may be stronger than in the ruthenium complex. Quantitative comparison between these distances and those reported for $[Pt(SnCl_3)_5]^{3-}$ is precluded by the unreliable nature of the bond lengths in the latter complex.

The geometry at germanium is considerably distorted from tetrahedral, with Pt-Ge-Cl angles in the range 116.0 (2)-124.0 (2)° (av 119.5°) while the Cl-Ge-Cl angles are in the range 95.0 (3)-102.0 (3)° (av 97.8°). This trend was also observed[21] in $Ru(CO)_4(GeCl_3)_2$. The Ge-Cl bond lengths are from 2.168 (7) to 2.235 (7) Å, with an average value of 2.194 Å, which are appreciably longer than the average (uncorrected for thermal motion) of 2.153 Å in *trans*-$Ru(CO)_4(GeCl_3)_2$ but are consistent with the reported sum of the covalent radii[22] of Ge and Cl. The coordination at the nitrogen in each of the cations is roughly tetrahedral, with C-N-C angles in the range 101 (3)-116 (3)° (av 109°). The C-N bond lengths are from 1.43 (3) to 1.58 (3) Å (av 1.53 Å).

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Registry No. $[N(CH_3)_4]_3Pt(GeCl_3)_5$, 41812-93-5.

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-73-2932.

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

Crystal and Molecular Structure of Dinitrato[2-(2-dimethylaminoethyl)pyridine]copper(II)

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The crystal and molecular structure of dinitrato[2-(2-dimethylaminoethyl)pyridine]copper(II), Cu(DMAEP)(NO$_3$)$_2$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell and cell constants of $a = 6.688$ (6), $b = 14.310$ (11), $c = 14.285$ (9) Å, and $\beta = 78.46$ (3)°. The observed and calculated densities are 1.64 (3) and 1.675 g cm^{-3} and the structure was refined by full-matrix least-squares procedures to a final value of R of 0.037 for 1576 independent reflections having $F^2 > 3\sigma(F^2)$. The copper(II) ions are unsymmetrically coordinated to two bidentate nitrate groups and to the nitrogen atoms of the DMAEP ligand. The geometry at the copper(II) ion is distorted octahedral with elongated axial positions occupied by oxygen atoms from both nitrate groups with Cu-O bond distances of 2.468 (4) and 2.479 (4) Å. The equatorial plane bond distances are considerably shorter, with Cu-N bond lengths of 1.966 (4) and 2.014 (4) Å and Cu-O bond lengths of 1.990 (3) and 2.019 (4) Å.

Introduction

Complexes of the type $CuLX_2$ where L is a substituted 2-(2-aminoethyl)pyridine and X a halogen were first reported by Uhlig and coworkers,[1,2] who suggested that the complexes are dimeric with five-coordinate geometry at the copper atom. Recent reports of the structures of $Cu(AEP)Br_2$[3] and $Cu(AEP)Cl_2$,[4] where AEP is 2-(2-aminoethyl)pyridine, have shown these complexes to be polymeric with six-coordinate geometry at the copper atom and both polymeric chain and pairwise copper-halogen-copper linkages.

The ability of the pseudo-halogen, nitrate, to act as a ligand in transition metal complexes has been well documented during the past 15 years.[5] Like the halogens, the nitrate group has been shown to act as a monodentate ligand or as a bifunctional bridge in both dimeric and polymeric cases. In addition, nitrate frequently serves as either a symmetrically or unsymmetrically bidentate ligand occupying two coordination sites on the same metal center. In view of the known polymeric nature of $Cu(AEP)Br_2$ and $Cu(AEP)Cl_2$ and the coordinating versatility of the nitrate group, a number of molecular geometries can be postulated for a substituted 2-(2-aminoethyl)pyridinecopper(II) nitrate complex. In order to further our investigations into the geometries of copper(II) chelates and the coordination of the nitrate group we have undertaken the three-dimensional structural determination of dinitrato[2-(2-dimethylaminoethyl)pyridine]copper(II).

Data Collection and Reduction

The complex was prepared by addition of equimolar amounts of 2-(2-dimethylaminoethyl)pyridine (DMAEP) and $Cu(NO_3)_2 \cdot 3H_2O$ in acetone. After several hours deep blue crystals which were suitable for X-ray examination appeared. *Anal.* Calcd for $CuC_9N_4O_6H_{14}$: C, 32.00; N, 16.59; H, 4.19. Found: C, 32.01; N, 16.50; H, 4.16.

Preliminary Weissenberg and precession photographs indicated that the crystals belong to the monoclinic system. The systematic absences which were observed are $0k0$ for k odd and $h0l$ for l odd which indicates that the space group is $P2_1/c$. The cell constants obtained by the least-squares procedure of Busing and Levy[6] are $a = 6.688$ (6), $b = 14.310$ (11), $c = 14.285$ (9) Å, and $\beta = 78.46$ (3)°;

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[1] E. Uhlig and M. Maaser, *Z. Anorg. Allg. Chem.*, **322**, 25 (1963).

[2] R. Krahmer, M. Maaser, K. Staiger, and E. Uhlig, *Z. Anorg. Allg. Chem.*, 354, 242 (1967).

[3] V. C. Copeland, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 1826 (1972).

[4] V. C. Copeland, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 12, 1340 (1973).

[5] C. D. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev., Chem. Soc.*, 25, 289 (1971).

[6] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967).

the observations were made at 23° with an assumed wavelength of $\lambda(\text{Mo K}\alpha) = 0.7093$ Å. The density of 1.675 g cm^{-3} calculated for four molecules in the cell is in agreement with the value of 1.64 (3) g cm^{-3} measured by flotation in dichloromethane–dibromoethane solution.

Diffraction data were collected from a plate-like crystal with faces (100), $(\bar{1}10)$, (010), $(0\bar{1}0)$, (001), and $(00\bar{1})$; the separations between parallel faces were: (010) and $(0\bar{1}0)$, 0.007 cm; (001) and $(00\bar{1})$, 0.019 cm. The distances between the (100) face and the intersections of the $(\bar{1}10)$, $(0\bar{1}0)$, and (001) faces and the $(\bar{1}10)$, (010), and $(00\bar{1})$ faces were 0.061 and 0.051 cm, respectively. The crystal was mounted approximately normal to the (100) planes, and data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator using Mo Kα radiation in the manner previously described.[7] A single form of the data $(-h, k, \pm l)$ was collected out to a value of $2\theta(\text{Mo}) = 48°$, a total of 2360 intensities being recorded. There were few intensities greater than background at values of $2\theta > 48°$.

Data processing was carried out as described by Corfield, Doedens, and Ibers.[8] The value of p in the expression[9]

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

was chosen as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption. The form of the Lorentz–polarization correction was

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

where θ_m is the monochromator angle.[10] The absorption coefficient for these atoms and Mo Kα radiation is 17.28 cm^{-1}, and for the present sample the transmission coefficients ranged from 0.729 to 0.988.

Solution and Refinement

Examination of a three-dimensional Patterson[11] function revealed the position of the independent copper atom. Two cycles of least-squares refinement, using the 1576 reflections whose intensities were greater than three times their estimated standard deviations, were run on this position. All least-squares refinements in this analysis were carried out on F, the function minimized being $w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In all the calculations of F_c, the atomic scattering factors for Cu were taken from Cromer and Waber,[12] those for C, O, and N from Ibers,[13] and that for H from Stewart, Davidson, and Simpson.[14] The effects of anomalous dispersion of copper were included in the final calculations of F_c,[15] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[16] After the two cycles of 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 0.420 and 0.515, respectively. The remaining nonhydrogen atoms were located by two sequences of difference Fourier synthesis followed by least-squares refinement. The final values of R_1 and R_2 after isotropic refinement of all nonhydrogen atoms using the data before the application of the absorption correction were 0.103 and 0.131.

Utilization of the absorption corrected data and anisotropic refinement for all nonhydrogen atoms reduced the values of R_1 and R_2 to 0.054 and 0.078 after two further cycles of least-squares refinement. A difference Fourier map revealed the positions of all of the anticipated hydrogen atoms. Owing to the small number of data, only the hydrogen atom positional and isotropic thermal parameters and the positional and anisotropic thermal parameters of atoms adjacent to hydrogen atoms were allowed to vary during the next two cycles of least-squares refinement. The final cycles of least-squares refinement were then run allowing all nonhydrogen atom positional and thermal parameters and all hydrogen isotropic thermal parameters to vary but fixing all hydrogen positional parameters at the values obtained in the previous refinement. This led to values of R_1 and R_2 of 0.037 and 0.045, respectively.

Table I. Positional Parameters for Cu(DMAEP)$(NO_3)_2$

Atom	x	y	z
Cu	0.16473 (8)	0.16430 (4)	0.17875 (3)
N(1)	0.1312 (7)	0.1534 (3)	0.0001 (3)
O(1)	0.2855 (5)	0.1693 (2)	0.0397 (2)
O(2)	0.1563 (6)	0.1564 (2)	−0.0868 (2)
O(3)	−0.0342 (5)	0.1363 (2)	0.0533 (2)
N(2)	0.2650 (8)	0.3414 (3)	0.1774 (3)
O(4)	0.0982 (5)	0.3011 (2)	0.1684 (2)
O(5)	0.2786 (7)	0.4261 (3)	0.1658 (3)
O(6)	0.4036 (6)	0.2925 (3)	0.1965 (2)
N(3)	−0.0135 (6)	0.1620 (3)	0.3061 (3)
C(1)	−0.1921 (9)	0.2064 (3)	0.3185 (4)
C(2)	−0.3157 (10)	0.2153 (4)	0.4158 (6)
C(3)	−0.2567 (16)	0.1802 (6)	0.4836 (6)
C(4)	−0.0793 (14)	0.1364 (5)	0.4726 (4)
C(5)	0.0505 (9)	0.1250 (4)	0.3823 (3)
C(6)	0.2464 (10)	0.0760 (5)	0.3639 (4)
C(7)	0.2597 (9)	0.0012 (4)	0.2882 (4)
N(4)	0.3041 (6)	0.0414 (3)	0.1898 (3)
C(8)	0.2469 (11)	−0.0293 (4)	0.1249 (5)
C(9)	0.5251 (8)	0.0591 (4)	0.1612 (4)
H(1)	−0.226 (9)	0.233 (4)	0.270 (5)
H(2)	−0.446 (10)	0.244 (4)	0.413 (4)
H(3)	−0.353 (15)	0.188 (6)	0.527 (6)
H(4)	−0.019 (12)	0.112 (5)	0.513 (5)
H(61)	0.361 (10)	0.129 (5)	0.339 (4)
H(62)	0.279 (10)	0.052 (5)	0.405 (4)
H(71)	0.141 (11)	−0.028 (5)	0.294 (5)
H(72)	0.361 (12)	−0.048 (5)	0.300 (5)
H(81)	0.100 (11)	−0.036 (4)	0.140 (4)
H(82)	0.283 (11)	−0.005 (4)	0.069 (4)
H(83)	0.314 (10)	−0.088 (4)	0.131 (4)
H(91)	0.556 (11)	0.095 (5)	0.095 (5)
H(92)	0.585 (11)	0.102 (5)	0.201 (5)
H(93)	0.608 (12)	0.009 (6)	0.169 (5)

Examination of the values of R_2 showed a marked dependence on $\sin\theta$, which suggested that our weighting scheme was inappropriate. The weights were modified by dividing the weights w for data with $2\theta < 15°$ by 2.0 and those for data with $15° \leqslant 2\theta \leqslant 20°$ by 1.3. A final cycle of least-squares refinement, in which no parameter shift was greater than its standard deviation, gave values of 0.037 and 0.043 for R_1 and R_2. A final difference Fourier map revealed no additional features with the largest peak being less than 0.35 e A^{-3}. A structure factor calculation using the 596 space group allowed data whose intensities were less than three times their estimated standard deviations demonstrated that none of these "unobserved" reflections had values of $|F_o| - |F_c| > 3.5\sigma(F_o)$. The positional and thermal parameters obtained from the final least-squares calculation, with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A compilation of the observed and calculated structure factors is also available.[17] An examination of these structure amplitudes suggested to us that no correction for secondary extinction was necessary, and none was applied.

Description of the Structure

The geometry of the molecule, which is depicted in Figure 1, may be described as a severely distorted octahedron. The bond distances and angles, along with their associated estimated standard deviations, are given in Tables III and IV. The coordination around the copper atom consists of the bidentate 2-(2-dimethylaminoethyl)pyridine (DMAEP) ligand and two unsymmetrically coordinated bidentate nitrate groups. The nearly square equatorial plane is formed by the two DMAEP nitrogen atoms [N(3) and N(4)] with Cu-N(3)

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

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

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

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

Table II. Thermal Parameters for Cu(DMAEP)$(NO_3)_2$

Atom	$\beta_{11}{}^a$ or B, A^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.01963 (15)	0.00390 (3)	0.00323 (3)	−0.00074 (6)	−0.00018 (4)	−0.00014 (3)
N(1)	0.0328 (14)	0.0043 (2)	0.0040 (2)	0.0041 (5)	−0.0011 (5)	0.0002 (2)
O(1)	0.0220 (9)	0.0067 (2)	0.0034 (2)	−0.0027 (4)	−0.0005 (3)	0.0002 (2)
O(2)	0.0430 (12)	0.0076 (2)	0.0033 (2)	0.0007 (5)	−0.0033 (4)	−0.0001 (2)
O(3)	0.0209 (9)	0.0062 (2)	0.0055 (2)	−0.0018 (4)	−0.0016 (4)	0.0003 (2)
N(2)	0.0317 (14)	0.0048 (3)	0.0053 (2)	−0.0018 (6)	−0.0012 (5)	−0.0003 (2)
O(4)	0.0213 (9)	0.0041 (2)	0.0062 (2)	−0.0005 (4)	−0.0027 (4)	−0.0001 (1)
O(5)	0.0411 (14)	0.0040 (2)	0.0133 (4)	−0.0035 (5)	−0.0057 (6)	0.0007 (2)
O(6)	0.0231 (10)	0.0056 (2)	0.0060 (2)	0.0004 (4)	−0.0028 (4)	−0.0004 (2)
N(3)	0.0216 (11)	0.0047 (2)	0.0046 (2)	−0.0019 (5)	0.0008 (4)	−0.0012 (2)
C(1)	0.0270 (18)	0.0040 (3)	0.0069 (4)	−0.0026 (6)	0.0029 (6)	−0.0010 (3)
C(2)	0.0252 (18)	0.0058 (4)	0.0113 (6)	−0.0053 (7)	0.0091 (9)	−0.0044 (4)
C(3)	0.0573 (32)	0.0088 (6)	0.0078 (5)	−0.0096 (11)	0.0146 (12)	−0.0045 (5)
C(4)	0.0577 (29)	0.0081 (5)	0.0035 (3)	−0.0108 (10)	0.0022 (9)	−0.0001 (3)
C(5)	0.0323 (17)	0.0052 (3)	0.0037 (3)	−0.0056 (6)	−0.0000 (5)	−0.0003 (2)
C(6)	0.0375 (20)	0.0091 (5)	0.0046 (3)	−0.046 (8)	−0.0058 (7)	0.0028 (3)
C(7)	0.0304 (17)	0.0053 (3)	0.0069 (3)	0.0005 (6)	−0.0030 (6)	0.0021 (3)
N(4)	0.0241 (11)	0.0046 (2)	0.0053 (2)	−0.0007 (4)	−0.0013 (4)	0.0001 (2)
C(8)	0.0450 (26)	0.0046 (3)	0.0083 (5)	−0.0002 (7)	−0.0036 (8)	−0.0008 (3)
C(9)	0.0194 (14)	0.0076 (4)	0.0076 (4)	0.0010 (7)	0.0004 (6)	0.0011 (3)
H(1)	2.3 (1)					
H(2)	4.4 (12)					
H(3)	10.2 (25)					
H(4)	3.9 (12)					
H(61)	4.9 (11)					
H(62)	5.2 (13)					
H(71)	4.3 (11)					
H(72)	5.2 (11)					
H(81)	3.5 (10)					
H(82)	3.6 (12)					
H(83)	11.8 (27)					
H(91)	6.6 (15)					
H(92)	6.9 (16)					
H(93)	7.5 (16)					

[a] The form of anisotropic 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. Internuclear Distances in Cu(DMAEP)$(NO_3)_2$

Atoms	Distance, Å	Atoms	Distance, Å
Cu–O(1)	1.990 (3)	N(3)–C(1)	1.334 (7)
Cu–O(3)	2.468 (4)	N(3)–C(5)	1.355 (7)
Cu–O(4)	2.019 (4)	C(1)–C(2)	1.358 (9)
Cu–O(6)	2.479 (4)	C(2)–C(3)	1.349 (12)
Cu–N(3)	1.966 (4)	C(3)–C(4)	1.323 (12)
Cu–N(4)	2.014 (4)	C(4)–C(5)	1.413 (8)
N(1)–O(1)	1.292 (5)	C(5)–C(6)	1.463 (8)
N(1)–O(2)	1.220 (5)	C(6)–C(7)	1.512 (8)
N(1)–O(3)	1.235 (5)	C(7)–N(4)	1.491 (6)
N(2)–O(4)	1.286 (6)	N(4)–C(8)	1.472 (7)
N(2)–O(5)	1.223 (6)	N(4)–C(9)	1.475 (7)
N(2)–O(6)	1.235 (6)		

Table IV. Internuclear Angles in Cu(DMAEP)$(NO_3)_2$

Atoms	Angle, deg	Atoms	Angle, deg
O(1)–Cu–O(3)	56.7 (1)	Cu–N(3)–C(5)	121.1 (3)
O(1)–Cu–O(4)	86.8 (1)	C(1)–N(3)–C(5)	119.9 (4)
O(1)–Cu–O(6)	86.2 (1)	N(3)–C(1)–C(2)	122.0 (7)
O(1)–Cu–N(3)	166.9 (1)	C(1)–C(2)–C(3)	119.9 (7)
O(1)–Cu–N(4)	90.5 (1)	C(2)–C(3)–C(4)	118.8 (6)
O(3)–Cu–O(4)	86.9 (1)	C(3)–C(4)–C(5)	122.4 (7)
O(3)–Cu–O(6)	130.3 (1)	C(4)–C(5)–N(3)	116.9 (6)
O(3)–Cu–N(3)	110.7 (2)	C(4)–C(5)–C(6)	125.7 (6)
O(3)–Cu–N(4)	103.9 (1)	N(3)–C(5)–C(6)	117.3 (4)
O(4)–Cu–O(6)	56.4 (1)	C(5)–C(6)–C(7)	112.9 (5)
O(4)–Cu–N(3)	89.0 (2)	C(6)–C(7)–N(4)	112.0 (4)
O(4)–Cu–N(4)	165.0 (2)	C(7)–N(4)–C(8)	107.6 (4)
N(3)–Cu–N(4)	96.7 (2)	C(7)–N(4)–C(9)	109.2 (4)
O(1)–N(1)–O(2)	118.7 (4)	C(8)–N(4)–C(9)	108.4 (4)
O(1)–N(1)–O(3)	117.4 (4)	Cu–N(4)–C(7)	113.7 (3)
O(2)–N(1)–O(3)	123.9 (5)	Cu–N(4)–C(8)	111.3 (3)
O(4)–N(2)–O(5)	118.3 (5)	Cu–N(4)–C(9)	106.2 (3)
O(4)–N(2)–O(6)	118.1 (5)		
O(5)–N(2)–O(6)	123.6 (5)		
Cu–O(1)–N(1)	103.1 (3)		
Cu–O(3)–N(1)	82.3 (3)		
Cu–O(4)–N(2)	102.8 (3)		
Cu–O(6)–N(2)	82.6 (3)		
Cu–N(3)–C(1)	118.1 (3)		

and Cu-N(4) bond distances of 1.966 (4) and 2.014 (4) Å and two oxygen atoms [O(1) and O(4)] from the two nitrate groups with Cu-O(1) and Cu-O(4) bond distances of 1.990 (3) and 2.019 (4) Å. The fifth and sixth (axial) coordination sites around copper are occupied at greater distances by two additional nitrate oxygens [O(3) and O(6)] with Cu-O(3) and Cu-O(6) bond distances of 2.468 (4) and 2.479 (4) Å.

As can be seen from Table V, the atoms of the equatorial region [N(3), N(4), O(1), and O(4)] deviate considerably from planarity, with an average deviation from the best least-squares plane (plane I) of 0.227 Å. The trans equatorial atoms N(3) and O(1) are both below the plane, while N(4) and O(4) are above it, which leads to the O(1)-Cu-N(3) and O(4)-Cu-N(4) angles of 166.9 (1) and 165.0 (2)°. These deviations from planarity are toward the axial coordination site occupied by the oxygen atom of the same nitrate group. Hence N(3) and O(1) are on the same side of the best least-squares plane as O(3), and N(4) and O(4) are similarily disposed with respect to O(6). There are good planes (II and III in Table V) through these atoms, with the average deviation for each group [Cu, N(3), O(1), and O(3) and Cu, N(4), O(4), and O(6)] from its best least-squares plane being 0.023 and 0.013 Å, respectively. It should be noted that these two planes are essentially perpendicular with their normals subtending an angle of 90° 20′, but both are tilted with respect to the equatorial plane with subtended angles of 99° 30′ and 81° 50′ for II and III with respect to I.

Further distortion is provided by the small bite of the nitrate groups, which averages 2.16 Å. This, in addition to the elongation along the axial positions, causes the O(1)-Cu-

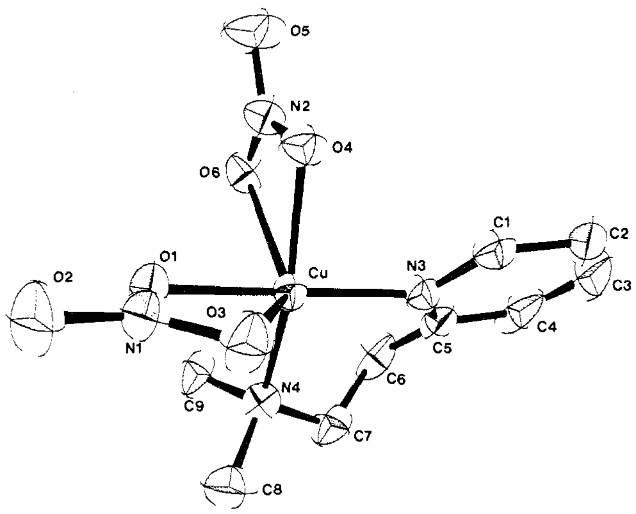

Figure 1. View of the Cu(DMAEP)$(NO_3)_2$ molecule. Thermal ellipsoids are drawn at the 40% probability level and hydrogen atoms are omitted for clarity.

Table V. Least-Squares Planes for Cu(DMAEP)$(NO_3)_2$

Atom	Deviation from best plane, Å
	Plane I
N(3)	+0.220
N(4)	−0.216
O(1)	+0.234
O(4)	−0.238
	Plane II
Cu	−0.042
N(3)	+0.022
O(1)	+0.024
O(3)	−0.005
	Plane III
Cu	−0.023
N(4)	+0.012
O(4)	+0.014
O(6)	−0.003

O(3) and O(4)-Cu-O(6) angles to be greatly reduced from 90°, the observed values being 56.7 (1) and 56.4 (1)°. Both of these values are in agreement with analogous values in other examples of unsymmetrically bound bidentate nitrate transition metal complexes.[18-23]

The unsymmetric coordination of the nitrate group is further demonstrated by the variation of the internal N-O bond distances. The increasing values of 1.220 (5), 1.235 (5), and 1.292 (5) Å for N(1)-O(2), N(1)-O(3), and N(1)-O(1), and 1.223 (5), 1.235 (5), and 1.286 (6) Å for N(2)-O(5), N(2)-O(6), and N(2)-O(4), respectively, mirror the copper-oxygen coordination with O(2) and O(5) being noncoordinated, O(3) and O(6) weakly coordinated, and O(1) and O(4) strongly coordinated. It should be noted, however, that the differences between the bond lengths involving the noncoordinated and weakly coordinated oxygen atoms are small. Application of the independent and riding model "corrections" for thermal motion[24] produces a result in which the bonds to the strongly coordinated oxygen atoms remain significantly longer than the other N-O bonds, but the differences between the bond lengths involving the noncoordinated and the weakly coordinated atoms become insignificant. The O-N-O angles are similar to other examples of unsymmetric bidentate coordination[18,23] with the angle defined by the two coordinating oxygens [O(1)-N(1)-O(3) and O(4)-N(2)-O(6)] having values of 117.4 (4) and 118.1 (4)°, which are less than those of the other two O-N-O angles. Both nitrate groups are also essentially planar with largest deviations from the best least-squares planes being 0.002 and 0.003 Å.

The coordination of the substituted aminoethylpyridine ligand is similar to that found in previous examples.[25-28] The nonaromatic portion of the ligand approximates the classic "boat" form with a considerable flattening effect as demonstrated by the values of 0.696 and 0.412 Å for the perpendicular distances between C(6) and Cu and the best least-squares plane formed by N(3), C(5), C(7), and N(4). The flattening is similar to that found in $[Cu(EAEP)OH]_2$-$[ClO_4]_2$[26] and α- $[Cu(DMAEP)OH]_2[ClO_4]_2$[25] but much greater than that found in the less sterically strained Cu-$(AEP)_2(ClO_4)_2$[27] and $Cu(AEP)_2I_2$[28] molecules. This flattening is also demonstrated by the N(4)-Cu-N(3) angle of 96.7 (2)° which is similar to the analogous values of 95.02 (9) and 96.3 (5) and 93.0 (5)° in α- $[Cu(DMAEP)OH]_2$-$[ClO_4]_2$ and $[Cu(EAEP)OH]_2[ClO_4]_2$ but much greater than the acute angles of 86.54 (7) and 86.8 (1)° found in Cu-$(AEP)_2(ClO_4)_2$ and $Cu(AEP)_2I_2$. The pyridine portion of the ligand is planar with the largest deviation from the best least-squares plane being 0.006 Å, and all bond lengths and angles are normal.

It is interesting to note that, despite the relatively large "hole" in the face defined by O(3), N(3), and O(4), the complex shows no tendency to increase its coordination number to seven. This is in contrast with the expanded coordination recently demonstrated for complexes of the type $M(py)_3(NO_3)_2$[19,20] in which the tightly bound oxygen atoms are trans while in the present example they are cis.

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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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2935.

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