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Crystal Structure of Bis[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) Perchlorate, $[Cu(C_4H_{12}N_2O)_2](ClO_4)_2$[1]

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The crystal structure of bis[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) perchlorate has been determined from three-dimensional X-ray diffraction data. The compound crystallizes in the space group $P2_1/n$ with cell dimensions $a = 15.914$ (3), $b = 12.710$ (1), $c = 9.041$ (2) Å, and $\beta = 101.39$ (2)°. The observed density is 1.74 (1) g/cm^3, while the calculated density is 1.741 g/cm^3 for four molecules in the unit cell. Intensities were measured for 3872 independent reflections on a Picker automated four-circle diffractometer. The structure was refined by least-squares methods to a conventional R factor of 0.079. The compound consists of discrete complex cations and perchlorate anions. Each of the *N*-(2-hydroxyethyl)ethylenediamine (hn) ligands is tridentate, coordinating in a facial configuration. The geometric arrangement of ligand donors about the central copper atom is a distorted octahedron with the chemically equivalent amino groups cis to each other at Cu–N distances of 2.012 (4), 2.018 (4), 2.036 (3), and 2.041 (3) Å, while the alcohol groups are trans to each other at Cu–O distances of 2.419 (3) and 2.518 (3) Å.

Introduction

For a number of years, studies on alkanolamine and alkanol-substituted ethylenediamine complexes by numerous physicochemical methods have been carried out in this laboratory. One conclusion of these studies has been that coordination could occur through an alcoholic oxygen in such complexes. This was indicated, for example, for a number of copper(II) complexes of mono-, di-, and triethanolamines.[3] In 1958, Hall and Dean[4] indicated that the ligand *N*-(2-hydroxyethyl)ethylenediamine (hn) could be tridentate in solution through coordination of the two nitrogen atoms and the oxygen atom of the alcohol group.

Very recently, Zimmerman and Hall[5] carried out a study on a number of crystalline copper(II) and nickel(II) complexes with each of three different alkanol-substituted ethylenediamines. The compounds were characterized by means of elemental analyses, by electronic and infrared spectra, and by magnetic moments. Concomitantly, we have initiated X-ray crystallographic studies of some of these compounds to facilitate the evaluation of the chemical data. This work, the crystal structure determination of $[Cu(hn)_2](ClO_4)_2$, is the first of these studies to be completed.

Experimental Section

Crystal Data. Dark blue crystals which display an elongated octahedral morphology were prepared by Zimmerman.[6] The crystal chosen for the collection of all diffraction data had the approximate dimensions 0.34 × 0.21 × 0.19 mm as measured between opposite apices of the octahedron.

Oscillation and Weissenberg photographs were taken using Cu Kα radiation with the crystal mounted along the c axis. The space group was found to be $P2_1/n$ ($C_{2h}{}^5$) from the systematic absences of the $0k0$ reflections with k odd and the $h0l$ reflections with $h + l$ odd. Cell dimensions were obtained by least-squares refinement of the 2θ values for 26 reflections collected at room temperature (*ca.* 25°) on a Picker automated diffractometer, using zirconium-filtered Mo Kα radiation (λ 0.71069 Å). The dimensions are $a = 15.914$ (3), $b = 12.710$ (1), $c = 9.041$ (2) Å, and $\beta = 101.39$ (2).° Accurate cell parameters and other properties of the complex were previously reported by Pajunen and Lehtonen.[7] Their parameters for the cell with space group $P2_1/c$ are $a = 9.041$ (6), $b = 12.710$ (4), $c = 16.662$ (1) Å, and $\beta = 110.54$ (2)°. A transformation of the basis vectors of this cell into those of the cell with space group $P2_1/n$ (with the matrix 101/010/–100) produces the dimensions $a = 15.926$ (2), $b = 12.710$ (4), $c = 9.041$ (6) Å, and $\beta = 101.57$ (4)°. In order to work in a more nearly orthogonal unit cell, the space group $P2_1/n$ was used. A crystal density of 1.74 (1) g/cm^3 was found by the flotation method using a mixture of carbon tetrachloride and methyl iodide. With four molecules in the unit cell, the calculated density is 1.741 g/cm^3. Other physical data for $[Cu(hn)_2](ClO_4)_2$ are mol wt 470.7, $V = 1795.4$ Å^3, and $F(000) = 972$ e.

Intensity Data Collection and Reduction. The intensity data were collected using zirconium-filtered Mo Kα radiation and the Picker automated (card-controlled) diffractometer. The θ–2θ scan method was employed, with the scan range set equal to $1.80 + 1.00 (\tan \theta)$ for all reflections having $2\theta \geqslant 10°$ as suggested by Alexander and Smith[8] for Mo Kα radiation. The scan ranges for several reflections having $2\theta < 10°$ were determined experimentally. The scan speed was 2°/min and 30-sec background counts were taken at each end of the scan range. For a number of reflections the maximum count rate during the scan was outside the linear range of the counter and these intensities were thus measured using an attenuator.

The intensities of 3872 symmetrically independent reflections were measured out to a 2θ value of 55°. Three strong reflections (040, 241, and 122) were measured every 3–4 hr to monitor the stability of the crystal and the diffraction equipment. These data were later used to scale the reflections measured at the various times to a common basis. The intensity sum of each set of standards was used to calculate the relative scale factor for the reflections measured between each set. The intensity of each standard reflection dropped fairly regularly during data collection and the net reduction in the total intensity of the standards was 11%.

The intensity of each reflection was evaluated as $I = (\mathrm{Qg})(\mathrm{At})[S - TB]$ where S is the scan count, B is the sum of the background counts, T is the ratio of the time spent in the reflection scan to the total time spent on the backgrounds, Qg is the gth group scale factor, and At corrects for the use of an attenuator (or is otherwise unity). The estimated standard deviations in the intensities were calculated by the relation $\sigma_I = (\mathrm{Qg})(\mathrm{At})[S + BT^2 + (\sigma_{\mathrm{Qg}}{}^2/\mathrm{Qg}^2 + \sigma_{\mathrm{At}}{}^2/\mathrm{At}^2)(S - TB)^2]^{1/2}$ in which $\sigma_{\mathrm{Qg}}{}^2$ and $\sigma_{\mathrm{At}}{}^2$ are the experimental variances in Qg and At, respectively. A total of 178 reflections had intensities which computed to be negative and were assigned an F_o of zero.

The data reduction process and all other computations were carried out using the "X-Ray 67" crystallographic computing system of Stewart.[9] Lorentz and polarization corrections were applied to the intensities but no correction was made for absorption. The linear absorption coefficient was 16 cm^{-1}. Considering the crystal dimension extremes, the largest absorption corrections would be about ±12%

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[1] Abstracted in part from the Ph.D. dissertation of T. L. D., West Virginia University, 1971.

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Table II[a]

Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^2$)

Atom	x	y	z	B_{11}	B_{22}	β_{33}	B_{12}	B_{13}	B_{23}
Cu	947 (1)	2292 (1)	3402 (1)	223 (2)	295 (2)	270 (2)	9 (2)	−5 (2)	31 (2)
Cl(1)	3089 (1)	71 (1)	7350 (1)	318 (6)	398 (6)	397 (6)	−47 (5)	−47 (5)	16 (5)
Cl(2)	3786 (1)	3500 (1)	3549 (1)	328 (6)	363 (6)	464 (6)	−2 (5)	0 (5)	37 (5)
O(1)	1164 (2)	4255 (3)	3470 (4)	581 (20)	578 (19)	382 (17)	−200 (16)	−106 (15)	0 (16)
O(2)	107 (2)	695 (2)	2977 (4)	435 (17)	402 (17)	632 (20)	−22 (14)	146 (15)	−97 (15)
O(3)	3978 (2)	156 (3)	7439 (5)	528 (22)	966 (30)	1618 (41)	−298 (21)	363 (24)	−417 (28)
O(4)	2840 (3)	611 (4)	8482 (6)	1388 (41)	1625 (46)	1308 (40)	−342 (35)	817 (34)	−752 (36)
O(5)	2662 (4)	417 (4)	6028 (5)	1862 (49)	1841 (50)	625 (28)	887 (41)	53 (29)	594 (31)
O(6)	2919 (2)	−1000 (3)	7441 (6)	621 (24)	574 (25)	1790 (45)	−74 (20)	−58 (26)	268 (26)
O(7)	3107 (2)	3696 (3)	4328 (4)	522 (20)	865 (26)	692 (23)	187 (18)	191 (17)	27 (19)
O(8)	3548 (2)	3894 (3)	2049 (4)	532 (19)	691 (22)	466 (19)	−39 (16)	−68 (15)	156 (16)
O(9)	4559 (2)	4015 (3)	4265 (4)	425 (18)	677 (22)	727 (23)	−171 (16)	−169 (16)	19 (18)
O(10)	3932 (2)	2394 (2)	3551 (4)	740 (22)	308 (17)	895 (22)	35 (16)	127 (18)	73 (17)
N(1)	1981 (2)	1487 (3)	3059 (4)	269 (17)	384 (20)	509 (22)	55 (22)	41 (16)	118 (17)
N(2)	829 (2)	2731 (3)	1205 (4)	241 (15)	334 (17)	351 (17)	−23 (15)	−14 (13)	38 (16)
N(3)	−232 (2)	2751 (3)	3726 (4)	288 (16)	347 (17)	352 (18)	18 (15)	65 (15)	−7 (16)
N(4)	1245 (2)	5673 (4)	1981 (2)	505 (22)	509 (22)	308 (19)	58 (19)	−65 (16)	41 (17)
C(1)	1950 (3)	1410 (4)	1396 (6)	457 (27)	439 (28)	600 (32)	93 (22)	228 (24)	−12 (24)
C(2)	1643 (3)	2422 (4)	719 (5)	419 (24)	560 (31)	333 (23)	58 (22)	117 (19)	84 (21)
C(3)	621 (3)	3860 (4)	921 (5)	323 (22)	460 (26)	342 (23)	3 (20)	44 (18)	124 (20)
C(4)	1198 (3)	4553 (4)	1977 (6)	487 (27)	287 (23)	603 (32)	−56 (21)	79 (24)	58 (22)
C(5)	−735 (3)	936 (4)	3182 (6)	356 (26)	473 (29)	714 (35)	−137 (22)	118 (24)	−80 (25)
C(6)	−932 (3)	2074 (4)	2959 (6)	256 (22)	490 (29)	662 (32)	−36 (20)	38 (21)	−81 (24)
C(7)	−173 (3)	2921 (4)	5347 (5)	494 (27)	697 (33)	381 (25)	110 (25)	186 (21)	27 (24)
C(8)	457 (4)	2166 (5)	6246 (6)	547 (30)	907 (39)	330 (30)	75 (30)	91 (22)	75 (26)

Positional Parameters ($\times 10^3$) and Thermal Parameters

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(1)	193 (2)	81 (3)	327 (4)	3.68	H(13)	5 (2)	66 (3)	213 (4)	4.53
H(2)	242 (2)	191 (3)	338 (4)	3.68	H(14)	−106 (2)	50 (3)	236 (4)	4.56
H(3)	151 (2)	85 (3)	105 (4)	4.66	H(15)	−83 (2)	72 (3)	429 (4)	4.56
H(4)	256 (2)	127 (3)	117 (4)	4.66	H(16)	−96 (2)	239 (3)	178 (4)	4.34
H(5)	158 (2)	239 (3)	−24 (4)	4.11	H(17)	−145 (2)	232 (3)	337 (4)	4.34
H(6)	210 (2)	307 (3)	107 (4)	4.11	H(18)	−35 (2)	345 (3)	345 (3)	2.99
H(7)	42 (2)	233 (3)	80 (4)	3.24	H(19)	11 (2)	370 (3)	545 (4)	4.47
H(8)	62 (2)	397 (3)	−11 (4)	3.41	H(20)	−68 (2)	285 (3)	565 (4)	4.47
H(9)	4 (2)	397 (3)	113 (4)	3.41	H(21)	28 (2)	128 (3)	598 (4)	5.52
H(10)	178 (2)	445 (3)	182 (4)	4.36	H(22)	49 (2)	235 (3)	736 (4)	5.52
H(11)	103 (2)	520 (3)	174 (4)	4.36	H(23)	152 (2)	284 (3)	594 (4)	4.21
H(12)	144 (2)	446 (3)	400 (4)	4.74	H(24)	167 (2)	159 (3)	606 (4)	4.21

[a] The estimated standard deviation in the least significant figure(s) is given in parentheses following each parameter. The temperature factor is defined as $\exp(-{}^1\!/_4 \Sigma_{i=1} \Sigma_{j=1} B_{ij} h_i h_j a_i^* a_j^*)$.

and were ignored. The estimated standard deviation in each relative structure factor amplitude was taken as $\sigma_F = [F^2 + (Lp)^{-1}\sigma_I]^{1/2} - F$.

Solution and Refinement of the Structure. Structure factors were first computed using the coordinates of the copper atom obtained from a Patterson synthesis and a temperature factor of 3.0 Å^2 as determined by a Wilson calculation. The resulting phase signs were used in a subsequent electron density calculation, the first of several such calculations through which all nonhydrogen atoms were located and their positions somewhat refined. In this early stage of solution the four primary atoms of the organic ligands were assumed to be oxygen atoms, but were later positively identified by a difference-Fourier synthesis.

All least-squares refinements were performed using the "X-Ray 67" version of ORFLS.[10] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. All reflections were included in the refinement with weights, w, assigned as σ_F^{-2}. The convergence pattern of the least-squares process was normal with the minor exception of the thermal parameters of the oxygen atoms belonging to one of the perchlorate groups. In their case, the thermal parameters became rather large suggesting possible disorder. Near the end of the refinement, the 24 hydrogen atoms were located by analysis of a difference-Fourier synthesis and verified by calculating the idealized positions assuming tetrahedral configurations about carbon, nitrogen, and oxygen atoms of the organic ligands. On the final cycle of refinement of the nonhydrogen atom parameters, the largest shift was 0.43σ and the average shift was 0.11σ. The conventional residual factor, $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, was 0.079 and the weighted residual, $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$, was 0.042. A final difference map proved to be fairly flat in all areas except for the vicinities about the copper atom and the atoms of the two perchlorate groups. Several positive maxima (the largest of which was 0.71 e/Å^3) were located along the edges and in the faces of the tetrahedron formed by the perchlorate group whose oxygen atoms had high temperature factors, another apparent consequence of the disorder.

Throughout the determination the scattering factors employed were those taken from ref 11 for neutral copper, chlorine, oxygen, nitrogen, and carbon and those reported by Stewart, *et al.*,[12] for hydrogen.

The observed and calculated structure factors are given in Table I.[13] Table II lists the final parameters with their estimated standard deviations. Figure 1 gives perspective diagrams of the complex cation and perchlorate anions, showing the nonhydrogen atom designations and the thermal ellipsoids. Table III gives the root-mean-square displacements for the nonhydrogen atoms.

Description of the Structure

The structure of bis[*N*-(2-hydroxyethyl)ethylenediamine]-copper(II) perchlorate consists of discrete $[Cu(hn)_2]^{2+}$ cations and perchlorate anions. Bond distances and angles with their estimated standard deviations are given in Table IV. Each of the hn ligands is tridentate, coordinating in a facial configuration. The geometric arrangement of ligand donors

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(10) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(11) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 213.

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

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

Table III. Root-Mean Square Displacements (Å) of Principal Axes of Thermal Ellipsoids for Nonhydrogen Atoms[a]

Atom	Axis 1	Axis 2	Axis 3
Cu	0.205	0.190	0.156
Cl(1)	0.236	0.220	0.194
Cl(2)	0.258	0.212	0.196
O(1)	0.333	0.250	0.181
O(2)	0.291	0.230	0.215
O(3)	0.482	0.327	0.217
O(4)	0.557	0.381	0.252
O(5)	0.589	0.418	0.191
O(6)	0.503	0.277	0.252
O(7)	0.347	0.296	0.228
O(8)	0.329	0.270	0.204
O(9)	0.358	0.292	0.181
O(10)	0.341	0.307	0.194
N(1)	0.272	0.213	0.173
N(2)	0.233	0.198	0.166
N(3)	0.214	0.209	0.189
N(4)	0.282	0.255	0.175
C(1)	0.288	0.251	0.193
C(2)	0.277	0.225	0.192
C(3)	0.262	0.204	0.182
C(4)	0.284	0.250	0.182
C(5)	0.306	0.260	0.183
C(6)	0.300	0.244	0.178
C(7)	0.308	0.249	0.193
C(8)	0.343	0.261	0.201

[a] Orientations of thermal ellipsoids may be seen by reference to Figure 1.

Table IV. Bond Lengths (Å) and Angles (deg)[a]

	Bond Lengths		
Cu-O(1)	2.518 (3)	Cl(2)-O(10)	1.424 (3)
Cu-O(2)	2.419 (3)	O(1)-C(4)	1.413 (7)
Cu-N(1)	2.012 (4)	O(2)-C(5)	1.421 (6)
Cu-N(2)	2.036 (3)	N(1)-C(1)	1.497 (7)
Cu-N(3)	2.041 (3)	N(2)-C(2)	1.499 (6)
Cu-N(4)	2.018 (4)	N(2)-C(3)	1.484 (6)
Cl(1)-O(3)	1.405 (4)	N(3)-C(6)	1.469 (5)
Cl(1)-O(4)	1.355 (6)	N(3)-C(7)	1.465 (6)
Cl(1)-O(5)	1.328 (5)	N(4)-C(8)	1.449 (7)
Cl(1)-O(6)	1.393 (4)	C(1)-C(2)	1.467 (7)
Cl(2)-O(7)	1.423 (4)	C(3)-C(4)	1.478 (6)
Cl(2)-O(8)	1.425 (4)	C(5)-C(6)	1.485 (7)
Cl(2)-O(9)	1.431 (3)	C(7)-C(8)	1.504 (7)
	Bond Angles		
O(1)-Cu-O(2)	154.7 (1)	O(7)-Cl(2)-O(10)	108.2 (2)
O(1)-Cu-N(1)	113.3 (1)	O(8)-Cl(2)-O(9)	108.2 (2)
O(1)-Cu-N(2)	74.8 (1)	O(8)-Cl(2)-O(10)	111.2 (2)
O(1)-Cu-N(3)	80.7 (1)	O(9)-Cl(2)-O(10)	109.0 (2)
O(1)-Cu-N(4)	92.3 (1)	Cu-O(1)-C(4)	105.9 (3)
O(2)-Cu-N(1)	89.6 (1)	Cu-O(2)-C(5)	107.7 (3)
O(2)-Cu-N(2)	97.7 (1)	Cu-N(1)-C(1)	108.8 (3)
O(2)-Cu-N(3)	76.6 (1)	Cu-N(2)-C(2)	107.2 (2)
O(2)-Cu-N(4)	96.6 (1)	Cu-N(2)-C(3)	114.1 (3)
N(1)-Cu-N(2)	84.8 (2)	C(2)-N(2)-C(3)	112.3 (3)
N(1)-Cu-N(3)	166.0 (1)	Cu-N(3)-C(6)	113.4 (3)
N(1)-Cu-N(4)	95.0 (2)	Cu-N(3)-C(7)	107.9 (3)
N(2)-Cu-N(3)	98.7 (1)	C(6)-N(3)-C(7)	116.8 (4)
N(2)-Cu-N(4)	165.7 (2)	Cu-N(4)-C(8)	108.6 (3)
N(3)-Cu-N(4)	84.9 (2)	N(1)-C(1)-C(2)	107.7 (4)
O(3)-Cl(1)-O(4)	111.1 (3)	C(1)-C(2)-N(2)	110.1 (4)
O(3)-Cl(1)-O(5)	110.8 (3)	N(2)-C(3)-C(4)	112.0 (3)
O(3)-Cl(1)-O(6)	106.0 (3)	C(3)-C(4)-O(1)	108.7 (4)
O(4)-Cl(1)-O(5)	109.8 (3)	O(2)-C(5)-C(6)	111.8 (4)
O(4)-Cl(1)-O(6)	111.2 (3)	C(5)-C(6)-N(3)	112.8 (4)
O(5)-Cl(1)-O(6)	107.9 (3)	N(3)-C(7)-C(8)	110.5 (4)
O(7)-Cl(2)-O(8)	108.9 (2)	C(7)-C(8)-N(4)	109.2 (4)
O(7)-Cl(2)-O(9)	111.4 (2)		

[a] The figures in parentheses are standard deviations of least significant digits.

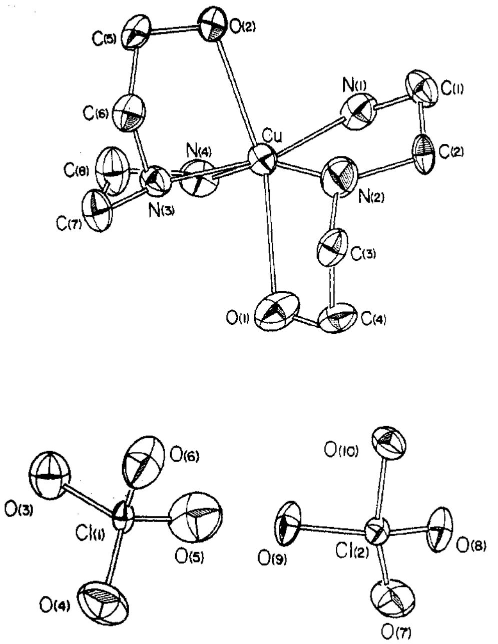

Figure 1. Thermal ellipsoids of the nonhydrogen atoms of bis[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) perchlorate.

about the central copper atom is a distorted octahedron with the chemically equivalent amino groups cis to each other at Cu-N distances of 2.012 (4), 2.018 (4), 2.036 (3), and 2.041 (3) Å, while the alcohol groups are trans to each other at Cu-O distances of 2.419 (3) and 2.518 (3) Å. On the basis of the standard deviations, the difference in the Cu-O bond lengths is significant. However, both distances are comparable to similar dimensions found in other axially elongated octahedral complexes of Cu(II).[14] The Cu-N distances are likewise in good agreement with the values found in several complexes of copper(II) with *N*-alkyl-substituted ethylenediamines.[15-18] The differences between the Cu-N(primary) and Cu-N(secondary) bond lengths may also be significant ($\Delta/\sigma > 3$).

In addition to the characteristic tetragonal elongation, there are two other distortions in the coordination configuration which appear to have been imparted by the mode of chelation. First, the O(1)-Cu-O(2) bond angle (154.7 (1)°) is considerably removed from the idealized value of 180°. This type of distortion has been found in other axial complexes where chelation occurs out of the equatorial plane.[19] Second, the four nitrogen atoms are not coplanar with the copper atom but rather are situated at the apices of a very flattened tetrahedron. The copper atom lies in the mean plane defined by the nitrogen atoms, but the nitrogen atoms themselves lie alternately above and below their mean plane (each by about 0.25 Å). These tetrahedral distortions from planarity would tend to accommodate the axial elongation, since each secondary nitrogen atom is displaced from the defining plane in the direction of the hydroxyethyl group to which it is attached.

Bond distances within the hn ligands concur rather well with previously reported values. The average C-N and C-C

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[18] A. Pajunen and J. Korvendanta, *Suom. Kemistilehti B*, 42, 261 (1969).

[19] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970).

Table V. Deviations (Å) of the Carbon Atoms from the Plane of the Copper Atom and Ligand Donors[a]

Equation of the plane	Defining atoms	Deviations
$8.430x + 10.156y + 1.576z - 3.662 = 0$	Cu, N(1), N(2)	C(1) −0.37, C(2) 0.30
$0.989x - 0.134y + 0.006z - 0.669 = 0$	Cu, N(2), O(1)	C(3) −0.49, C(4) 0.18
$1.202x - 2.891y + 8.469z - 2.333 = 0$	Cu, N(3), O(2)	C(5) 0.00, C(6) −0.54
$4.711x + 12.120y - 0.033z - 3.213 = 0$	Cu, N(3), N(4)	C(7) 0.23, C(8) −0.39

[a] x, y, z are the coordinates in terms of the unit cell basis vectors.

Table VI. Hydrogen Bond Lengths and Angles[a]

A	B	A–B, Å	A–H, Å	H–B, Å	A–H–B, deg
N(1)–H(2)- - -	O(10)	3.259 (5)	0.88 (3)	2.46 (3)	151 (3)
N(2)–H(7)- - -	O(9)^{vi}	3.269 (5)	0.85 (3)	2.44 (3)	165 (3)
N(3)–H(18)- - -	O(3)^{vi}	3.075 (5)	0.93 (3)	2.18 (3)	160 (3)
N(4)–H(24)- - -	O(5)	3.152 (7)	1.03 (3)	2.17 (4)	159 (3)
N(4)–H(23)- - -	O(6)^{viii}	3.019 (6)	0.95 (3)	2.15 (3)	152 (3)

[a] See footnote *a*, Table VII, on symmetry transformations.

Table VII. Interionic Contact Distances[a]

A	B	A–B, Å	A	B	A–B, Å
O(3)- - -	N(3)^{iv}	3.08	O(7)- - -	C(6)^{iv}	3.48
O(3)- - -	C(3)^{iv}	3.42	O(8)- - -	O(2)^{vii}	3.14
O(4)- - -	O(1)^{ix}	3.37	O(8)- - -	N(1)^{vii}	3.40
O(4)- - -	C(1)^{i}	3.38	O(9)- - -	O(2)^{iv}	3.32
O(5)- - -	N(4)	3.15	O(9)- - -	O(2)^{vii}	3.06
O(5)- - -	N(1)	3.01	O(9)- - -	O(9)^{iii}	3.04
O(6)- - -	N(4)^{ix}	3.02	O(9)- - -	N(2)^{iv}	3.27
O(6)- - -	C(5)^{ii}	3.41	O(10)- - -	N(2)^{iv}	3.47
O(6)- - -	C(6)^{ii}	3.40	O(10)- - -	N(1)	3.26
O(7)- - -	O(1)	3.12	O(10)- - -	C(3)^{iv}	3.48
O(7)- - -	N(1)	3.41	O(10)- - -	C(7)^{v}	3.49

[a] Symmetry transformations with respect to the coordinates listed in Table II are as follows: none, x, y, z; i, $x, y, 1 + z$; ii, $-x, -y, 1 - z$; iii, $1 - x, 1 - y, 1 - z$; iv, $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; v, $^1/_2 + x, ^1/_2 - y, -^1/_2 + z$; vi, $-^1/_2 + x, ^1/_2 - y, -^1/_2 + z$; vii, $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$; viii, $^1/_2 - x, ^1/_2 + y, ^3/_2 - z$; ix, $^1/_2 - x, -^1/_2 + y, ^3/_2 - z$.

distances are 1.477 (8) and 1.483 (8) Å, respectively. The C–O bond lengths are in good agreement with the mean of several such distances found in hydroxycarboxylate complexes (1.426 (7) Å).[20]

There is some evidence of angular strain within the two ligands. The largest of these distortions occurs at the secondary nitrogen atoms; the Cu–N(2)–C(3) (114.1 (3)°) and C(6)–N(3)–C(7) (116.8 (4)°) angles are 15σ and 18σ, respectively, from the strain free tetrahedral value. Analogous distortions have been found at the asymmetric nitrogen atoms in a few triethylenetetramine complexes.[21]

One of the perchlorate groups [Cl(1), O(3), O(4), O(5), O(6)] is disordered and the Cl–O bond lengths for that group are observed to be somewhat shorter than the normal distance (*ca.* 1.43 Å).[22] Both the large vibrational displacements of the group's oxygen atoms and the apparent contraction of the Cl–O bond lengths would suggest that the disorder is dynamic.

Conformations of the hn Chelate Rings. The geometries of the copper–ethylenediamine cycles in $[Cu(hn)_2]^{2+}$ are generally accordant with the results of the classical calculations of Corey and Bailar.[23] The N–Cu–N ring angles (84.8 (2) and 84.9 (2)°) are near to the suggested strain-free value of 86.2°. The corresponding N–Cu–O ring angles (74.8 (1) and 76.6 (1)°) are significantly smaller and reflect the strain imparted by the axial attachment of the alcoholic oxygen atoms. The dihedral angles about the C–C bonds are as follows: C(1)–C(2), 51.6°; C(3)–C(4), 55.6°; C(5)–C(6), 48.9°; C(7)–C(8), 45.4°.

Table V gives the deviations of the carbon atoms from the plane of the copper atom and ligand donors. The ring associated with ligand donors N(1) and N(2) adopts a nearly symmetrical-skew conformation. The other conformations are unsymmetrical, particularly that of the ring associated with donors N(3) and O(2) where the so-called eclipsed envelope conformation is formed; *i.e.*, the four atoms Cu, N(3), O(2), and C(5) are coplanar, while C(6) is off this plane at a distance of 0.54 Å.

Another interesting aspect of the structure is noted in the various ring conformations. The copper–ethylenediamine cycles have opposite chiralities (δλ or λδ), whereas the rings formed by the chelation of the *N*-2-hydroxyethyl groups are similar in handedness (δδ or λλ).[24] The relative helicities of

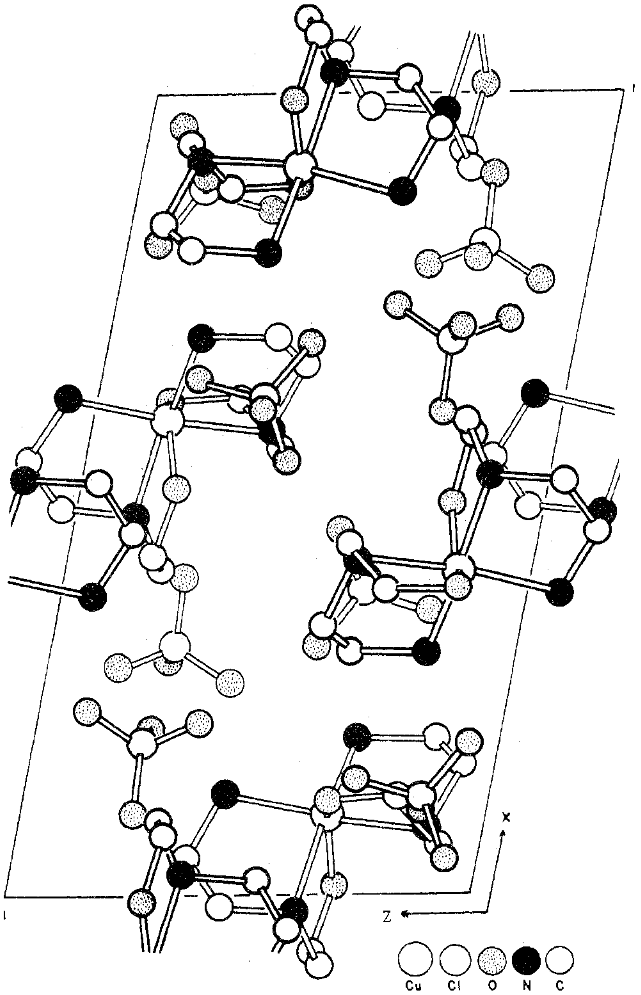

Figure 2. Projection of the unit cell along the *b* axis of bis[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) perchlorate.

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the conformers indicate that in one of the ligands (with donors N(3), N(4), O(2)) the rings have inverted conformations, while in the other ligand (with donors N(1), N(2), O(1)) the chiralities are alike.

Hydrogen Bonding and Nonbonded Contacts. Table VI gives pertinent data relevant to the hydrogen bonding. Nonbonded contacts less than 3.5 Å are listed in Table VII. Figure 2 shows a projection of the unit cell along the *b* axis.

Each complex cation is involved in five N-H- - -O hydrogen bonds with three neighboring perchlorate groups. Two of the bonds appear to be weak. Their N-O distances (3.259 (5) and 3.269 (5) Å) are longer than the upper limit listed by Pimentel and McClellan[25] for such bonds. However, the H-O distances for these bonds (2.46 (3) and 2.44 (3) Å) are significantly shorter than the sum of the van der Waals radii for an oxygen atom and a hydrogen atom (2.6 Å).[26] The N-H- - -O angles each deviate from linearity and range from 151 (3) to 165 (3)°.

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Registry No. $[Cu(C_4H_{12}N_2O)_2](ClO_4)_2$, 36539-67-0.

Supplementary Material Available. Table I, 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 $5.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2621.

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An Unsymmetrical *trans*-Dinitrocobalt(III) Complex. A Crystal Structure Determination

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The crystal structure of *trans*-dinitro-2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone)dioximatocobalt(III), $[Co(PnAO\text{-}H)(NO_2)_2]^0$, $C_{13}H_{27}N_6O_6Co$, has been determined from three-dimensional X-ray diffraction data. Unit cell dimensions are $a = 8.563 \pm 0.008$ Å, $b = 16.62 \pm 0.02$ Å, $c = 17.54 \pm 0.02$ Å, and $\beta = 133.4 \pm 0.1°$; the space group is $P2_1/c$. The density by flotation is 1.55 g/cm^3; four formula units in the unit cell give a calculated density of 1.547 g/cm^3. The basic structure was obtained from film data. The final parameters were obtained by refinement using the intensities of 2963 independent reflections measured with a Picker diffractometer using a scintillation counter. Three-dimensional Patterson and Fourier methods, followed by full-matrix least-squares refinement, gave a conventional *R* factor of 3.5%. The structure consists of discrete neutral molecules with near-octahedral coordination about the cobalt atom. The nitro groups are nitrogen bound and are in the trans configuration. The nitro nitrogens are different distances from the cobalt atom (1.984 ± 0.003 and 1.937 ± 0.003 Å) with the cobalt slightly out of the plane of the amine and oxime nitrogens toward the nitro nitrogen with the short Co-N distance. Weak intramolecular hydrogen bonding may occur between one set of the nitro oxygens and the amine hydrogens. The O- - -O distance for the characteristic intramolecular hydrogen bond formed between the oxime groups is 2.432 ± 0.003 Å.

Introduction

The molecule described in this paper is of special interest from two points of view. First, it contains a short intramolecular hydrogen bond which may be nearly symmetrical.[1] Structures of similar planar complexes of α-amine oxime ligands[2,3] with Ni(II) and Pt(II) have been determined and compared with the dimethylglyoximates[4] and glyoximates[5,6] of these metals. Modifications in the hydrogen bond due to a small metal ion such as Co(III) and to an octahedral geometry could lead to a better understanding of the nature of all hydrogen bonds. Second, this complex is related to vitamin B_{12} in having a strongly planar inducing ligand and apical positions containing more labile groups. Numerous chemical studies have been made on the cobalt(II)-cobalt(III)-bis(dimethylglyoxime) system which has been called a model system[7] for the B_{12} moiety. Of consequence is the possibility that the apical positions are not equivalent and that one may have considerably more π-bonding capability than the other. If a difference exists, then the cause, steric or electronic, becomes important. This paper summarizes a structure determination on a complex with a strong tetradentate ligand PnAO (Figure 1) in the planar positions and nitro groups in the trans positions. Before and during this structural study, chemical experiments were being conducted investigating the kinetic behavior toward substitution of the trans nitro groups. A substantial difference in lability for the two nitro groups was observed.

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