry at the copper in this complex is much different from that in either the corresponding bromide or iodide. There is an inverse correlation in these complexes between anion contact volume and the copper coordination number with the largest anion forming a four-coordinate complex, the intermediate size anion a five-coordinate complex, and the smallest anion a six-coordinate complex. This would be expected from consideration of steric principles but has not been previously demonstrated in similar circumstances. Moreover, though change in coordination with diverse anions has been postulated for similar copper(II) systems on the basis of electronic spectra and epr data, these predictions show no similar correlation between anion size and copper coordination number. With this established correlation in these three AEP complexes there is an opportunity to examine more closely this relationship between electronic spectra and solid-state structure and possibly enhance the reliability of electronic spectra as diagnostic structural tools. Further studies in this area are presently being conducted.

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Registry No. $Cu(AEP)_2(ClO_4)_2$, 42294-83-7.

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, 20× 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-74-143.

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

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

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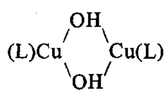
The crystal structure of α-di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridine]dicopper(II) perchlorate, α-$[Cu(DMAEP)OH]_2(ClO_4)_2$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the triclinic space group $P\bar{1}$ with one dimeric molecule in a cell of dimensions $a = 9.164$ (5), $b = 10.049$ (5), and $c = 8.953$ (5) Å; and $\alpha = 82.30$ (2), $\beta = 56.72$ (2), and $\gamma = 68.52$ (2)°. The observed and calculated densities are 1.71 (2) and 1.716 g cm^{-3}, respectively. Independent intensities (2134) greater than 3 times their estimated standard deviations were used in the full-matrix least-squares refinement, and the final value of the conventional R factor is 0.027. The complex consists of pairs of copper atoms linked by two hydroxo bridges and two intramolecular bidentate perchlorate groups. The geometry at each copper atom is distorted octahedral, the equatorial plane consisting of two hydroxo oxygen atoms and two nitrogen atoms from a DMAEP ligand with Cu–O bond distances of 1.947 (2) and 1.936 (2) Å and Cu–N bond distances of 2.017 (2) and 2.056 (2) Å, while the axial coordination sites are occupied by perchlorate oxygen atoms with Cu–O bond distances of 2.716 (3) and 2.782 (2) Å. The effect of the bidentate perchlorate coordination on the infrared spectra in the region 1000–1300 cm^{-1} is also discussed.

Introduction

A number of recent structural investigations[1-4] have demonstrated the existence of the dimeric structural unit



for complexes of stoichiometry $[Cu(L)(OH)]_2^{2+}$ where L may be any of a number of bidentate ligands. Corresponding magnetic susceptibility and electron paramagnetic resonance data for these complexes present a wide range of antiferromagnetic and ferromagnetic[5-8] interactions which appear to be the result of minor structural changes in the geometry of the hydroxo bridge of the dimeric unit. Further correlation between these structural changes and the resulting magnetic behavior is of great importance if the nature of the magnetic interactions is to be understood.

Uhlig and coworkers,[9] on the basis of electronic spectroscopy and magnetic susceptibility data, suggested that copper(II)-hydroxo complexes with N-substituted 2-(2-aminoethyl)pyridines should be formulated as dimers of this type. Our recent determination of the crystal structure of the 2-(2-ethylaminoethyl)pyridine (EAEP) analog[1] confirms this hypothesis for the case of the monosubstituted ligand. The magnetic susceptibility measurements of Uhlig and coworkers further suggest that there may be significant struc-

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tural differences between the monosubstituted and disubstituted cases, since for the methyl- and isopropyl-substituted complexes the magnetic data show large antiferromagnetic interactions with susceptibility maxima at 116 and 202°, respectively, whereas the dimethyl-substituted case appears to follow Curie-Weiss behavior above 80°K. Our recent magnetic measurements[5] on the ethyl-substituted complex tend to confirm these findings.

In order to understand the basis of this apparent magnetic difference between the mono- and disubstituted complexes, we have undertaken a complete three-dimensional crystal structure study of one form of the dimethyl complex, α-$[Cu(DMAEP)OH]_2(ClO_4)_2$, where DMAEP is 2-(2-dimethylaminoethyl)pyridine. This experiment was also performed in order to test further the validity of our hypothesis[1,8] that the value of $2J$, the singlet-triplet splitting, for dihydroxo-bridged copper(II) complexes is inversely proportional to the value of the Cu-O-Cu bridging angle.

Data Collection and Reduction

Crystals of $[Cu(DMAEP)OH]_2(ClO_4)_2$ were prepared[9] by addition of equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and DMAEP to a methanol-ether mixture. After several days two types of well-formed crystals, dark blue plates and dark blue needles, were observed and elemental analysis confirmed similar compositions for both crystal types. Preliminary Weissenberg and precession photography indicated that the plates belong to the triclinic system, the space group being either C_1^1-$P1$ or C_i^1-$P\bar{1}$ (the centrosymmetric $P\bar{1}$ being demonstrated during the refinement (*vide infra*)) whereas the needles belong to the monoclinic system. We report here the three-dimensional crystal structure of the triclinic form, α-$[Cu(DMAEP)OH]_2(ClO_4)_2$, and will consider the monoclinic form, β-$[Cu(DMAEP)OH]_2(ClO_4)_2$, in a future report. From an examination of the magnetic behavior of these two isomers, it is evident that the material originally prepared and investigated by Uhlig and coworkers[9] is the triclinic α form. The cell constants, obtained by least-squares procedure[10] on 20 independent reflections, are $a = 9.164$ (5), $b = 10.049$ (5), and $c = 8.953$ (5) Å; and $\alpha = 82.30$ (2), $\beta = 56.72$ (2), and $\gamma = 68.52$ (2)°; observations were made at 23° with an assumed wavelength λ (Mo $K\alpha_1$) 0.7093 Å. The calculated density of 1.716 g cm^{-3} for one dimeric unit per cell agrees well with the value of 1.71 (2) g cm^{-3} obtained by flotation in dichloromethane–dibromoethane solution. Hence, in the space group $P\bar{1}$ there must be an inversion center in the middle of the dimer.

Diffraction data were collected on a four-circle Picker automatic diffractometer using Mo Kα radiation and a graphite monochromator in the manner previously described.[11] The scan rate was 1.0°/min, and the scan range was from 0.95° in 2θ below the calculated $K\alpha_1$ peak maximum to 0.95° in 2θ above the calculated $K\alpha_2$ peak maximum. The data were collected from a parallelepiped crystal with faces (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001), and $(00\bar{1})$ and having separation between parallel faces of 0.035 cm for (100) and $(\bar{1}00)$, 0.009 cm for (010) and $(0\bar{1}0)$, and 0.025 cm for (001) and $(00\bar{1})$. One form $(+h, \pm k, \pm l)$ of the data set was collected out to a value of 2θ (Mo) = 53°, and more than 50 strong Friedel pairs were additionally collected in the event that the space group proved noncentrosymmetric. At values of $2\theta > 53°$ there were few intensities greater than the background. A total of 2524 independent intensities was obtained.

Data processing was carried out as described by Corfield, Doedens, and Ibers.[12] The value of p in the expression[13] $\sigma(I) = (C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2)^{1/2}$ was chosen as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects, the form of the Lorentz–polarization correction being

$$1/Lp = (2 \sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)$$

where θ_m is the monochromator angle.[14]

Table I. Positional Parameters for α-$[Cu(DMAEP)OH]_2(ClO_4)_2$

Atoms	x	y	z
Cu	0.034320 (4)	−0.09429 (3)	0.12620 (4)
Cl	0.1282 (1)	−0.29904 (7)	−0.23802 (9)
O(1)	0.1740 (2)	−0.0278 (3)	−0.1081 (3)
O(2)	0.0046 (3)	−0.1648 (2)	−0.2476 (3)
O(3)	0.0736 (4)	−0.3139 (3)	−0.0553 (3)
O(4)	0.1183 (5)	−0.4138 (3)	−0.3025 (4)
O(5)	0.3138 (3)	−0.2970 (3)	−0.3379 (4)
C(1)	0.4117 (4)	−0.1557 (3)	0.0314 (4)
C(2)	−0.4184 (4)	−0.2246 (4)	0.0120 (5)
C(3)	−0.3927 (5)	−0.3512 (4)	0.0914 (5)
C(4)	0.4657 (4)	−0.4032 (3)	0.1825 (5)
C(5)	0.2966 (4)	−0.3302 (3)	0.1971 (4)
C(6)	0.1361 (5)	−0.3816 (3)	0.3009 (5)
C(7)	−0.0368 (4)	−0.2676 (4)	0.4418 (4)
C(8)	−0.2509 (5)	−0.2190 (4)	0.3467 (5)
C(9)	−0.2658 (5)	−0.0328 (4)	0.5025 (4)
N(1)	0.2708 (3)	−0.2061 (2)	0.1203 (3)
N(2)	−0.1374 (3)	−0.1586 (2)	0.3688 (3)
H(91)	−0.343 (5)	0.041 (4)	0.460 (5)
H(92)	0.352 (5)	0.049 (4)	0.376 (5)
H(93)	−0.203 (5)	−0.000 (4)	0.529 (5)
H(81)	−0.346 (5)	−0.233 (4)	0.460 (5)
H(82)	−0.312 (5)	−0.157 (4)	0.300 (5)
H(83)	−0.177 (5)	−0.301 (4)	0.272 (5)
H(71)	−0.005 (5)	−0.219 (4)	0.491 (4)
H(72)	0.119 (4)	0.314 (3)	0.464 (3)
H(61)	0.163 (4)	−0.464 (3)	0.363 (4)
H(62)	0.119 (4)	−0.416 (3)	0.226 (4)
H(4)	−0.524 (5)	−0.491 (4)	0.240 (4)
H(3)	−0.290 (5)	−0.397 (3)	0.070 (4)
H(2)	0.330 (5)	0.181 (3)	0.055 (4)
H(1)	0.389 (4)	−0.071 (3)	−0.014 (4)
HO	−0.223 (4)	0.086 (3)	0.171 (4)

Solution and Refinement of Structure

Examination of the three-dimensional Patterson function[15] revealed the positions of the copper atom and the bridging oxygen atom; five cycles of least-squares refinement were run on these positions. 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,[16] that for H was from Stewart, Davidson, and Simpson,[17] and those for C, O, and N were from the tabulation of Ibers.[18] The effects of anomalous dispersion were included in calculations of F_c,[19] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer.[20] Only the 2134 independent intensities which were greater than 3 times their estimated standard deviations were used in the refinement of the structure.

The two atoms were initially assigned isotropic thermal parameters and after the five cycles of least-squares refinement 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 0.459 and 0.520, respectively.

A difference Fourier map then revealed the positions of the remaining nonhydrogen atoms. An absorption correction was applied to the data, the absorption coefficient for these atoms and Mo Kα radiation being 19.2 cm^{-1}; the transmission coefficients were found to range from 0.64 to 0.875. After several more cycles of least-squares refinement with the addition of anomalous dispersion effects the values of R_1 and R_2 were 0.097 and 0.129, respectively. Refinement in the noncentrosymmetric space group $P1$ did not produce a significant improvement in R_2; moreover, the average deviation

(10) The logic used is that of Hamilton's MODE1 program.

(11) D. L. Lewis and D. J. Hodgson, *Inorg. Chem.*, 12, 1682 (1973).

(12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

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(14) S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 10, 2604 (1971).

(15) In addition to various local programs for the IBM 370/165, 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, Johnson's ORTEP plotting program, Doedens' RSCAN program, and Zalkin's Fourier program.

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

(18) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.3.1A.

(19) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(20) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

Table II. Thermal Parameters of α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$

Atom	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.01175 (7)	0.00801 (4)	0.01272 (6)	−0.00330 (4)	−0.00774 (5)	0.00327 (3)
Cl	0.0216 (2)	0.00920 (8)	0.0182 (1)	−0.0049 (1)	−0.0128 (1)	0.00239 (8)
O(1)	0.0120 (4)	0.0081 (2)	0.0122 (3)	−0.0026 (2)	−0.0069 (3)	0.0025 (2)
O(2)	0.0236 (5)	0.0104 (3)	0.0263 (5)	−0.0038 (3)	−0.0187 (4)	0.0030 (3)
O(3)	0.0387 (8)	0.0146 (3)	0.0210 (5)	−0.0071 (4)	−0.0185 (5)	0.0053 (3)
O(4)	0.0570 (10)	0.0114 (3)	0.0445 (8)	−0.0111 (5)	−0 0379 (8)	0.0028 (4)
O(5)	0.0185 (5)	0.0141 (3)	0.0314 (6)	−0.0028 (3)	−0.0090 (5)	0.0015 (4)
C(1)	0.0166 (6)	0.0099 (4)	0.0216 (6)	−0.0047 (4)	−0.0128 (5)	0.0037 (4)
C(2)	0.0158 (6)	0.0135 (4)	0.0269 (8)	−0.0053 (4)	−0.0138 (6)	0.0023 (5)
C(3)	0.0178 (7)	0.0124 (4)	0.0306 (8)	−0.0008 (4)	−0.0182 (7)	0.0004 (4)
C(4)	0.0223 (7)	0.0090 (4)	0.0268 (8)	−0.0016 (4)	−0.0181 (7)	0.0027 (4)
C(5)	0.0174 (6)	0.0075 (3)	0.0167 (5)	−0.0025 (3)	−0.0119 (5)	0.0020 (3)
C(6)	0.0233 (7)	0.0084 (3)	0.0239 (7)	−0.0059 (4)	−0.0160 (6)	0.0063 (4)
C(7)	0.0211 (7)	0.0119 (4)	0.0159 (6)	−0.0067 (4)	−0.0116 (5)	0.0070 (4)
C(8)	0.0179 (7)	0.0141 (5)	0.0211 (7)	−0.0091 (5)	−0.0107 (6)	0.0061 (5)
C(9)	0.0216 (8)	0.0126 (5)	0.0131 (6)	−0.0044 (5)	−0.0048 (6)	0.0014 (4)
N(1)	0.0136 (4)	0.0084 (3)	0.0159 (4)	−0.0031 (3)	−0.0095 (3)	0.0024 (5)
N(2)	0.0156 (4)	0.0094 (3)	0.0142 (4)	−0.0051 (3)	−0.0080 (3)	0.0039 (3)
H(91)	5.0 (8)					
H(92)	6.4 (9)					
H(93)	5.3 (9)					
H(81)	5.5 (8)					
H(82)	5.4 (8)					
H(83)	5.3 (9)					
H(71)	4.8 (8)					
H(72)	3.6 (6)					
H(61)	4.3 (7)					
H(62)	3.5 (6)					
H(4)	4.9 (7)					
H(3)	4.1 (7)					
H(2)	4.2 (7)					
H(1)	3.7 (6)					
HO	2.9 (7)					

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

between 20 of the most intense Friedel pairs examined was only 1.6% and was less than the average esd for these data. Hence, the centrosymmetric space group $P\bar{1}$ was used for the remainder of the analysis. All nonhydrogen atoms were then assigned variable anisotropic thermal parameters, and the values of R_1 and R_2 after two additional cycles of least-squares refinement were reduced to 0.047 and 0.071, respectively.

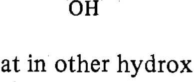
Examination of a difference Fourier map then revealed the locations of all the hydrogen atoms and these positions were verified by calculation of the theoretical positions based on tetrahedral geometry. It was decided, since the number of data per variable was sufficiently high, to allow the positional and isotropic thermal parameters of the hydrogen atoms to vary. After two further cycles of least-squares refinement, with the hydrogen atoms included, the values of R_1 and R_2 were reduced to 0.030 and 0.038. Upon examination of the most intense low-order data it was decided that correction for secondary extinction was necessary and after two further cycles of least-squares refinement with a variable extinction parameter of the kind described by Zachariasen[21] the values of R_1 and R_2 were 0.027 and 0.036.

In the last cycle of least-squares refinement no parameter shifted greater than 0.5 times its standard deviation, and, hence, the refinement was considered to have converged. The final value of R_2 showed little dependence either on sin θ or on $|F_o|$ which indicates that our choice of 0.04 for p is essentially correct. A final difference Fourier revealed no peaks higher than 0.3 e Å^{-3} which compares favorably with the average values of 7.0 and 5.5 e Å^{-3} earlier found for oxygen and carbon, respectively. 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 I and II. A table of observed and calculated structure amplitudes is available.[22] The final value of the extinction coefficient was 3.5(2) × 10^{-7}.

Description of the Structure

The structure consists of dimeric [Cu(DMAEP)OH]$_2^{2+}$ ions which are coordinated to two perchlorate groups. The overall geometry, as shown in Figure 1, can be best described as two trans-distorted octahedra which share a common edge. The equatorial planes of both octahedra are formed by the two oxygen atoms of the bridging hydroxyl groups and the two nitrogen atoms of the DMAEP ligand while the more distant axial positions are occupied by oxygen atoms from both perchlorate groups. This geometry at copper is unusual in that other documented hydroxo-bridged Cu(II) dimers are either square pyramidal as in the cases of the nitrate and sulfate salts of [Cu(OH)bipy]$_2^{2+}$ [3,4] (where bipy = 2,2′-bipyridine) and [Cu(EAEP)OH]$_2$(ClO$_4$)$_2$[1] or square planar as demonstrated by [Cu(tmen)OH]$_2$Br$_2$[2] (where tmen = N,N,N',N'-tetramethylethylenediamine).

The geometry of the dimer unit



is comparable with that in other hydroxo-bridged structures. The five atoms which describe the equatorial plane of the octahedron (copper, the bridging oxygen atoms, and the ligand nitrogen atoms) are coplanar, with no atom deviating from the least-squares plane by more than 0.045 Å. Hence, of course, the eight atoms which form the equatorial planes of the two octahedra are coplanar. This geometry is similar to that found in the nitrate salt of the bipy complex, in the tmen complex, and in the perchlorate salt of EAEP with the exception of the out-of-plane copper displacement which was found in the five-coordinate complexes. This minor difference can be directly attributed to the change in perchlorate coordination and the resultant change in the copper inner-sphere coordination as mentioned previously; any displacement of copper in the present example, where the

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(21) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967).

(22) See paragraph at end of paper regarding supplementary material.

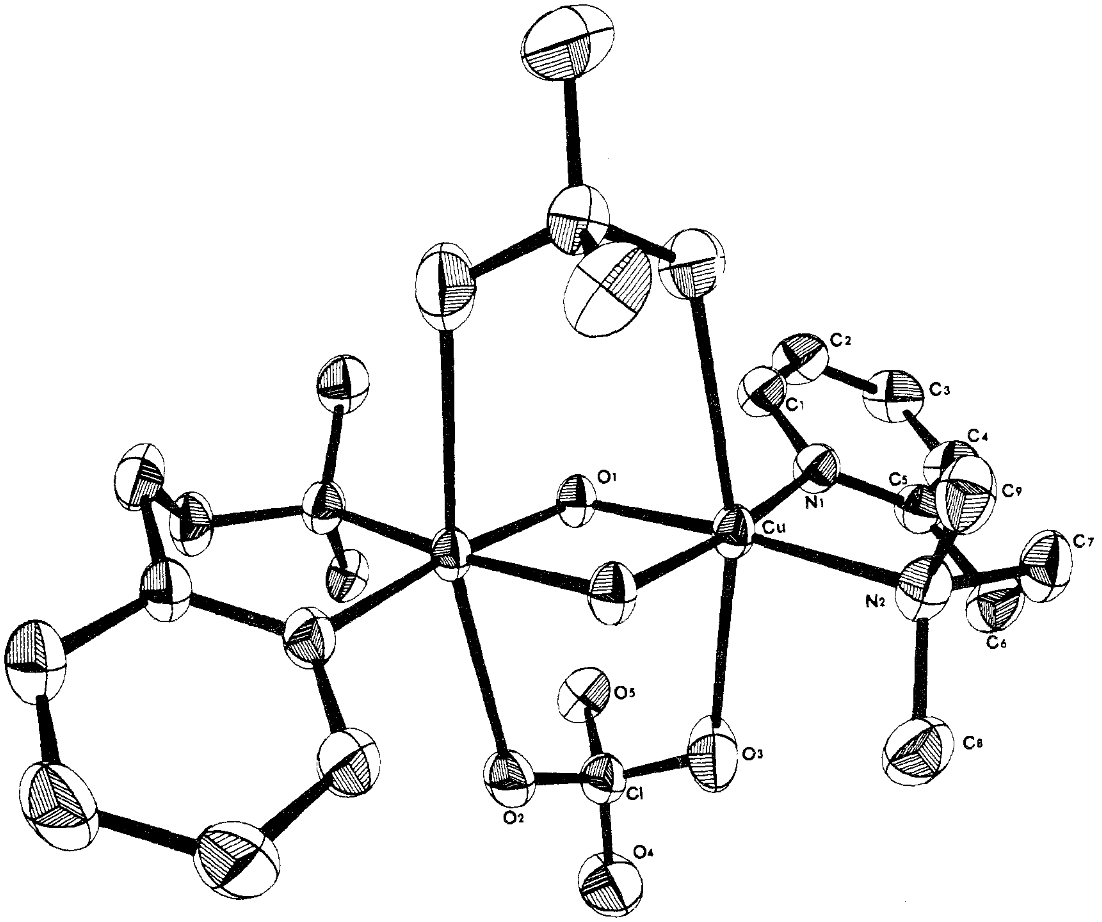

Figure 1. View of the dimeric molecule α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$. Thermal elipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

bonding above and below the dimeric plane is essentially equal, would be unexpected.

The bond lengths and angles for this portion of the complex, as given in Tables III and IV, compare with those found in similar structures. The Cu-Cu′ separation of 2.938 (1) Å is in the range of 2.78-3.00 Å found in other di-μ-hydroxo-copper(II) complexes[1-4,23] yet is significantly longer than the range of 2.63-2.65 Å found in complexes[24-26] in which copper-copper bonding interactions are postulated. The Cu-O bridging distances of 1.947 (2) and 1.936 (2) Å are also similar to those values found in the bipy, tmen, and EAEP examples, and the O(1)-Cu-O(1)′ and Cu(1)-O(1)-Cu(1)′ angles of 81.65 (9) and 98.35 (8)° fall well within the expected range. The Cu-N(1) and Cu-N(2) distances of 2.017 (2) and 2.056 (2) Å, respectively, compare with the range of 1.97-2.07 Å found in other examples of copper complexes of amines and substituted pyridines, with the copper to pyridine bond of 2.017 Å shorter than the copper to amine bond of 2.056 Å as expected.[27-36]

Table III. Internuclear Distances in α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$

Atoms[a]	Distance, Å	Atoms[a]	Distance, Å	Atoms[a]	Distance, Å
Cu-Cu′	2.938 (1)	C(2)-C(3)	1.379 (5)	C(3)-H(3)	0.80 (3)
Cu-O(1)	1.947 (2)	C(3)-C(4)	1.358 (5)	C(4)-H(4)	0.96 (3)
Cu-O(1)′	1.936 (2)	C(4)-C(5)	1.389 (4)	C(6)-H(61)	0.97 (3)
Cu-O(2)′	2.782 (2)	C(5)-N(1)	1.347 (3)	C(6)-H(62)	0.90 (3)
Cu-O(3)	2.716 (3)	C(5)-C(6)	1.490 (4)	C(7)-H(71)	0.91 (4)
Cu-N(1)	2.017 (2)	C(6)-C(7)	1.509 (5)	C(7)-H(71)	0.97 (3)
Cu-N(2)	2.056 (2)	C(7)-N(2)	1.486 (3)	C(7)-H(72)	0.94 (3)
Cl-O(2)	1.437 (2)	N(2)-C(8)	1.487 (4)	C(8)-H(81)	0.90 (4)
Cl-O(3)	1.429 (2)	N(2)-C(9)	1.479 (4)	C(8)-H(82)	0.91 (4)
Cl-O(4)	1.409 (3)	O(1)-O(5)	3.042 (4)	C(8)-H(83)	1.02 (4)
Cl-O(5)	1.428 (3)	OH-O(5)	2.36 (3)	C(9)-H(91)	0.97 (4)
N(1)-C(1)	1.341 (4)	C(1)-H(1)	0.90 (3)	C(9)-H(92)	0.90 (4)
C(1)-C(2)	1.371 (4)	C(2)-H(2)	0.93 (3)	C(9)-H(93)	0.70 (3)
				O(1)-OH	

[a] The numbering scheme for the atoms is shown in Figure 1.

The geometry of the DMAEP ligand is normal with the atoms of the pyridine ring being coplanar; the largest deviation from the least-squares plane is 0.006 Å. The bond distances and angles of the pyridine ring are comparable to those found in several other examples of substituted and nonsubstituted pyridine ring systems.[29,32,33,36] The plane

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Table IV. Internuclear Angles in α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$

Atoms	Angle, deg	Atoms	Angles, deg
Cu–O(1)–Cu′	98.35 (9)	O(3)–Cl–O(4)	109.6 (2)
O(1)–Cu–O(1)′	81.65 (9)	O(3)–Cl–O(5)	107.6 (2)
O(1)–Cu–O(2)′	82.81 (9)	O(4)–Cl–O(5)	111.5 (2)
O(1)–Cu–O(3)	86.02 (9)	C(1)–N(1)–C(5)	118.2 (2)
O(1)–Cu–N(1)	91.21 (8)	N(1)–C(1)–C(2)	123.6 (3)
N(1)–Cu–N(2)	94.95 (9)	C(1)–C(2)–C(3)	118.0 (3)
N(1)–Cu–O(2)′	94.33 (7)	C(2)–C(3)–C(4)	119.1 (3)
N(1)–Cu–O(3)	92.43 (9)	C(3)–C(4)–C(5)	120.8 (3)
N(2)–Cu–O(1)	92.29 (9)	C(4)–C(5)–N(1)	120.3 (3)
N(2)–Cu–O(2)′	98.81 (8)	C(4)–C(5)–C(6)	122.3 (2)
N(2)–Cu–O(3)	91.57 (8)	N(1)–C(5)–C(6)	117.4 (2)
O(1)′–Cu–O(2)′	82.17 (8)	C(5)–C(6)–C(7)	111.5 (3)
O(1)′–Cu–O(3)	89.73 (9)	C(6)–C(7)–N(2)	113.2 (2)
O(2)–Cu–O(3)	167.05 (7)	C(7)–N(2)–C(8)	108.7 (2)
O(2)–Cl–O(3)	108.6 (1)	C(7)–N(2)–C(9)	107.7 (2)
O(2)–Cl–O(4)	110.2 (2)	C(8)–N(2)–C(9)	108.2 (3)
O(2)–Cl–O(5)	109.2 (1)	O(1)–OH–O(5)	165 (3)

of the pyridine ring is inclined to the plane of the central dimeric unit at an angle of 30°, this angle being somewhat less than the angle of 44° found in the EAEP complex. Several of the atoms of the DMAEP moiety (C(5), C(6), C(7), N(1), N(2)) form a six-membered ring with Cu. The geometry of this ring approximates the classic "boat" form with N(1), C(5), N(2), and C(7) forming a "base plane" and Cu and C(6) the two out-of-plane atoms. The atoms N(1), C(5), N(2), and C(7) are not completely planar, the average deviation from the best least-squares plane being 0.13 Å, but the boat concept serves as a useful approximation. The other two atoms, Cu and C(6), are displaced 0.32 and 0.71 Å from the least-squares plane, respectively. This formation of a six-membered "boat" is also found in the EAEP complex with similar C(6) to "base plane" distances, the average being 0.67 Å, but longer Cu to "base plane" distances, the average being 0.57 Å. The effect of this reduced Cu to base plane distance in the DMAEP moiety is a general flattening of the "boat" with respect to the equatorial plane of the copper octahedron as compared to the similar circumstance in EAEP. This flattening is accompanied by a lessening of the tilt of the base plane of the boat with respect to the equatorial plane of the copper octahedron as demonstrated by the angles of 30 and 15° subtended by the perpendicular to these planes in the EAEP and DMAEP complexes, respectively. This further results in the movement of C(6) away from the sixth coordination site of the copper atom and a reduction in possible steric hindrance at that axial site.

The perchlorate anion possesses a coordination geometry which to our knowledge has not been structurally documented previously. Structural evidence for a unidentate perchlorate was first presented by Cotton and Weaver in 1965[37] after its presence in various complexes had been postulated from infrared data. Since that time several other examples of that type of perchlorate coordination have been presented.[1,38-41] During this same period a number of other structures have been proposed in which the perchlorate group acts as a bidentate chelate.[42-44] The proposals are largely based on examination of infrared data and its correlation with theoretical symmetry considerations. Recently, crystallographic evidence has been presented for an *intermolecular* bidentate perchlorate of a polymeric nature in Cu(bipy)$_2$(ClO$_4$)$_2$,[45] but the corresponding infrared data are inconclusive. Here we present crystallographic and infrared evidence for an *intramolecular* bidentate perchlorate group which functions as a bridging ligand between two metal atoms (Figure 1). Although this mode of coordination has been observed for the sulfate ion,[46,47] to our knowledge it is unique in perchlorate chemistry.

The perchlorate group is positioned directly above or below the central dimeric unit with Cu-O(2) and Cu-O(3) bond lengths of 2.782 (3) and 2.716 (3) Å. The copper-oxygen bonds deviate several degrees from the perpendicular to the dimeric plane as demonstrated by the O(1)-Cu-O(2)′, O(1)-Cu-O(3), O(1)′-Cu-O(2)′, and O(1)′-Cu-O(3) bond angles of 82.8 (1), 86.0 (1), 82.2 (1), and 89.7 (1)°. This is to be expected as the perchlorate bite (the O(2)-O(3) separation) of 2.328 (3) Å is much less than the copper–copper separation of 2.938 (1) Å. Further contact with the dimeric cation is provided by a hydrogen bond involving a third perchlorate oxygen atom O(5) and the bridging hydroxyl hydrogen atom, as shown in Figure 2. The O(1)-O(5) contact of 3.042 (4) Å is similar to the sum of the van der Waals radii of the atoms. More significantly, both the O(1)-H and O(5)· · ·H separations of 0.70 (3) and 2.36 (3) Å are considerably less than the sum of the van der Waals radii of oxygen and hydrogen; this has been proposed as the best criterion for the presence of hydrogen bonding.[48] The O(1)-H-O(5) bond angle of 165 (2)° is within the range expected for O-H-O hydrogen bonds. The O(1)-H bond is directed out of the plane of the dimeric unit so as to point toward the perchlorate group, with Cu-O(1)-OH and Cu′-O(1)-OH bond angles of 107 (3) and 107 (3)°, respectively.

This perchlorate coordination is a direct extension of that found in the EAEP complex. As shown in Figure 3, each perchlorate in [Cu(EAEP)OH]$_2$(ClO$_4$)$_2$ is unidentate and occupies the fifth coordination site of a single copper. The sixth coordination sites of these copper atoms are not occupied, but atoms O(8) and O(3) of the perchlorate groups appear to be approaching these positions with Cu(1)-O(3) and Cu(2)-O(8) distances of 3.27 (1) and 3.34 (1) Å. Further approach of these oxygens would be severely sterically hindered by C(6) of the EAEP ligand and its associated hydrogens, as demonstrated by the calculated hydrogen to oxygen distance, for either O(8) or O(3) in a bonding position, of 2.37 Å as compared to the present average distance of 2.64 (3) Å in the EAEP complex. The ability of the perchlorate group of α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$ to occupy these sixth coordination sites is dependent on the steric opening of the sites by small changes in the boat portion of the substituted aminopyridine ligand (*vide supra*). As a result of these shifts the perchlorate oxygen, when in bonding position, is not as sterically hindered by the hydrogens of C(6), with a hydrogen to oxygen distance of 2.78 (3) Å.

The internal perchlorate geometry is totally consistent

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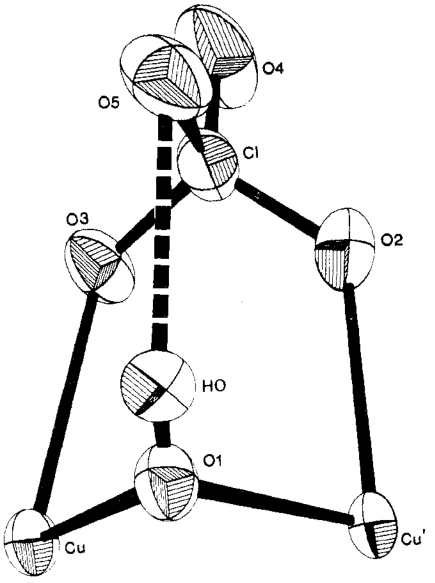

Figure 2. View of the perchlorate coordination in α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$.

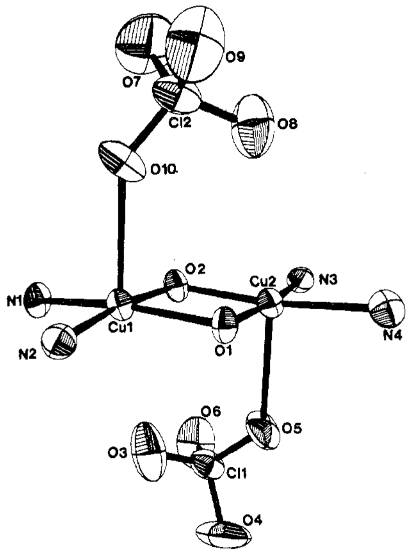

Figure 3. View of the coordination geometry around the copper atoms in [Cu(EAEP)OH]$_2$(ClO$_4$)$_2$(from data in ref 1).

with this external environment. The three bonded oxygen atoms, O(2), O(3), and O(5), have greater Cl-O bond distances, 1.437 (2), 1.429 (2), and 1.428 (3) Å, than the nonbonded oxygen, O(4), which has a Cl-O separation of 1.409 (3) Å. The O-Cl-O angles are roughly tetrahedral but with greater deviations from the mean than would be expected for an uncoordinated perchlorate.

Further evidence of the novel perchlorate coordination is found in an examination of the infrared spectra of the complex. The infrared spectrum of the Nujol mull of the complex (recorded on a Digilab FTS-14D Fourier transform spectrometer) shows a broad peak of medium intensity at 3550 cm^{-1}. This broad peak is indicative of a weak hydrogen bond, since free hydroxides give rise to sharp, intense peaks near 3620 cm^{-1}.[49] Nakamoto, *et al.*,[50] have shown that the frequency of the O-H stretch is markedly dependent on the O(1)· · ·O(5) distance, and by extrapolation from their data we deduce that a frequency of 3550 cm^{-1} corresponds to an O· · ·O separation (for a linear hydrogen bond) of 2.90-3.00 Å; this is in reasonable agreement with our observed O(1)· · ·O(5) separation of 3.042 (4) Å.

Hathaway and Underhill[51] have shown that examination of the region 1000-1300 cm^{-1} is instrumental in determining the symmetry and, hence, the nature of the bonding of perchlorate anions. For bidentate perchlorate, symmetry C_{2v}, this region should have three bands (ν_1, ν_6, ν_8) as compared to the single band expected for ionic perchlorate (ν_3) of T_d symmetry. Several groups[42,44] have observed this additional splitting and this has been the major evidence for the presence of bidentate perchlorates until this time. The solid-state spectra of α-[Cu(DMAEP)OH]$_2$[ClO$_4$]$_2$ tend to confirm the validity of this postulate. Very intense peaks are found at 1145, 1128, and 1072 cm^{-1} (ν_8, ν_6, and ν_1, respectively) which fall quite near the ranges of 1130-1208, 1093-1125, and 1025-1058 cm^{-1} previously assigned. The splitting pattern appears to be less pronounced than that previously observed, but it should be noted that the perchlorate-copper bond length is indicative of a fairly weak interaction and, hence, as evidenced by the small deviations in chlorine to oxygen bond lengths, the perturbation of the perchlorate from tetrahedral geometry is correspondingly small.

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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, 20× 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-74-147.

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