unexceptional. The lengths of the two independent P-S bonds within each ligand vary inversely with the lengths of the adjoining Bi-S bonds, as is plausible to maintain bond order conservation around sulfur. The two sets of distances average 1.999 and 1.954 Å, differing by about five standard deviations. The six P-O bonds are equivalent within two standard deviations of the average 1.572 Å. In agreement with those in other structures containing this ligand, the S-P-S angles (averaging 112°) are larger than the O-P-O angles (averaging 100°).

Conclusion

We have shown that $Bi(dtp)_3$ adopts a configuration consistent with the VSEPR theory, a valence-bonding scheme which accounts for observed trends in molecular architecture of nontransition elements. Owing to *a priori* equivalency of the sulfur atoms, discrete molecules of the type $:M(S_2X)_3$, where M is trivalent As, Sb, or Bi and S_2X represents thio bidentate ligands, have emerged as an excellent source of complexes for studying seven-coordination in which a nonbonding electron pair occupies a coordination site. There exists a wide range of as yet unexplored ligands suitable for further study of $:ML_6$ coordination, including L_2COR, L_2CNR_2, $L_2P(OR)_2$, $L_2P(R)(OR)$, and L_2PR_2, where L = S or Se and R = H, CH_3, F, Cl, Br, or I, just to name a few. Krishnan and Zingaro, for example, have reported the preparation of $As[(C_2H_5O)_2PSe_2]_3$, $Sb[(C_2H_5O)_2PSe_2]_3$, and $Bi[(C_2H_5O)_2PSe_2]_3$.[43] A definitive resolution of $:ML_6$ coordination might sharpen our overall understanding of lone pair-bond pair interactions in the more crowded seven-coordination spheres.

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Registry No. $Bi[(i\text{-}C_3H_7O)_2PS_2]_3$, 42294-79-1; $(i\text{-}C_3H_7O)_2PSSH \cdot {}^1/_3Bi$, 42282-62-2.

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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-135.

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Molecular Structure of Diperchloratobis[2-(2-aminoethyl)pyridine]copper(II)

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The crystal structure of diperchloratobis[2-(2-aminoethyl)pyridine]copper(II), $Cu(AEP)_2(ClO_4)_2$, has been determined from three-dimensional X-ray data obtained from a four-circle automatic diffractometer using Mo Kα radiation. The complex crystallizes in the space group $P\bar{1}$ of the triclinic system with cell constants $a = 8.275\ (3)$, $b = 9.772\ (4)$, $c = 7.894\ (4)$ Å; $\alpha = 126.88\ (2)$, $\beta = 82.20\ (3)$, $\gamma = 111.22\ (3)^\circ$. The observed and calculated densities for one molecule per unit cell are 1.75 (3) and 1.779 g cm^{-3}, and the structure was refined by full-matrix least-squares methods to a final value of the R factor of 0.030 for 2275 independent reflections whose intensities were greater than 3 times their estimated standard deviations. The molecule is a six-coordinate monomer with tetragonally distorted octahedral geometry at the copper atom; four nitrogen atoms from two AEP ligands form the equatorial plane and oxygen atoms from two perchlorate groups occupy the axial sites. The perchlorate groups are weakly coordinated with a Cu-O bond length of 2.883 (2) Å, as compared to the Cu-N bond lengths of 2.005 (2) and 2.024 (2) Å for the AEP coordination.

Introduction

The preparation of complexes of the formulation $Cu(AEP)_2X_2$ where AEP is 2-(2-aminoethyl)pyridine and X is a halogen was first reported by Uhlig and Maaser,[1] who assumed their conformation to be six-coordinate and monomeric. Recently, the structural determinations of $Cu(AEP)_2Br_2$[2] and $Cu(AEP)_2I_2$[3] have shown this assumption to be incorrect as these complexes have been demonstrated to be five- and four-coordinate, respectively. This change in coordination with diverse anions is not unique as Hathaway and coworkers[4] and McWhinnie and coworkers[5,6] have postulated similar trends in other copper complexes. Hathaway, *et al.*,[4] have shown that from electronic and epr spectra several diverse conformations would be anticipated for various $Cu(bipy)_2X_2$ and $Cu(bipy)_2XY$ complexes (where bipy is 2,2′-bipyridine). Similarly, McWhinnie, *et al.*, have concluded that complexes of the type $Cu(bipyam)_2X_2$ (where bipyam is 2,2′-bipyridylamine) may assume at least three different geometries depending upon the choice of anion.[5,6] Confirmation of these trends by three-dimensional crystal structure determination has not yet been completed.

As an extention of the recently compiled data on $Cu(AEP)_2I_2$ and $Cu(AEP)_2Br_2$, characterization of other AEP complexes with the remaining halogens or pseudohalogens would be valuable. Also, recent work with the pseudohalogen perchlo-

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rate[7–11] has shown this anion to be very adaptable to diverse bonding situations and to possess a relatively small bonding volume compared to iodide or bromide. Hence, to gain a better understanding of the effect of anion size on the copper coordination sphere and of the coordination preferences of the perchlorate anion we report the three-dimensional X-ray structure of diperchloratobis[2-(2-aminoethyl)pyridine]-copper(II).

Data Collection and Reduction

Violet crystals of $Cu(AEP)_2(ClO_4)_2$ were prepared by mixing a 2:1 molar ratio of AEP and $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol.[1] After several days crystals suitable for X-ray diffraction precipitated from the solution, and their composition was confirmed by elemental analysis. Precession and Weissenberg photographs indicated that the crystals belong to the triclinic system, the space group being either $C_1{}^1$-P_1 or $C_i{}^1$-$P\bar{1}$. The cell constants obtained by the least-squares procedure of Busing and Levy[12] on 12 independent reflections are a = 8.275 (3), b = 9.772 (4), c = 7.894 (4) Å; α = 126.88 (2), β = 82.20 (3), and γ = 111.22 (3)°, the observations being made at 23° and with Mo Kα_1 radiation with an assumed wavelength of 0.7093 Å. The density of 1.779 g cm^{-3} calculated for one molecule per unit cell agrees well with the experimental density of 1.75 (3) g cm^{-3} determined by flotation in dichloromethane–iodomethane solution.

Diffraction data were collected on a platelike crystal with faces (101), ($\bar{1}0\bar{1}$), ($\bar{1}10$), ($10\bar{1}$), ($01\bar{1}$), ($\bar{2}\bar{4}3$), and ($2\bar{4}3$), with the separation between the parallel faces (101) and ($\bar{1}0\bar{1}$) being 0.014 cm. Additional distances between faces and intersections of faces were as follows: ($01\bar{1}$) to [($\bar{2}\bar{4}3$), (101)], 0.018 cm; ($01\bar{1}$) to [($\bar{2}\bar{4}3$), ($10\bar{1}$)], 0.013 cm; ($\bar{1}10$) to [($10\bar{1}$), ($01\bar{1}$)], 0.069 cm; ($\bar{1}10$) to [($\bar{1}0\bar{1}$), ($2\bar{4}3$)], 0.076 cm; ($01\bar{1}$) to [($10\bar{1}$), ($2\bar{4}3$), ($\bar{1}0\bar{1}$)], 0.008 cm; ($01\bar{1}$) to [($10\bar{1}$), ($2\bar{4}3$), (101)], 0.011 cm. The crystal was mounted approximately perpendicular to the ($\bar{1}10$) planes, and data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator and using Mo Kα radiation in the manner previously described.[13] The scan rate was 1°/min with a takeoff angle of 1.0°, a total scan range of 0.85° below and above the calculated positions for Kα_1 and Kα_2, respectively, and a total stationary background count of 40 sec.

A single form of the data ($+h,\pm k,\pm l$) was collected out to a value of 2θ(Mo Kα) of 58°, above which there were few reflections with intensities greater than background. A total of 2752 reflections was recorded, including several strong Friedel pairs in the event the space group proved to be noncentrosymmetric. Data processing was carried out as described by Corfield, Doedens, and Ibers,[14] the value of p in the expression[15]

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

being chosen as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects, using the expression[16]

$$\frac{1}{Lp} = \frac{2 \sin 2\theta}{\cos^2 2\theta_m + \cos^2 2\theta}$$

where θ_m is the monochromator angle, and for absorption. The absorption coefficient for the sample with Mo radiation is 15.35 cm^{-1}, and the transmission coefficients for the data crystal were found to range from 0.80 to 0.86. Of the 2752 reflections, 2275 were independent reflections having intensities greater than 3 times their estimated standard deviations. Three standard reflections were examined after every 100 reflections and showed a steady decline in intensity throughout the run; the intensity of a typical standard at the end of the data collection was approximately 93% of its original value.

Table I. Positional Parameters for $Cu(AEP)_2(ClO_4)_2$

Atom	x	y	z
Cu	0.00000	0.00000	0.00000
Cl	−0.32230 (5)	0.29522 (5)	0.18496 (6)
O(1)	−0.2643 (3)	0.1424 (2)	0.0652 (3)
O(2)	−0.1742 (2)	0.4614 (2)	0.3045 (3)
O(3)	−0.4091 (3)	0.2960 (3)	0.0410 (3)
O(4)	−0.4394 (2)	0.2811 (3)	0.3281 (3)
N(1)	−0.1081 (2)	−0.0034 (2)	0.2439 (2)
C(1)	−0.1368 (3)	0.1445 (2)	0.4171 (3)
C(2)	−0.2308 (3)	0.1403 (3)	0.5721 (3)
C(3)	−0.3022 (3)	−0.0222 (3)	0.5480 (3)
C(4)	−0.2728 (3)	−0.1748 (3)	0.3712 (3)
C(5)	−0.1747 (2)	−0.1620 (2)	0.2212 (3)
C(6)	−0.1369 (3)	−0.3211 (3)	0.0272 (3)
C(7)	−0.2249 (3)	−0.3864 (2)	−0.1778 (3)
N(2)	−0.1979 (2)	−0.2347 (2)	−0.1915 (3)
H(1)	−0.087 (3)	0.263 (4)	0.430 (4)
H(2)	0.246 (5)	−0.246 (5)	0.315 (7)
H(3)	0.367 (4)	0.028 (4)	0.354 (5)
H(4)	−0.325 (4)	−0.291 (5)	0.347 (5)
H(61)	−0.010 (4)	−0.289 (4)	0.021 (4)
H(62)	−0.164 (4)	−0.414 (5)	0.041 (6)
H(71)	0.346 (5)	0.456 (5)	0.195 (6)
H(72)	0.187 (4)	0.476 (5)	0.295 (6)
HN(1)	0.288 (5)	0.202 (4)	0.152 (5)
HN(2)	0.194 (3)	0.278 (4)	0.322 (5)

Solution and Refinement of Structure

Examination of a three-dimensional Patterson function[17] revealed eleven reliable copper–light atom vectors. Two cycles of least-squares refinement were run on these eleven positions with the copper atom fixed at the origin and all atoms were assigned variable isotropic thermal parameters. All least-squares refinements in the 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,[18] those for C, O, and N were from Ibers,[19] and that for H was from Stewart, Davidson, and Simpson.[20] The effects of anomalous dispersion of copper and chlorine were included in the final calculation of F_c,[21] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[22] After the two cycles of least-squares refinement using those nonabsorption-corrected data with intensities greater than 3 times their estimated standard deviations and assuming the space group $P\bar{1}$, 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 0.213 and 0.294, respectively. A difference Fourier map revealed the locations of the remaining nonhydrogen atoms, and two further cycles of least-squares refinement on these positions resulted in values of R_1 and R_2 of 0.094 and 0.131.

At this stage of refinement the data were corrected for the approximately linear decay in standards (*vide supra*), and the absorption correction was applied. After two cycles of least-squares refinement, during which the atom thermal parameters were allowed to vary anisotropically, the values of R_1 and R_2 were 0.044 and 0.071. A difference Fourier map then revealed all hydrogen atom locations, and after two further cycles of least-squares refinement, with anisotropic refinement of all nonhydrogen atoms and isotropic refinement

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Table II. Thermal Parameters for $Cu(AEP)_2(ClO_4)_2$

Atom	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00997 (6)	0.00921 (6)	0.01315 (8)	0.00155 (4)	0.00147 (4)	0.00702 (5)
Cl	0.01169 (7)	0.01156 (8)	0.01732 (11)	0.00334 (6)	0.00153 (6)	0.00882 (7)
O(1)	0.0218 (3)	0.0139 (3)	0.0276 (5)	0.0083 (3)	0.0002 (3)	0.0095 (3)
O(2)	0.0155 (3)	0.0135 (3)	0.0288 (5)	0.0000 (2)	0.0013 (3)	0.0076 (3)
O(3)	0.0246 (4)	0.0278 (4)	0.0270 (5)	0.0140 (4)	0.0034 (3)	0.0191 (4)
O(4)	0.0168 (3)	0.0268 (4)	0.0272 (5)	0.0043 (3)	0.0061 (3)	0.0192 (4)
N(1)	0.0108 (2)	0.0094 (2)	0.0150 (3)	0.0029 (2)	0.0019 (2)	0.0076 (2)
C(1)	0.0149 (3)	0.0089 (3)	0.0153 (4)	0.0037 (2)	0.0018 (3)	0.0068 (3)
C(2)	0.0184 (4)	0.0123 (3)	0.0145 (4)	0.0071 (3)	0.0049 (3)	0.0070 (3)
C(3)	0.0164 (3)	0.0164 (4)	0.0175 (4)	0.0062 (3)	0.0061 (3)	0.0119 (4)
C(4)	0.0156 (3)	0.0120 (3)	0.0186 (4)	0.0041 (3)	0.0039 (3)	0.0111 (3)
C(5)	0.0114 (3)	0.0093 (2)	0.0149 (4)	0.0040 (2)	0.0021 (2)	0.0077 (3)
C(6)	0.0176 (4)	0.0109 (3)	0.0192 (5)	0.0079 (3)	0.0054 (3)	0.0092 (3)
C(7)	0.0164 (4)	0.0082 (3)	0.0178 (4)	0.0030 (3)	0.0019 (3)	0.0058 (3)
N(2)	0.0109 (2)	0.0112 (2)	0.0169 (4)	0.0018 (2)	0.0001 (2)	0.0081 (3)
H(1)	2.9 (5)					
H(2)	5.1 (7)					
H(3)	3.9 (6)					
H(4)	4.3 (6)					
H(61)	3.0 (5)					
H(62)	4.7 (7)					
H(71)	4.3 (6)					
H(72)	4.3 (7)					
HN(1)	4.0 (6)					
HN(2)	2.9 (5)					

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

of hydrogen atoms and with all positional parameters except Cu being allowed to vary, the values of R_1 and R_2 were 0.031 and 0.045. Examination of the values of $|F_o|$ and $|F_c|$ for the strong low-order reflections suggested that the data were subject to secondary extinction, and a correction of the type described by Zachariasen[23,24] was applied. The value of R_2 showed some dependence on sin θ, which suggested that our weighting scheme was inappropriate. The weights were modified by multiplying the weight, w, for data with $2\theta < 30°$ by 0.25. Two final cycles of least-squares refinement gave values of 0.030 and 0.039 for R_1 and R_2; the final value of the extinction coefficient was $1.0\ (17) \times 10^{-8}$. In the last cycle of least-squares refinement, the greatest shift in any parameter was 0.3 times its estimated standard deviation and the refinement was considered to have converged. The final values of R_1 and R_2 were considered evidence that our choice of the space group $P\overline{1}$ was correct. A final difference Fourier revealed no additional strong peaks, with the largest peak being less than 0.4 e Å^{-3}. 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 compilation of observed and calculated structure amplitudes is available.[25] A structure factor calculation using the 385 data whose intensities were less than 3 times their estimated standard deviations demonstrated that none of these "unobserved" reflections had $|F_o - F_c| > 3.9\sigma(F_o)$.

Table III. Internuclear Distances in $Cu(AEP)_2(ClO_4)_2$

Atoms	Dist, Å	Atoms	Dist, Å	Atoms	Dist, Å
Cu-N(1)	2.024 (2)	C(1)-C(2)	1.373 (3)	C(4)-H(4)	0.96 (4)
Cu-N(2)	2.005 (2)	C(2)-C(3)	1.377 (3)	C(6)-H(61)	0.98 (3)
Cu-O(1)	2.833 (2)	C(3)-C(4)	1.379 (3)	C(6)-H(62)	0.92 (4)
Cl-O(1)	1.433 (2)	C(4)-C(5)	1.385 (3)	C(7)-H(71)	0.96 (4)
Cl-O(2)	1.436 (2)	C(5)-C(6)	1.492 (3)	C(7)-H(72)	0.93 (4)
Cl-O(3)	1.430 (2)	C(6)-C(7)	1.517 (3)	N(2)-HN(1)	0.86 (4)
Cl-O(4)	1.424 (2)	C(7)-N(2)	1.484 (3)	N(2)-HN(2)	0.85 (3)
N(1)-C(1)	1.343 (2)	C(1)-H(1)	1.02 (3)	C(2)-H(2)	0.91 (4)
N(1)-C(5)	1.347 (2)	C(3)-H(3)	0.90 (3)	O(1)′-H(61)	2.46 (3)

Table IV. Internuclear Angles in $Cu(AEP)_2(ClO_4)_2$

Atoms	Angle, deg	Atoms	Angle, deg
N(1)-Cu-N(2)	86.54 (7)	C(2)-C(3)-C(4)	118.9 (2)
N(1)′-Cu-N(2)	93.46 (7)	C(3)-C(3)-H(3)	120.3 (20)
N(1)-Cu-O(1)	79.02 (7)	C(4)-C(3)-H(3)	120.8 (20)
N(2)-Cu-O(1)	80.60 (7)	C(3)-C(4)-C(5)	119.6 (2)
N(1)′-Cu-O(1)	100.98 (7)	C(3)-C(4)-H(4)	120.5 (20)
N(2)′-Cu-O(1)	99.40 (7)	C(5)-C(4)-H(4)	119.8 (20)
O(1)-Cl-O(2)	109.2 (1)	C(4)-C(5)-C(6)	122.4 (2)
O(1)-Cl-O(3)	109.0 (1)	C(4)-C(5)-N(1)	121.3 (2)
O(1)-Cl-O(4)	109.9 (1)	N(1)-C(5)-C(6)	116.3 (2)
O(2)-Cl-O(3)	109.9 (1)	C(5)-C(6)-C(7)	113.2 (2)
O(2)-Cl-O(4)	109.2 (1)	C(5)-C(6)-H(61)	109.8 (16)
O(3)-Cl-O(4)	109.6 (1)	C(5)-C(6)-H(62)	110.0 (23)
Cu-O(1)-Cl	148.8 (1)	C(7)-C(6)-H(61)	109.4 (16)
Cu-N(1)-C(1)	120.8 (1)	C(7)-C(6)-H(62)	112.2 (23)
Cu-N(1)-C(5)	119.9 (1)	C(6)-C(7)-N(2)	112.7 (2)
C(1)-N(1)-C(5)	118.7 (1)	C(6)-C(7)-H(71)	110.0 (22)
N(1)-C(1)-C(2)	122.5 (2)	C(6)-C(7)-H(72)	110.1 (21)
N(1)-C(1)-H(1)	117.5 (15)	N(2)-C(7)-H(71)	112.0 (21)
C(2)-C(1)-H(1)	120.0 (15)	N(2)-C(7)-H(72)	110.9 (21)
C(1)-C(2)-C(3)	119.1 (2)	C(7)-N(2)-Cu	117.3 (1)
C(1)-C(2)-H(2)	117.5 (24)	C(7)-N(2)-HN(1)	108.9 (22)
C(3)-C(2)-H(2)	123.3 (24)	C(7)-N(2)-HN(2)	106.6 (18)

Description of the Structure

The structure consists of monomeric, six-coordinate $Cu(AEP)_2(ClO_4)_2$ units as postulated by Uhlig and Maaser[1] for all $Cu(AEP)_2X_2$ complexes. The geometry of the complex may be best described as a tetragonally distorted octahedron and is shown in Figure 1. The bond distances and angles and their associated estimated standard deviations are given in Tables III and IV. The equatorial plane of the complex is formed by nitrogen atoms, N(1), N(2), N(1)′, and N(2)′ (where primed atoms denote centrosymmetric equivalence), from two AEP groups, and the axial coordination sites are occupied by perchlorate oxygen atoms O(1) and O(1)′. The equatorial plane forms a nearly square-planar array with Cu-N(1) and Cu-N(1)′ bond distances of 2.024 (2) and 2.005 (2) Å and N(1)-Cu-N(2) and N(1)′-Cu-N(2) bond angles of 86.54 (7) and 93.46 (7)°, the unit being constrained to planarity by the inversion center at Cu. The axial Cu-O(1) bond distance of 2.833 (2) Å is much greater than those found in the equatorial plane, this elongation being a common feature of many copper(II) complexes.[26] The Cu-O(1) separation observed here, however, is considerably greater than those found in a wide variety of copper(II) complexes with unidentate perchlorate groups, which

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Table V. Comparison of the Chelating Geometries of Aminoethylpyridine Ligands in Several Copper(II) Complexes

Measurement	$Cu(AEP)_2(ClO_4)_2$	$Cu(AEP)_2I_2$	$[Cu(EAEP)OH]_2[ClO_4]_2$ (av value)	α-$[Cu(DMAEP)OH]_2[ClO_4]_2$
Cu-boat plane, Å	0.97	0.91	0.57	0.32
C(6)-boat plane, Å	0.62	0.64	0.67	0.71
N(1)-N(2), Å	2.76		2.95	3.00
N(1)-Cu-N(2), deg	86.54	86.8	94.61	95.02
H(61)-O(1), Å	2.46		2.64	2.77

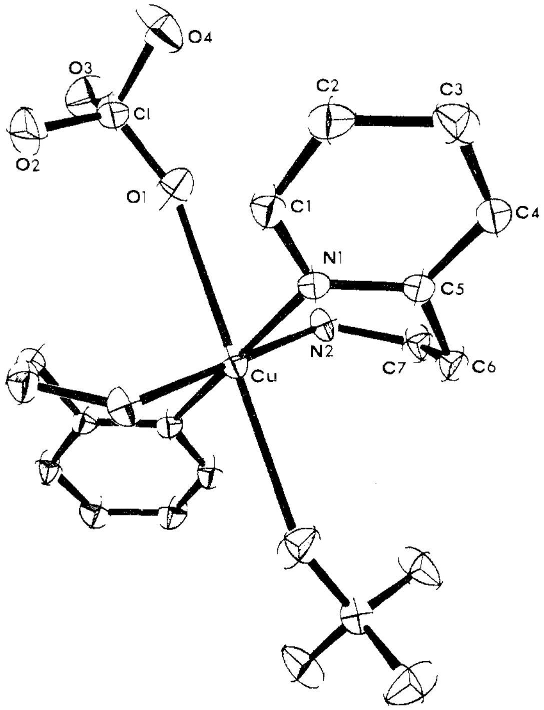

Figure 1. View of the $Cu(AEP)_2(ClO_4)_2$ molecule. Thermal ellipsoids are drawn at the 40% probability level and hydrogen atoms are omitted for clarity.

fall in the range 2.52-2.68 Å;[8-10,27-31] in nickel(II) and cobalt(II) complexes the metal-oxygen bonds are even shorter with a range of 2.10-2.34 Å.[32-35] Hence, the very long Cu-O(1) separation observed here suggests that the interaction between the perchlorate group and the metal might be best described as what Hathaway and coworkers[36] have called "semicoordination." The Cu-O(1) vector also deviates slightly from the perpendicular to the equatorial plane with N(1)-Cu-O(1), N(2)-Cu-O(1), N(1)′-Cu-O(1), and N(2)′-Cu-O(1) bond angles of 79.02 (7), 80.60 (7), 100.98 (7), and 99.40 (7)°, respectively, causing an additional slight distortion from octahedral geometry.

The geometry of the perchlorate group is essentially tetrahedral with Cl-O(1), Cl-O(2), Cl-O(3), and Cl-O(4) bond distances of 1.433 (2), 1.436 (2), 1.430 (2), and 1.424 (2) Å and O-Cl-O bond angles ranging from 109.0 (1) to 109.9 (1)°.

As Hathaway and coworkers[36] have noted, semicoordination has little influence on the geometry of the ligand, and the observed Cl-O bond lengths of 1.424 (2)-1.436 (2) Å and O-Cl-O angles of 109.2 (1)-109.9 (1)° are consistent with this concept. The infrared spectrum of a solid sample (Nujol mull) obtained on a Digilab FTS-14 Fourier spectrometer indicates only slight splitting of the Cl-O stretching band (ν_3 in T_d symmetry) at 1085 cm^{-1}, showing two peaks at 1070 and 1100 cm^{-1} (ν_1 and ν_4 in C_{3v} symmetry). Hence, the spectrum also indicates that the perchlorate is weakly bound to the metal.

Additional evidence for the extremely loose bonding of the perchlorate is the Cu-O(1)-Cl bond angle of 148.8 (1)°, which is considerably greater than the expected value of approximately 120° but still within the range found in similarly coordinated perchlorate complexes.[8-11,27-31]

The AEP ligand geometry, which is compared in Table V with that in several related complexes, is similar to other substituted aminoethylpyridine moieties with the chelating portion of the group retaining the classic six-membered-ring boat conformation. The basal portion of the ring, defined by N(1), C(5), C(7), and N(2), approximates planarity with an average deviation from the best least-squares plane of 0.076 Å. The remaining two atoms of the ring, Cu and C(6), are displaced from the least-squares plane by 0.97 and 0.62 Å, respectively. These displacement distances are very similar to the values of 0.91 and 0.640 Å found in[3] $Cu(AEP)_2I_2$ but considerably different from the average values[27] of 0.57 and 0.67 Å found in $[Cu(EAEP)OH]_2[ClO_4]_2$ and those of 0.32 and 0.71 Å found in α-$[Cu(DMAEP)OH]_2[ClO_4]_2$.[11] Similarly, the N(1)-Cu-N(2) bond angle of 86.54 (7)° is very near that of 86.8 (1)° found in $Cu(AEP)_2I_2$ but much smaller than the values found in $[Cu(EAEP)OH]_2[ClO_4]_2$ and α-$[Cu(DMAEP)OH]_2[ClO_4]_2$ which range from 92.7 to 96.3°. It appears that the structural form of AEP found in $Cu(AEP)_2(ClO_4)_2$ and $Cu(AEP)_2I_2$ is the preferred low-energy configuration of the ligand when additional steric constraints are not present. In both of these cases the axial copper coordination site is either vacant or occupied by a small ligand which is weakly bound and directed away from the protruding C(6) atom; the Cu-O(1) vector is displaced from the perpendicular by approximately 10° away from the C(6) atom in $Cu(AEP)_2(ClO_4)_2$ (*vide supra*). In $[Cu(EAEP)OH]_2[ClO_4]_2$ and α-$[Cu(DMAEP)OH]_2[ClO_4]_2$ the ligand assumes a flattened form allowing a closer approach by the axial ligand to the copper atom. It appears that in these cases the substituted aminoethylpyridine ligand assumes a higher energy conformation which allows the molecule, as a whole, to gain a more stable conformation by closer coordination of axial ligands. In all cases involving perchlorate coordination the final result of the aminoethylpyridine deformation is that C(6) maintains a "steric free" relationship with O(1) of the perchlorate group as demonstrated by

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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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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.

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

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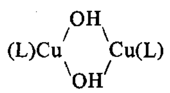
The crystal structure of α-di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridine]dicopper(II) perchlorate, α-[Cu(DMAEP)-OH]$_2$(ClO$_4$)$_2$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the triclinic space group $P\bar{1}$ with one dimeric molecule in a cell of dimensions a = 9.164 (5), b = 10.049 (5), and c = 8.953 (5) Å; and α = 82.30 (2), β = 56.72 (2), and γ = 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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