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

Crystal and Molecular Structure of Dinitratobis[2-(2-diethylammonioethyl)pyridine]copper(II) Nitrate

DAVID L. LEWIS and DEREK J. HODGSON*

Received December 18, 1972

The crystal and molecular structure of dinitratobis[2-(2-diethylammonioethyl)pyridine]copper(II) nitrate, $[Cu(DEAEPH)_2(NO_3)_2](NO_3)_2$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a cell of dimensions a = 8.320 (6), b = 8.639 (7), c = 11.096 (11) Å; α = 102.38 (5), β = 99.95 (7), γ = 89.85 (7)°. The observed and calculated densities are 1.43 (2) and 1.454 g cm^{-3}, respectively, and the structure was refined by full-matrix least-squares methods to a final value of the conventional R factor of 0.037 for 2948 independent reflections having $F^2 > 3\sigma(F^2)$. The copper(II) ions are unsymmetrically coordinated to two bidentate nitrate ions with Cu–O distances of 1.992 (2) and 2.562 (3) Å and to the pyridine nitrogen atoms of two DEAEPH ligands with Cu–N distances of 1.984 (2) Å. The amine nitrogen atoms of the ligand are protonated, which causes the ligands to be unidentate and positively charged. The amine nitrogen atoms are hydrogen bonded to the uncoordinated nitrate ions.

Introduction

Copper(II) complexes of chelating nitrogen bases like ethylenediamine,[1] aminoethylpyridines,[2-6] 2,2′-bipyridine,[7-10] and 1,10-phenanthroline[11,12] have been of great interest recently, and we and others have investigated their structural and spectral properties. In all reported cases the ligands are bidentate and uncharged, coordinating to the metal through both nitrogen atoms. In the course of our systematic study of a series of these complexes with substituted aminoethylpyridines we have prepared a purple copper nitrate complex of 2-(2-diethylaminoethyl)pyridine (DEAEP) which contains four nitrate ions and two ligands per copper; hence, assuming that the formal oxidation state of the metal was 2+, it appeared that we had protonated the ligand.

In order to determine the site of protonation and the resulting coordination geometry of this novel complex, we have undertaken a three-dimensional X-ray structure analysis. Of particular interest was the coordination around copper; the presence of four potentially bidentate nitrate ions and two potentially bidentate ligands gives rise to numerous possible geometries at the metal.

Data Collection and Reduction

The complex was prepared by adding several drops of water to 0.70 g of the neat ligand and mixing this solution with a solution of 1.03 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 30 ml of acetone. After several minutes the resulting precipitate was removed by filtration. Purple crystals appeared in the blue filtrate after several days. *Anal.*[13] Calcd for $CuC_{22}N_8O_{12}H_{38}$: C, 39.43; H, 5.72; N, 16.72; O, 28.65. Found: C, 39.38; H, 5.87; N, 16.52; O, 27.29. Preliminary precession and Weissenberg photography indicated that the crystals belong to the triclinic system, the space group being either C_1^1-$P1$ or C_i^1-$P\bar{1}$

Diffraction data were collected from a parallelepiped crystal with faces (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001), and $(00\bar{1})$, the separations between opposite pairs of faces being as follows: (100) and $(\bar{1}00)$, 0.056 cm; (010) and $(0\bar{1}0)$, 0.026 cm; (001) and $(00\bar{1})$, 0.033 cm. The crystal was mounted roughly normal to the (100) planes, and in this orientation intensity data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator and using Mo Kα radiation. The cell constants, obtained by the least-squares procedure of Busing and Levy[14] using twelve reflections, are a = 8.320 (6), b = 8.639 (7), c = 11.096 (11) Å; α = 102.38 (5), β = 99.95 (7), δ = 89.85 (7)°. The density of 1.454 g cm^{-3} calculated for one molecule per unit cell is in acceptable agreement with the value of 1.43 (2) g cm^{-3} obtained by flotation in dibromoethane–dichloromethane solution. Hence, in space group $P\bar{1}$, the copper atom is constrained to lie on a crystallographic inversion center.

The intensity data were collected at a takeoff angle of 1.0°. The receiving aperture was 5.0 mm × 5.0 mm and was located 32 cm from the crystal. Peaks were scanned at a rate of 1°/min, from −0.75° in 2θ below the calculated Kα_1 peak position to +0.75° in 2θ above the Kα_2 peak position; stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan.

A single form $(-h, \pm k, \pm l)$ of the data was collected out to a value of 2θ(Mo) = 54°, above which angle there were very few intensities above background. The intensities of three standard reflections, measured after every 100 reflections, remained essentially constant throughout the run. A total of 3700 independent intensities was recorded, and 54 strong reflections of the form $(+h, \pm k, \pm l)$ were also obtained in order to assist in choosing the enantiomorph in the event the space group proved to be noncentrosymmetric ($P1$).

Data processing was carried out as described by Corfield, Doedens, and Ibers.[15] The value of p in the expression[15,16]

$$\sigma(I) = (C + 0.25(t_s/t_b)^2(B_h + B_l) + (pI)^2)^{1/2}$$

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.[17]

Solution and Refinement of Structure

Owing to instrument failure a preliminary data set of approximately 1400 independent reflections was manually collected on the

---

[1] D. S. Brown, J. D. Lee, B. F. A. Melsome, B. J. Hathaway, G. M. Procteur, and A. A. G. Tomlinson, *Chem. Commun.*, 369 (1967).

[2] D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 2216 (1972).

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

[4] P. Singh, V. C. Copeland, W. E. Hatfield, and D. J. Hodgson, *J. Phys. Chem.*, 76, 2887 (1972).

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

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

[7] R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 74, 3497 (1970).

[8] A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970).

[9] H. Nakai, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jap.*, 43, 577 (1970).

[10] H. Nakai, *Bull. Chem. Soc. Jap.*, 44, 2412 (1970).

[11] C. M. Harris, E. Sinn, W. R. Walker, and P. R. Woolliams, *Aust. J. Chem.*, 21, 631 (1968).

[12] D. D. Perrin and V. S. Sharma, *J. Inorg. Nucl. Chem.*, 28, 1271 (1966).

[13] Analysis performed by Meade Microanalytical Laboratory and Galbraith Laboratories.

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

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

[16] W. R. Busing and H. A. Levy, *J. Chem. Phys.*, 26, 563 (1957).

[17] S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 11, 2604 (1971).

Table I. Positional Parameters for $[Cu(DEAPH)_2(NO_3)_2](NO_3)_2$

Atom	*x*	*y*	*z*
Cu	0.0	0.0	0.0
N1	−0.1119 (2)	−0.1877 (2)	0.0290 (1)
C1	−0.1489 (2)	−0.1955 (2)	0.1408 (2)
C2	−0.2179 (3)	−0.3340 (2)	0.1568 (2)
C3	−0.2515 (3)	−0.4623 (3)	0.0592 (2)
C4	−0.2149 (3)	−0.4529 (3)	−0.0554 (2)
C5	−0.1445 (3)	−0.3143 (2)	−0.0666 (2)
C6	−0.1166 (3)	−0.0514 (2)	0.2462 (2)
C7	−0.2740 (3)	0.0078 (3)	0.2849 (3)
N2	−0.2458 (2)	0.1587 (2)	0.3850 (2)
C8	−0.2785 (3)	0.3046 (3)	0.3341 (2)
C81	−0.4540 (4)	0.3252 (4)	0.2844 (4)
C9	−0.3341 (3)	0.1476 (3)	0.4901 (2)
C91	−0.2957 (5)	0.2854 (4)	0.5999 (3)
N3	0.2905 (3)	−0.1090 (2)	0.0768 (2)
O1	0.2479 (3)	−0.0199 (2)	0.1680 (2)
O2	0.1925 (2)	−0.1315 (2)	−0.0287 (1)
O3	0.4188 (3)	−0.1774 (3)	0.0826 (3)
N4	0.1673 (2)	0.2717 (2)	0.4660 (2)
O10	0.3063 (2)	0.3042 (2)	0.5254 (2)
O11	0.0776 (2)	0.1803 (2)	0.5007 (2)
O12	0.1139 (3)	0.3226 (3)	0.3720 (2)
H2	−0.226 (4)	−0.343 (3)	0.226 (3)
H3	−0.305 (3)	−0.561 (3)	0.068 (2)
H4	−0.241 (3)	−0.550 (3)	−0.124 (2)
H5	−0.122 (4)	−0.302 (3)	−0.142 (3)
H61	−0.069 (3)	0.028 (3)	0.220 (2)
H62	−0.053 (3)	−0.082 (3)	0.313 (2)
H71	−0.337 (4)	−0.082 (4)	0.323 (3)
H72	−0.369 (4)	0.014 (3)	0.222 (3)
HN2	−0.147 (3)	0.167 (3)	0.417 (2)
H81	−0.218 (4)	0.280 (4)	0.263 (3)
H82	−0.234 (3)	0.391 (3)	0.399 (2)
H811	−0.456 (4)	0.435 (4)	0.258 (3)
H812	−0.502 (5)	0.320 (5)	0.341 (4)
H813	−0.482 (4)	0.252 (4)	0.215 (3)
H91	−0.454 (3)	0.136 (3)	0.451 (2)
H92	−0.296 (4)	0.062 (3)	0.522 (3)
H911	−0.348 (4)	0.383 (4)	0.579 (3)
H912	−0.333 (6)	0.263 (5)	0.663 (4)
H913	−0.194 (4)	0.291 (3)	0.621 (3)

Picker diffractometer. Examination of a three-dimensional Patterson function[18] did not reveal any reliable copper–light atom vectors. Five cycles of least-squares refinement were run with a single copper atom positioned at the origin and assigned a variable isotropic thermal parameter. 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 were taken from Cromer and Waber,[19] those for C, O, and N were from Ibers,[20] and that for H was from Stewart, Davidson, and Simpson.[21] The effects of anomalous dispersion of copper were included in the final calculations of F_c,[22] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[23]

After five cycles of refinement using 1181 reflections which were greater than 3 times their estimated standard deviations, 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 0.55 and 0.58. Examination of a Wilson plot strongly suggested that the space group was noncentrosymmetric, and further refinement was conducted in the space group $P1$. The locations of the remaining nonhydrogen atoms were obtained by the normal sequence of least-squares calculation followed by difference Fourier synthesis; the final values of R_1 and R_2 after isotropic refinement of all nonhydrogen atoms were 0.092 and 0.129. Further refinement was discontinued at this time until a full data set could be collected with the diffractometer in the automatic mode.

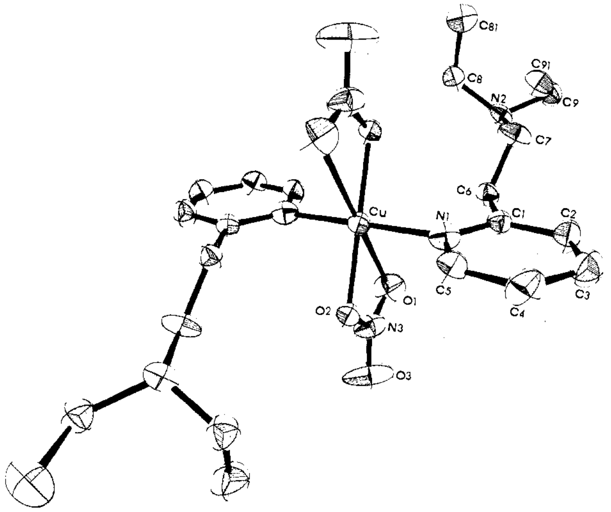

Figure 1. View of the $[Cu(DEAEPH)_2(NO_3)_2]^{2+}$ cation. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

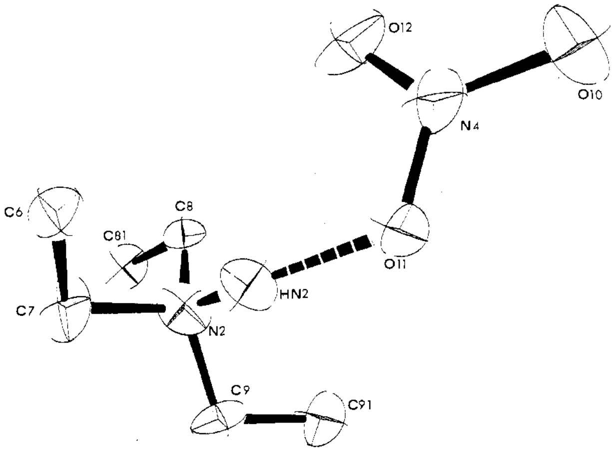

Figure 2. View of the hydrogen-bonding scheme involving the amine nitrogen of DEAEPH and the uncoordinated nitrate.

The full data set, consisting of 2948 independent reflections with intensities greater than 3 times their estimated standard deviations, was then collected (*vide supra*). An absorption correction was immediately applied; the absorption coefficient for these atoms and Mo Kα radiation is 8.2 cm^{-1} and the transmission coefficients for the sample used were found to range from 0.760 to 0.836. Only the 2948 intensities which were greater than 3 times their estimated standard deviations were used in the refinement of the structure.

Examination of a least-squares calculation at this stage showed very high correlation coefficients between many pairs of parameters and suggested that the structure might be centric, and all further refinements were carried out in $P\bar{1}$. A difference Fourier map revealed the locations of all of the anticipated hydrogen atoms; in addition to these peaks, there was a high peak within 1.0 Å of the amine nitrogen which we interpreted as a hydrogen atom. Examination of the geometry around this nitrogen atom strongly supported this assignment, since the C–N–C angles were all close to those expected for tetrahedral geometry at N rather than those predicted for trigonal coordination. Two cycles of least-squares were run with anisotropic refinement for all nonhydrogen atoms and isotropic refinement for all hydrogen atoms; the positional and thermal parameters of all atoms (including hydrogens) were varied, and the values of R_1 and R_2 were 0.038 and 0.051. 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[24,25] was applied. The value of R_2 showed some dependence

---

(18) 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, Zalkin's FORDAP Fourier program, Johnson's ORTEP plotting program, and Doeden's RSCAN program.

(19) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(20) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.31A.

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

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

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

(24) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

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

Table II. Thermal Parameters for $[Cu(DEAPH)_2(NO_3)_2](NO_3)_2$

Atom	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.01353 (6)	0.00906 (5)	0.00617 (3)	0.00181 (4)	0.00317 (3)	0.00201 (3)
N1	0.0142 (3)	0.0097 (2)	0.0061 (1)	0.0014 (2)	0.0025 (2)	0.0016 (1)
C1	0.0118 (3)	0.0088 (2)	0.0062 (2)	0.0014 (2)	0.0023 (2)	0.0015 (2)
C2	0.0202 (5)	0.0104 (3)	0.0081 (2)	−0.0002 (3)	0.0049 (3)	0.0024 (2)
C3	0.0203 (5)	0.0095 (3)	0.0108 (2)	−0.0011 (3)	0.0042 (3)	0.0018 (2)
C4	0.0204 (5)	0.0097 (3)	0.0084 (2)	0.0001 (3)	0.0017 (3)	−0.0004 (2)
C5	0.0189 (4)	0.0108 (3)	0.0060 (2)	0.0006 (3)	0.0024 (2)	0.0008 (2)
C6	0.0124 (3)	0.0099 (3)	0.0058 (2)	0.0003 (2)	0.0026 (2)	0.0010 (2)
C7	0.0112 (3)	0.0135 (3)	0.0104 (2)	−0.0003 (3)	0.0023 (2)	−0.0034 (2)
N2	0.0105 (2)	0.0109 (2)	0.0078 (2)	0.0001 (2)	0.0029 (2)	−0.0007 (2)
C8	0.0152 (4)	0.0136 (3)	0.0091 (2)	−0.0004 (3)	0.0037 (2)	0.0024 (2)
C81	0.0179 (5)	0.0200 (5)	0.0141 (4)	0.0043 (4)	0.0031 (4)	0.0058 (4)
C9	0.0160 (4)	0.0133 (3)	0.0095 (2)	0.0017 (3)	0.0053 (3)	0.0029 (2)
C91	0.0213 (6)	0.0229 (6)	0.0090 (3)	0.0017 (5)	0.0055 (3)	−0.0005 (3)
N3	0.0149 (3)	0.0108 (2)	0.0138 (2)	0.0008 (2)	0.0002 (2)	0.0020 (2)
O1	0.0244 (3)	0.0176 (3)	0.0100 (2)	0.0019 (3)	0.0010 (2)	0.0007 (2)
O2	0.0144 (3)	0.0120 (2)	0.0092 (2)	0.0023 (2)	0.0023 (2)	0.0018 (2)
O3	0.0154 (4)	0.0200 (4)	0.0262 (4)	0.0058 (3)	−0.0052 (3)	−0.0034 (3)
N4	0.0132 (3)	0.0129 (3)	0.0087 (2)	−0.0001 (2)	0.0039 (2)	0.0011 (2)
O10	0.0109 (3)	0.0230 (3)	0.0148 (2)	−0.0035 (2)	0.0019 (2)	0.0023 (2)
O11	0.0131 (3)	0.02390 (3)	0.0111 (2)	−0.0049 (3)	0.0006 (2)	0.0077 (2)
O12	0.0235 (4)	0.0301 (4)	0.0143 (2)	−0.0031 (4)	0.0028 (3)	0.0123 (3)
H2	5.8 (7)					
H3	4.7 (6)					
H4	4.6 (6)					
H5	4.9 (6)					
H61	3.8 (5)					
H62	3.7 (5)					
H71	6.5 (7)					
H72	5.4 (6)					
HN2	2.9 (5)					
H81	6.7 (8)					
H82	3.8 (5)					
H811	6.4 (7)					
H812	7.8 (11)					
H813	5.4 (7)					
H91	4.1 (5)					
H92	5.3 (6)					
H911	7.0 (8)					
H912	10.7 (14)					
H913	5.1 (7)					

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

on sin θ, which suggested that our weighting scheme was inappropriate. The weights were modified by multiplying $\sigma(F)$ for data with $2\theta < 30°$ by 1.43. Two final cycles of least-squares refinement gave values of 0.037 and 0.050 for R_1 and R_2; the final value of the extinction coefficient was 7.7 (6) × 10^{-6}. In the last cycle of least-squares refinement, the greatest shift in any parameter was 0.8 times its estimated standard deviation and the refinement was considered to have converged. A final attempt to refine the structure in the noncentrosymmetric space group was unsuccessful which indicates that our eventual choice of $P\bar{1}$ is 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.[26] A structure factor calculation using the 335 data whose intensities were less than 3 times their estimated standard deviations demonstrated that none of these "unobserved" reflections had $||F_o| - |F_c|| > 3.2\sigma(F_o)$.

Table III. Internuclear Distances in $[Cu(DEAEPH)_2(NO_3)_2](NO_3)_2$

Atoms	Dist, Å	Atoms	Dist, Å
Cu-N1	1.984 (2)	C3-C4	1.376 (4)
Cu-O1	2.562 (3)	C4-C5	1.373 (3)
Cu-O2	1.992 (2)	C1-C6	1.503 (3)
N3-O1	1.237 (3)	C6-C7	1.502 (3)
N3-O2	1.283 (3)	C7-N2	1.510 (3)
N3-O3	1.218 (3)	N2-C8	1.494 (3)
N4-O10	1.228 (3)	N2-C9	1.501 (3)
N4-O11	1.249 (2)	N2-HN2	0.83 (2)
N4-O12	1.231 (3)	N2-O11	2.762 (3)
N1-C1	1.344 (3)	C8-C81	1.493 (4)
N1-C5	1.342 (3)	C9-C91	1.500 (4)
C1-C2	1.387 (3)	HN2-O11	1.93 (3)
C2-C3	1.364 (3)		

Description of the Structure

The structure consists of a dinitratobis[2-(2-diethylammonioethyl)pyridine]copper(II), $[Cu(DEAEPH)_2(NO_3)_2]$, cation in close proximity to two nitrate anions. The geometry of the complex cation may be best described as a severely distorted octahedron and is shown in Figure 1. The bond distances and angles, along with their associated estimated standard deviations, are given in Tables III and IV. The coordination around the copper(II) ion consists of two pyridine nitrogen atoms and four nitrate oxygen atoms from two nitrate ions and is very similar to that found[27] in the pyrazine complex. The two nitrogen atoms, N1 and N1′, and two of the nitrate oxygens, O2 and O2′, form a nearly square-planar array with Cu-N1 and Cu-O2 bond distances of 1.984 (2) and 1.992 (2) Å and N1-Cu-O2 and N1-Cu-O2′ bond angles of 88.95 (9) and 91.05 (9)°. The coordinated nitrate ions

---

(26) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1682.

(27) A. Santoro, A. D. Mighell, and C. W. Riemann, *Acta Crystallogr., Sect. B*, 26, 979 (1970).

Table IV. Internuclear Angles in $[Cu(DEAEPH)_2(NO_3)_2](NO_3)_2$

Atoms	Angle, deg	Atoms	Angle, deg
N1-Cu-O1	92.29 (9)	C1-C2-C3	120.5 (2)
N1-Cu-O2	88.95 (9)	C2-C3-C4	119.1 (2)
O1-Cu-O2	54.85 (8)	C3-C4-C5	118.4 (2)
O1-N3-O2	117.8 (2)	C4-C5-N1	122.6 (2)
O1-N3-O3	123.5 (2)	C1-C6-C7	110.3 (2)
O2-N3-O3	118.7 (2)	C6-C7-N2	111.3 (2)
O10-N4-O11	118.7 (2)	C7-N2-C8	113.1 (2)
O10-N4-O12	122.7 (2)	C7-N2-C9	110.3 (2)
O11-N4-O12	118.6 (2)	C7-N2-HN2	108.3 (15)
C1-N1-C5	119.2 (2)	C8-N2-C9	114.4 (2)
C1-N1-Cu	122.9 (1)	C8-N2-HN2	104.6 (15)
C5-N1-Cu	117.7 (1)	C9-N2-HN2	105.6 (15)
N1-C1-C2	120.0 (2)	N2-C8-C81	114.7 (2)
N1-C1-C6	118.8 (2)	N2-C9-C91	113.2 (2)
C2-C1-C6	121.1 (2)	N2-HN2-O11	175.3 (22)

act as bidentate ligands, the fifth and sixth coordination sites around copper being occupied by two additional oxygen atoms, O1 and O1′, from the nitrates. The Cu-O1 bond distance of 2.562 (3) Å is much longer than those found in the equatorial plane. This elongation, resulting in four short and two long bonds, is a common feature of many copper(II) complexes[27] and can be considered the result of strong bonding in the *xy* plane with a corresponding decrease of bond strength along the *z* axis. The combination of the Cu-O1 elongation and the relatively short bite of the chelating nitrate (approximately 2.15 Å) results in a large deviation of the Cu-O1 vector from the perpendicular to the square-planar base. This deviation is evidenced by the relatively small O1-Cu-O2 bond angle of 54.85 (8)°; this value is similar to the analogous value of 56.11 (17)° found[27] in $Cu(NO_3)_2$-$(C_4N_2H_4)$.

The unsymmetrical nature of the bidentate nitrate is reflected in the variation of the three internal nitrogen-oxygen bond distances. The monotonically decreasing distances of 1.283 (3), 1.237 (3), and 1.218 (3) Å for N3-O2, N3-O1, and N3-O3, respectively, parallel the copper-oxygen coordination with O2 being strongly bonded, O1 weakly bonded; and O3 nonbonded. The O1-Cu-O2 angle of 54.85 (8)° is in the range of 48.8-56.0° found[28-34] for a variety of bidentate nitrate complexes. This value is much smaller than the O-Cu-O angle of 66.38 (8)° subtended[35] at copper by the chelating carbonate ligand in $Cu(NH_3)_2CO_3$ because of the stronger Cu-O binding in the latter case.

The coordination of the DEAEP moiety is unusual since other examples[2-4] of transition metal complexes of substituted aminoethylpyridines have been shown to involve bidentate ligand coordination. In the present case this chelation is precluded by the protonation of the second potential coordination site (N2), which gives the ligand a formal positive charge. Though no longer included in the copper(II) coordination sphere, this site plays an important role in the overall molecular geometry. The geometry around N2 is roughly tetrahedral, and the hydrogen atom (HN2) has an additional contact of 1.93 (3) Å with an oxygen atom (O11) of the uncoordinated nitrate (see Figure 2). This contact and the subsequent N2-HN2-O11 angle of 175 (2)° suggest[36] a strong N-H· · ·O hydrogen bond since the H· · ·O distance is less than the sum of the van der Waals radii of these atoms[37,38] and the N-H· · ·O angle is nearly linear. Further evidence for the validity of this postulated hydrogen bond is found in the nitrogen-oxygen bond distances of the uncoordinated nitrate anion. The N4-O11 bond distance of 1.249 (3) Å is significantly greater than the N4-O10 and N4-O12 bond distances of 1.228 (3) and 1.231 (3) Å, respectively, which strongly suggests an interionic interaction involving O11. Additional evidence is provided by the infrared spectrum of the complex (obtained using both a KBr disk and a Nujol mull) which shows a medium-strength band at approximately 2720 cm^{-1} which we assign to the N-H stretching mode. Nakamoto, *et al.*,[39] have shown that such a low-energy N-H stretch would be expected for hydrogen bonded N-H· · ·O distances of less than 2.8 Å.

The geometry of the DEAEP group is as expected. The pyridine ring is essentially planar, with no deviations from the best least-squares plane greater than 0.007 Å. The bond distances and angles of the ring and the side chain are similar to those found in a wide variety of transition metal complexes of substituted pyridines.[2-4,40-42]

Registry No. $[Cu(DEAEPH)_2(NO_3)_2](NO_3)_2$, 39561-38-1.

Acknowledgments. This research was supported by the Materials Research Center of the University of North Carolina through contract with the National Science Foundation and by an equipment grant (GP-10300) from the National Science Foundation.

---

(28) A. F. Cameron, D. W. Taylor, and R. H. Nuttal, *J. Chem. Soc., Dalton Trans.*, 1603 (1972).

(29) A. F. Cameron, D. W. Taylor, and R. H. Nuttal, *J. Chem. Soc., Dalton Trans.*, 1608 (1972).

(30) A. F. Cameron, D. W. Taylor, and R. H. Nuttal, *J. Chem. Soc., Dalton Trans.*, 58 (1972).

(31) B. Matkovic, B. Ribar, B. Zelenko, and S. W. Peterson, *Acta Crystallogr.*, 21, 719 (1966).

(32) T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, **7**, 715 (1968).

(33) F. A. Cotton and J. G. Bergmann, *J. Amer. Chem. Soc.*, 86, 2941 (1964).

(34) J. C. Taylor, M. H. Mueller, and R. L. Hitterman, *Acta Crystallogr.*, 20, 842 (1966).

(35) M. H. Meyer, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Acta Crystallogr., Sect. B*, 28, 1607 (1972).

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

(37) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y.

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

(39) K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, 77, 6480 (1955).

(40) P. Singh, D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 11, 1657 (1972).

(41) V. F. Duckworth and N. C. Stephenson, *Acta Crystallogr., Sect. B*, 25, 1795 (1969).

(42) G. Davey and F. S. Stephens, *J. Chem. Soc. A*, 1917 (1971).