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The Crystal and Molecular Structure of Bis-(1,4-diazacycloheptane)copper(II) Nitrate Hemihydrate*

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Bis-(1,4-diazacycloheptane)copper(II) nitrate hemihydrate,



crystallizes in the monoclinic space group $P2_1/n$ with $a=20.92$, $b=15.79$, $c=10.04 \text{ \AA}$ and $\beta=91.7^\circ$. There are four formula units per unit cell. The structure was solved by Patterson and Fourier techniques and refined by least-squares calculations, based on 3845 reflections measured on a Picker automatic diffractometer; the final R index was 0.11. The copper atoms in the $[\text{Cu}(\text{dach})_2\text{NO}_3]^+$ and $[\text{Cu}(\text{dach})_2\text{H}_2\text{O}]^{2+}$ cations have approximately square pyramidal coordination with average equatorial Cu-N and average axial Cu-O bond lengths of 2.01 and 2.34 Å, respectively. The chelated 1,4-diazacycloheptane moieties are in double-boat conformation. This is the first structural analysis of a bis complex of a cyclic diamine with a transition metal.

Introduction

Pentacoordinated copper complexes may have either trigonal bipyramidal (D_{3h}) or square pyramidal (C_{4v}) structures. Copper(II) complexes of 6-methyl-2-picolyamine (Sutton, 1963; Utsuno & Sone, 1966) and tris-(2-dimethylaminoethyl)amine with Cl^- , Br^- or ClO_4^- ions occupying the fifth position (Ciampolini & Nardi, 1966) are examples of the former structure. The square pyramidal arrangement around copper(II) has been

observed in N,N' -ethylene-bis(acetylacetonimine)copper(II) monohydrate (Hall, Morgan & Waters, 1966), in N,N' -disalicylidene-propane-1,2-diaminecopper(II) monohydrate (Llewellyn & Waters, 1960) and in 4-methylpyridine-bis-(*o*-hydroxyacetophenonato)-copper(II) (Duckworth, Graddon, Mockler & Stephenson, 1967).

Recently the preparation and characterization of copper(II) complexes of 1,4-diazacycloheptane (dach) have been reported (Musker & Hussain, 1967). It was concluded that addition of tetraethylammonium chloride or bromide to bis-(1,4-diazacycloheptane)copper(II) perchlorate in nitromethane resulted in pentacoordinated species, in which the substituent at the assumed apical position could be varied systematically

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without affecting the coordination of the ligand itself. Only one of the perchlorate groups in $[\text{Cu}(\text{dach})_2](\text{ClO}_4)_2$ could be exchanged with chloride, bromide, thiocyanate or nitrate, forming an assumed pyramidal structure of the type $[\text{Cu}(\text{dach})_2\text{X}]\text{ClO}_4$ where X is any one of these anions. The visible absorption spectra of $[\text{Cu}(\text{dach})_2\text{NO}_3]\text{ClO}_4$ and $\text{Cu}(\text{dach})_2(\text{NO}_3)_2$ were identical, suggesting that both complexes have the same cation, $[\text{Cu}(\text{dach})_2\text{NO}_3]^+$, and that the dinitrate should be formulated as $[\text{Cu}(\text{dach})_2\text{NO}_3](\text{NO}_3)$. It was anti-

cipated that the present crystal-structure determination would be useful in correlating the spectra and structures of copper complexes of 1,4-diazacycloheptane.

Prior to this study no crystal structure of a transition metal chelate was known in which two cyclic bidentate amino ligands were attached to the metal atom. The complexes of medium-ring ligands reported in the literature (Gillard & Irving, 1965) are those with 1,4-diheterocyclohexanes as ligands, with N, O, S, Se, P

Table 1. *The final fractional coordinates and isotropic temperature factors (\AA^2) for one $[\text{Cu}(\text{dach})_2\text{H}_2\text{O}](\text{NO}_3)_2 \cdot [\text{Cu}(\text{dach})_2(\text{NO}_3)]\text{NO}_3$ unit*

The estimated standard deviations given in parentheses refer to the last decimal position.

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	
	Cu(1)*	0.35145 (7)	0.50961 (10)	0.26004 (16)	—	
	Cu(2)*	0.87142 (7)	0.50580 (10)	0.22003 (17)	—	
Cation <i>A</i>	N(3)	0.3593 (4)	0.6266 (5)	0.1828 (9)	3.0 (2)	
	C(4)	0.3120 (5)	0.6782 (7)	0.2478 (11)	3.1 (2)	
	C(5)	0.3072 (5)	0.6525 (7)	0.3983 (12)	3.3 (2)	
	N(6)	0.3527 (4)	0.5811 (5)	0.4252 (9)	2.7 (1)	
	C(7)	0.4192 (5)	0.6142 (7)	0.4529 (12)	3.6 (2)	
	C(8)	0.4399 (6)	0.6796 (8)	0.3552 (14)	4.4 (2)	
	C(9)	0.4261 (6)	0.6581 (8)	0.2074 (13)	4.3 (2)	
	N(10)	0.3654 (4)	0.4402 (5)	0.0961 (9)	3.4 (2)	
	C(11)	0.3266 (7)	0.3597 (9)	0.1144 (15)	4.5 (3)	
	C(12)	0.3272 (6)	0.3360 (7)	0.2619 (13)	3.8 (2)	
	N(13)	0.3690 (4)	0.3951 (6)	0.3390 (10)	3.3 (2)	
	C(14)	0.4373 (8)	0.3739 (10)	0.3274 (17)	5.4 (3)	
	C(15)	0.4557 (6)	0.3518 (8)	0.1861 (13)	7.5 (2)	
	C(16)	0.4349 (7)	0.4197 (10)	0.0892 (16)	5.3 (3)	
	O(17)	0.2407 (4)	0.5005 (5)	0.2474 (9)	4.3 (2)	
	Nitrate group I	O(18)	0.3654 (5)	0.8740 (6)	0.3417 (10)	5.1 (2)
		O(19)	0.4334 (5)	0.9134 (6)	0.4706 (10)	4.9 (2)
N(20)		0.3768 (4)	0.9141 (5)	0.4369 (9)	2.9 (2)	
O(21)		0.3383 (4)	0.9584 (5)	0.5010 (8)	3.8 (1)	
Nitrate group II	O(22)	0.4283 (7)	0.0353 (11)	0.1981 (16)	8.4 (3)	
	N(23)	0.4078 (4)	0.1041 (6)	0.1990 (9)	3.1 (2)	
	O(24)	0.3497 (5)	0.1193 (7)	0.1819 (11)	5.4 (2)	
	O(25)	0.4436 (7)	0.1613 (9)	0.2346 (14)	7.3 (3)	
Cation <i>B</i>	N(26)	0.9461 (4)	0.4320 (5)	0.1778 (9)	3.1 (2)	
	C(27)	0.9238 (6)	0.3757 (8)	0.0686 (14)	4.6 (2)	
	C(28)	0.8530 (6)	0.3541 (8)	0.0891 (14)	4.3 (2)	
	N(29)	0.8309 (4)	0.3908 (6)	0.2081 (10)	3.6 (2)	
	C(30)	0.8482 (7)	0.3391 (9)	0.3263 (15)	4.6 (3)	
	C(31)	0.9191 (7)	0.3138 (9)	0.3311 (15)	5.0 (3)	
	C(32)	0.9654 (6)	0.3821 (8)	0.2994 (14)	4.2 (2)	
	N(33)	0.9169 (4)	0.6129 (5)	0.2795 (9)	2.9 (2)	
	C(34)	0.8774 (6)	0.6834 (8)	0.2292 (13)	4.1 (2)	
	C(35)	0.8065 (6)	0.6627 (8)	0.2365 (14)	4.4 (2)	
	N(36)	0.7998 (4)	0.5748 (6)	0.2933 (9)	3.5 (2)	
	C(37)	0.8066 (8)	0.5742 (10)	0.4404 (16)	5.4 (3)	
	C(38)	0.8624 (8)	0.6296 (11)	0.4919 (17)	5.9 (3)	
C(39)	0.9246 (6)	0.6141 (9)	0.4244 (14)	4.6 (2)		
Nitrate group III	O(40)	0.8141 (5)	0.8866 (7)	0.2169 (11)	6.0 (2)	
	O(41)	0.8859 (6)	0.8802 (8)	0.3788 (13)	6.8 (2)	
	N(42)	0.8322 (5)	0.8980 (6)	0.3282 (10)	3.5 (2)	
	O(43)	0.7968 (7)	0.9270 (9)	0.4126 (14)	7.8 (3)	
Nitrate group IV	O(44)	0.8361 (10)	0.0828 (12)	0.1158 (21)	10.9 (5)	
	O(45)	0.9233 (14)	0.0731 (20)	0.1646 (29)	14.7 (7)	
	N(46)	0.8751 (8)	0.0934 (10)	0.1999 (16)	6.6 (3)	
	O(47)	0.8409 (8)	0.1031 (12)	0.3103 (19)	10.3 (4)	

* The anisotropic thermal parameters for Cu(1) and Cu(2) are given in Table 2.

or a combination of these as hetero atoms, but for chelation these cyclohexanes must attain a rather constrained boat conformation, and no such compound has been reported to form a chelate with a first-row transition metal. The six-membered 1,4-diazacyclohexane (piperazine) ring does not form complexes with copper(II) and nickel(II) and only hydroxides are formed (Obear, 1960). However, the expansion from a six-membered cyclic diamine to a seven- or eight-membered diamine rendered possible the formation of chelated complexes with copper(II) and nickel(II) in aqueous, as well as in non-aqueous, solvents (Musker & Hussain, 1966, 1969). One of the objectives of the present investigation was to establish the conformation of the five- and six-membered chelate rings formed by the 1,2-diaminoethane or 1,3-diaminopropane moieties of the ligands.

Experimental

Bis(1,4-diazacycloheptane)copper(II) nitrate hemihydrate was prepared by adding an excess of 1,4-diazacycloheptane in anhydrous ether to an ethanolic solution of copper(II) nitrate trihydrate containing 10–15 ml of 2,2-dimethoxypropane. By very slow evaporation at room temperature of a 10^{-3} M solution of the compounds in nitromethane, bright maroon-colored plates were obtained. The crystals were stable in the atmosphere as well as under X-radiation for several days.

The space group was determined from rotation and Weissenberg photographs taken with Cu $K\alpha$ radiation. The density was measured by the flotation method in a mixture of benzene and carbon tetrachloride. The cell dimensions were calculated by a least-square treatment based on twelve angles measured on a diffractometer.

Crystal data

[Cu(dach)₂(NO₃)]NO₃. [Cu(dach)₂H₂O](NO₃)₂.

Monoclinic.

$a = 20.92 \pm 0.02$, $b = 15.79 \pm 0.02$, $c = 10.04 \pm 0.01$ Å;

$\beta = 91.7 \pm 0.1^\circ$.

$V = 3316$ Å³.

$D_m = 1.60 \pm 0.03$ g.cm⁻³, $D_{calc} = 1.58$ g.cm⁻³, $Z = 4$;

$F(000) = 1664$.

Absent spectra: $0k0$ when k is $2n+1$, $h0l$ when $h+l$ is $2n+1$; space group, $P2_1/n$. All atoms occupy the general fourfold set of positions $\pm(x, y, z)$ and $\pm(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

The crystal used for gathering three-dimensional intensity data was a plate with approximate dimensions $0.5 \times 0.25 \times 0.07$ mm³. The data were collected on a Picker automatic diffractometer equipped with a full-circle goniostat. The needle axis of the crystal was mounted close to the ϕ axis. The radiation used was Cu $K\alpha$ filtered through a nickel foil placed in the incident beam collimator. A total of 5362 unique reflections accessible below $2\theta = 133^\circ$ were scanned by the $2\theta-\theta$ technique at a scan speed of 2° min^{-1} . The scan range for all reflections was from $[2\theta(\alpha_1) - 0.75^\circ]$ to $[2\theta(\alpha_2) + 0.75^\circ]$. Stationary-counter background counts of 10 seconds duration were taken at each end of the scan range. To keep coincidence losses low, the automatic attenuator mechanism was set to add an attenuation filter when the count rate exceeded 10,000 counts per second during the scan. As a check on electronic and crystal stability during the period of data collection, the intensities of three standard test reflections (18, 0, 0, 0, 16, 0 and 0, 0, 6) were measured periodically. No systematic drift in these reflections was observed. Altogether 3845 reflections for which the net intensity exceeded three times its estimated standard deviation (from counting statistics) were recorded as observed; other reflections were not included in subsequent calculations. The intensities were corrected for the usual Lorentz and polarization effects but no correction was made for absorption.

Solution and refinement of the structure

The structure was solved by the heavy-atom method. From a sharpened three-dimensional Patterson map the x and z coordinates for the two copper atoms were readily derived. Both y coordinates were found to be close to zero (or one-half); from the elongation of one of the Cu–Cu($2x, 2y, 2z$) peaks, one of the copper atoms was assigned a y coordinate of 0.01 while the other was placed at $y = 0$. An electron-density synthesis based on the phases from these parameters indicated more reliable displacements from $y = 0$ for the two copper atoms, but the rest of the structure could not be easily recognized. A second Fourier synthesis based on the improved copper parameters clearly showed the positions of the atoms in the ligand molecules including one nitrate group. A third Fourier synthesis, based on phases from all atoms located so far, revealed the positions of a water oxygen atom bonded to one copper atom and the remaining nitrate groups, although two of the nitrate groups appeared with rather ill-defined peaks; a reasonable explanation of these ir-

Table 2. Final anisotropic thermal parameters and their standard deviations ($\times 10^5$) for copper atoms

B_{ij} are coefficients in the temperature factor expression $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	108 (5)	319 (6)	584 (5)	13 (1)	-30 (3)	80 (3)
Cu(2)	127 (6)	245 (5)	499 (4)	-10 (1)	-33 (3)	-38 (2)

Table 3. Observed and calculated structure factors
In the three columns are listed h, |Fo| and |Fc| in that order.

Table with multiple columns containing numerical data for structure factors. The table is organized into several vertical sections, each with its own header (e.g., h, |Fo|, |Fc|). The data consists of integers and some negative values, representing the observed and calculated structure factors for various reflections.

Table 3 (cont.)

Table with multiple columns of numerical data and labels such as K* 10, L* 6, K* 5, L* 7, K* 1, L* 8, K* 9, L* 8, K* 5, L* 9. The table contains a dense grid of numbers and symbols, likely representing crystallographic or spectroscopic data.

regularities, arrived at near the end of the refinement, appeared to be that at least one, and possibly, both of these nitrate groups were disordered. With an overall temperature coefficient B of 4 \AA^2 the R index at this stage was 0.25, and a total difference synthesis calculated showed no disturbing features other than some residual electron density around the apparently disordered nitrate groups. Inspection of the list of observed and calculated structure factors revealed some large differences for some of the very intense low-angle reflections, indicating sizeable secondary extinction effects. This observation, together with our decision not to include hydrogen atoms in the calculations, and the already rather lengthy computer runs, led us to exclude all reflections with $\sin \theta/\lambda$ values below 0.23 (about 300 reflections) from the least-squares refinement. The full-matrix program* could adjust a maximum of 163 parameters on an IBM 7044 computer. Therefore the refinement was accomplished by processing about one-half of the 47 atoms in the structure at a time. The first complete cycle (two runs), carried out with isotropic temperature factors for all atoms, reduced R from 0.25 to 0.13. Anisotropic temperature factors were then introduced for copper, and four more refinement cycles were executed. Refinement was concluded when all shifts were less than 10% of the corresponding estimated standard deviation. The final value of the R index is 0.11 for all observed reflections above $\sin \theta/\lambda = 0.23$. No allowance was made for the hydrogen atoms.

In Table 1 the final positional parameters and isotropic temperature coefficients B together with estim-

* The program was a local version of *ACA* 317 written for the IBM 7090 by P. K. Gantzel, R. A. Sparks, R. E. Long & K. N. Trueblood. The weighting scheme used for the observed reflections in this investigation was that of Hughes (1941) with $4F_o(\text{min}) = 56$. In all calculations of F_c the atomic scattering factors for neutral atoms tabulated by Hanson, Herman, Lea & Skillman (1964) were used for Cu, N, O and C. The real part of the dispersion correction ($\Delta f' = 2.1$) for Cu $K\alpha$ radiation was applied to the form factor of Cu, but the imaginary part was ignored. The standard deviations were estimated from the inverse matrix of the normal equations. R is defined by $R = \Sigma [(F_o - |F_c|)] / \Sigma F_o$. The program minimizes the weighted sum of the square of the quantity $(KF_o - G|F_c|)$, where F_o is the input structure factor, K is its scale factor, F_c is the calculated structure factor, and G is its scale factor.

ated standard deviations are given for all atoms. Anisotropic temperature coefficients for the two copper atoms are given in Table 2. A comparison of observed and calculated structure factors is given in Table 3. The parameters given in Tables 1 and 2 were used in the calculation of F_c 's.

Introduction of anisotropic temperature factors for C, N, and O probably would lead to a lower R index. We felt, however, that for the present purpose the structure is adequately described. The excellent agreement between the geometrical parameters of the two crystallographically independent cations may be taken as an indication that our error estimates are realistic.

Description of the structure

Packing considerations

The crystal structure is constructed from $[\text{Cu}(\text{dach})_2\text{H}_2\text{O}]^{2+}$, $[\text{Cu}(\text{dach})\text{NO}_3]^+$ and NO_3^- units. Projection of a part of the unit cell is shown in Fig. 1. The $[\text{Cu}(\text{dach})_2]^{2+}$ portions of the two crystallographically independent cations are oriented in such a way that a plane passing through the four amine nitrogen of the cation with Cu(1) as the central atom is approximately perpendicular to the corresponding plane for the molecule with Cu(2) as the central atom. The complex ions and the nitrate groups are bound together by a network of hydrogen bonds. Each of the nitrogen atoms of the cations has an oxygen atom of a neighboring nitrate group at a reasonable distance (3.1 Å or less) to account for all the possible hydrogen bonds (Table 4). The coordinated water molecule also participates in hydrogen bonding and is at distances of 2.97 Å and 2.77 Å from two oxygen atoms [O(18) and O(24)] of nitrate groups. Because the coordinates for the hydrogen atoms were not determined and because of the disorder of the nitrate groups (see below), detailed discussion of hydrogen bonding would be unjustified.

Coordination of copper(II)

The bond distances and angles in the cations are given in Fig. 2. In both cations the four nitrogen atoms of the two ligand molecules are at the corners of a rectangle, with an average Cu---N distance of 2.01 Å. In cation *A*, the oxygen atom of a water molecule

Table 4. Possible A-H...B bonds with A...B distances less than 3.15 Å

Atom A is at position x, y, z .

A	Distance	B	Position of atom B
N(3)	3.120 (16) Å	O(41)	$x - \frac{1}{2}, -y + \frac{1}{2} + 1, z - \frac{1}{2}$
N(6)	3.103 (14)	O(40)	$x - \frac{1}{2}, -y + \frac{1}{2} + 1, z + \frac{1}{2}$
N(10)	2.980 (21)	O(47)	$x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$
N(13)	2.904 (23)	O(44)	$x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$
N(26)	2.980 (14)	O(19)	$-x + \frac{1}{2} + 1, y - \frac{1}{2}, -z + \frac{1}{2}$
N(29)	2.957 (17)	O(43)	$-x + \frac{1}{2} + 1, y - \frac{1}{2}, -z + \frac{1}{2}$
N(33)	3.035 (17)	O(25)	$-x + \frac{1}{2} + 1, y + \frac{1}{2}, -z + \frac{1}{2}$
N(36)	3.014 (23)	O(44)	$-x + \frac{1}{2} + 1, y + \frac{1}{2}, -z + \frac{1}{2}$
O(17)	2.771 (14)	O(24)	$-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$
O(17)	2.969 (13)	O(18)	$-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$

completes the pyramidal arrangement at a distance of 2.32 Å, while in cation *B* an oxygen atom of a nitrate ion is coordinated at the fifth position with a Cu---O distance of 2.36 Å. The rectangles around the copper atoms have an average length of 3.09 Å and a width of 2.53 Å. The copper atoms in both cations are situated close to the center of the rectangle, being slightly (0.2 Å) displaced toward the oxygen atoms. The magnitude of the displacement is the same in both cations, although in cation *A* the fifth ligand is a neutral molecule, while in cation *B* the fifth ligand is part of a negatively charged group. The Cu-O bond in each cation is almost perpendicular to the mean CuN₄ plane.

The coordination of two 1,4-diazacycloheptane molecules to the copper atom results in the formation of two five-membered and two six-membered chelate rings around copper. For chelation the ligand molecules attain a seven-membered boat conformation. Calculated positions of the hydrogen atoms show that hydrogens of the trimethylene groups effectively block

one axial position of the copper atoms while the other axial position is less screened by the hydrogens on the ethylene groups of the five-membered chelate rings. Such an arrangement around the metal atom results in a bowl-type structure in which axial ligation is possible from one side only, resulting in a pyramidal complex.

The nitrate groups

Interatomic distances and angles of the nitrate groups are listed in Table 5. Nitrate groups I through III are essentially planar, as was evident from the least-square plane defined by the four atoms of a particular group, and by the equivalence of the non-bonding O-O distances (average 2.11 Å). The average N-O bond distance is 1.22 Å and the sum of the O-N-O angles is close to 360°. The isotropic temperature factors of the oxygen atoms in these groups are larger than those of the nitrogen atoms. The oxygen atom, O(21), which is coordinated to Cu(2) is positioned most precisely, with a smaller isotropic tem-

Table 5. *Interatomic distances and bond angles in the nitrate groups*

	Distances		Angles	
Nitrate group I	N(20)-O(18)	1.214 (13) Å	O(18)-N(20)-O(21)	118.5 (0.9)°
	N(20)-O(19)	1.222 (13)	O(21)-N(20)-O(19)	119.6 (0.9)
	N(20)-O(21)	1.258 (11)	O(19)-N(20)-O(18)	121.9 (1.0)
Nitrate group II	N(23)-O(22)	1.169 (19)	O(22)-N(23)-O(24)	122.4 (1.2)
	N(23)-O(24)	1.246 (14)	O(24)-N(23)-O(25)	119.1 (1.1)
	N(23)-O(25)	1.221 (16)	O(25)-N(23)-O(22)	117.8 (1.2)
Nitrate group III	N(42)-O(40)	1.184 (15)	O(43)-N(42)-O(40)	121.5 (1.2)
	N(42)-O(41)	1.250 (16)	O(40)-N(42)-O(41)	127.5 (1.2)
	N(42)-O(43)	1.230 (17)	O(41)-N(42)-O(43)	110.8 (1.2)
Nitrate group IV	N(46)-O(44)	1.170 (26)	O(44)-N(46)-O(47)	103.5 (1.8)
	N(46)-O(45)	1.125 (34)	O(47)-N(46)-O(45)	142.7 (2.2)
	N(46)-O(47)	1.346 (26)	O(45)-N(46)-O(44)	110.2 (2.2)

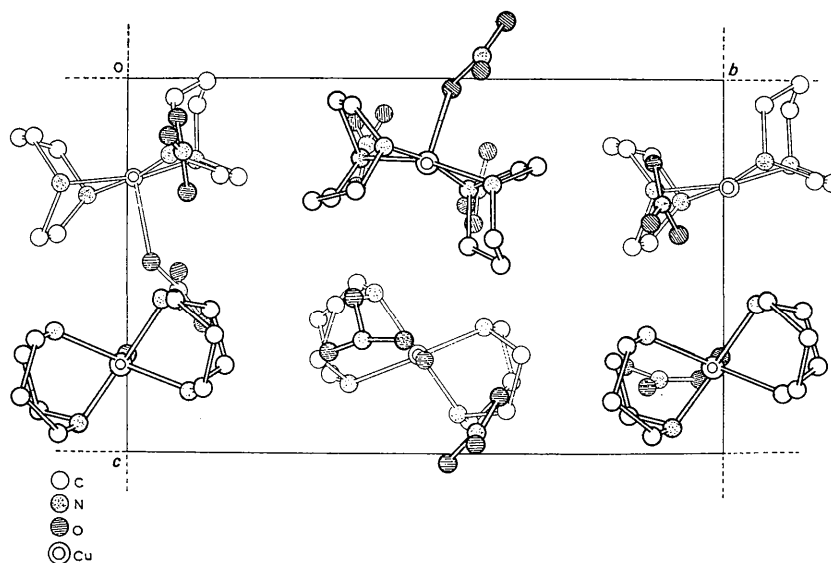


Fig. 1. Projection of one-half of the unit cell showing molecular packing. The portion from $x = \frac{1}{2}$ to $x = 1$ is shown viewed along the *a* axis. Heavily outlined molecules are in one layer and the lightly outlined are in the second. Only two layers are shown.

perature factor than the other oxygen atoms of the nitrate groups.

The situation in regard to the nitrate group IV is less satisfactory. Here the thermal parameters for the oxygen atoms are rather unreasonable. The bond distances between the N and O atoms range from 1.17 to 1.35 Å and the angles from 103 to 142°. The difference map indicated a rotational disorder about the axis O(47)–N(46). However, the nitrate group IV as described by the parameters of Table 1 is a fair approximation to the plane trigonal ion expected.

Since our principal interest was in the cations, the problem of disorder of the nitrate groups was not treated in any further detail. This problem has not led to any ambiguity in regard to the coordination of the cations and the parameters of the remainder of the structure appear to be determined with fairly good precision. Similar disorder of the nitrate groups has been observed by other workers (Marsh & Schaefer, 1968).

Discussion

Comparison with related structures

To the best of our knowledge no structural analysis has been reported for a bis-complex of a transition metal having medium-ring diamines as ligands. Thus, a strict comparison between different structures is not possible. The Cu---N, C–C and N–C distances found in this complex are similar to those found in ethylenediamine complexes (Table 6). The N---Cu---N angles, however, are quite different from corresponding angles previously found. The chelate N---Cu---N angles have an average value of 78.6 degrees in the present complex, compared to 90 degrees in ethylenediamine copper complexes. The narrowing of the N---Cu---N angles is connected with the eclipsed conformation of the ethylenediamine moiety (see below), which also leads to a shortening of the nonbonded N–N distance (2.53 Å) in the present complex as compared with the corresponding distance (2.80 Å) in the [Cu(en)₂](ClO₄)₂ complex. The out-of-plane displacement (0.21 Å) of the copper atom toward the oxygen atom of the water molecule or the coordinated nitrate ion is in agreement with other tetragonal pyramidal copper complexes (Hall *et al.*, 1966; Hall, Rae & Waters, 1963). In

N,N'-ethylenbis(acetylacetonimine)copper(II) monohydrate (Hall *et al.*, 1966) and *N,N'*-disalicylidene-propane-1,2-diaminecopper(II) monohydrate (Llewellyn & Waters, 1960), out-of-plane displacements of 0.19 Å and 0.24 Å, respectively, were observed in the directions of the water molecules.

Conformation of the chelate rings

The six-membered (trimethylenediamine) chelate rings which are a part of the bicyclic ring system are in the chair form. For example, the central carbon, C(8), of the trimethylene portion of one of the rings (Fig. 2) is 0.54 Å from the least-squares plane defined by N(3), N(6), C(7) and C(9), whereas the Cu(1) atom is 1.41 Å toward the opposite side of the plane from C(8). The dihedral angles between the above-mentioned plane and the planes defined by either N(3), N(6) and Cu(1) or by (C7), C(9) and C(8) are 109° and 110°, respectively. In both cations, the six-membered chelate rings exhibit the same overall features. A similar conformation was reported by Bosnich, Mason, Pauling, Robertson & Tobe (1966) in the complex dichloro-1,4,8,11-tetraazacyclotetradecanenickel(II); in contrast, the six-membered chelate rings in the complex tris(octamethylpyrophosphoramidate)copper(II) perchlorate (Joesten, Hussain, Lenhart & Venable, 1968) have been found to be essentially planar. The carbon atoms of the five-membered chelate rings are *cis* with respect to the coordinated nitrogen atoms. The average distance of the copper atoms from the least-squares plane defined by the atoms in the ethylenediamine moiety is 1.16 Å, and the dihedral angle between this plane and a plane defined by the copper atom and two amine nitrogen atoms is 106°. The two ethylene carbon atoms are coplanar with the nitrogen atoms. The hydrogen atoms of the five-membered chelate rings are eclipsed, in contrast to the staggered conformation observed in the corresponding chelate rings in ethylenediamine complexes. This eclipsed conformation appears to be a requirement for the five-coordination as found here. If one attempts to twist the five-membered ring so as to let the methylene group in question attain a staggered conformation, one of the methylene hydrogen atoms will move in towards the z axis of the complex, thereby blocking the access in that direction.

Table 6. Comparison of bond lengths and angles with those of related structures

Compound ^a	Stereo-chemistry	Distances (Å) ^b				Angles (°) ^b		Reference
		Cu–N	N–N	N–N'	Cu–O	N–Cu–N	N–Cu–N'	
Cu(en) ₂ (ClO ₄) ₂	Distorted octahedral	2.055 (20)	2.80	3.01	2.61	85.8 (8)	—	<i>c</i>
Cu(C ₁₇ H ₁₈ O ₃ N ₂)	Square pyramidal	1.87	—	—	2.53	83.0	—	<i>d</i>
[Cu(dach) ₂ H ₂ O] (NO ₃) ₂	Square pyramidal	2.007 (9)	2.543 (13)	3.078 (12)	2.322 (9)	78.6 (4)	100.2 (4)	<i>e</i>
[Cu(dach) ₂ NO ₃]NO ₃	Square pyramidal	2.011 (9)	2.528 (13)	3.103 (13)	2.355 (8)	77.9 (4)	100.9 (4)	<i>e</i>

^a en: ethylenediamine; C₁₇H₁₈O₃N₂: *N,N'*-disalicylidene-propane-1,2-diamine. ^b N–N corresponds to the non-bonding distance between amine nitrogen atoms of the same chelate ring whereas N–N' is the distance between the nitrogen atoms of two different chelate rings. (*c*) Pajunen (1967). (*d*) Llewellyn & Waters (1960). (*e*) This work.

cis-Configuration of the ligands

It is possible for two 1,4-diazacycloheptane rings to coordinate to the central metal atom in two different ways. The two carbon chains can both be on the same side of the plane formed by the four nitrogen atoms (*cis* form) or they can be on the opposite side of the plane (*trans* form). In a four-coordinated complex the more symmetric *trans* form would be sterically allowed. In any case of five coordination, steric requirements lead to a *cis* configuration as observed in the two complex ions in the present compound. The dissimilarity of the fifth ligand in the two cations does not seem to have any effect on the disposition of the ligand molecules around the metal atom.

The absorption spectra of the copper(II) complexes of 1,4-diazacycloheptane are solvent- and anion-dependent (Musker & Hussain, 1969). This can be explained by assuming that in the presence of coordinating solvents or anions the *cis* form can easily accommodate a fifth ligand, forming a pyramidal structure and thus changing the spectral properties,

whereas with non-coordinating solvents and anions, a major influence on the metal atom will be exerted only by the four coordinated nitrogen atoms.

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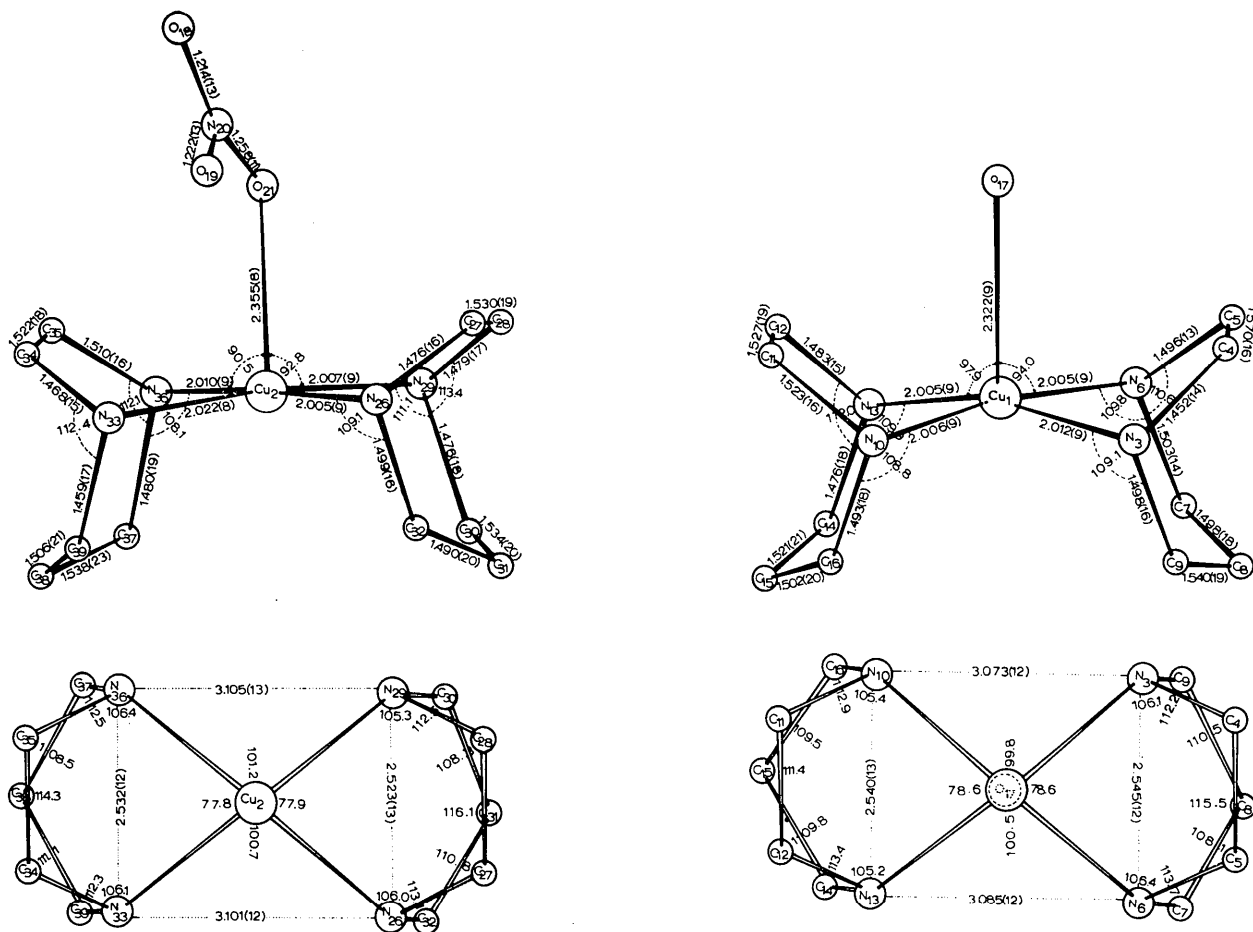


Fig. 2. Perspective views of the cations showing bond lengths and angles. Numbers in parentheses are estimated standard deviations in the least significant digits.

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The Crystal Structure of Hydroxylammonium Perchlorate ($\text{NH}_3\text{OH}^+\text{ClO}_4^-$) at -150°C

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Three crystalline phases of hydroxylammonium perchlorate have been examined by X-ray diffraction. The crystal structure of the most stable phase, which is orthorhombic with space group $P2_1cn$ and cell dimensions $a=7.52(2)$, $b=7.14(1)$, $c=15.99(2)$ Å at 25°C , has been determined at -150°C with data collected by the use of the equi-inclination photographic technique. The final $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.09$ for 1757 observed reflections. The structure consists of chains of perchlorate ion tetrahedra held together by hydrogen bonding from parallel chains of NH_3OH^+ ions. The NH_3OH^+ ions may be rotating with the N-O vector as axis.

Introduction

Hydroxylammonium perchlorate (HAP) crystallizes as colorless but very hygroscopic needles from a mixture of ethanol and chloroform. When the crystals so obtained (called phase A here) are heated, they crack near 55°C (*i.e.* $54\text{--}56^\circ\text{C}$) but retain their external form. Simultaneously, colors appear under the polarizing microscope in a crystal which previously had been in an extinction position. Differential thermal analysis (DTA) studies (Cziesla, 1966; Crisler, 1966) on phase A crystals show an absorption of heat at about 55°C . The above evidence is consistent with a phase change. The phase change is apparently not immediately reversible, although absorption of heat in the DTA studies reappears after the high temperature phase has either been cooled to liquid nitrogen temperatures or has been allowed to stand for about a week.

As part of the elucidation of this phase change and as part of a study of the physical and chemical properties of HAP, the crystal structure at -150°C of the room temperature form (phase A) has been determined and crystals of the high temperature form (phase B,

melting at about $89\text{--}91^\circ\text{C}$) were examined at 70°C . A third phase (phase C) which melts at about 58°C at atmospheric pressure, presumably the phase the possible existence of which was suggested earlier in order to explain anomalous DTA results (Cziesla, 1966), has been grown in capillaries and examined by single-crystal X-ray diffraction.

Since phase A undergoes the phase transition near 55°C and the closely related phases B and C melt near 90°C and near 58°C respectively, and since disorder or rotation has been reported in perchlorate groups (Gomes de Mesquita, MacGillavry & Eriks, 1965; Karle & Karle, 1966; Sundaralingam & Jensen, 1966) and NH_4^+ groups (Smith & Levy, 1962), the X-ray data on phase A were collected at about -150°C with a Weissenberg camera which had been modified slightly (Dickens, 1966) for routine low temperature work.

Determination of the structure

Roughly cylindrical needle-like crystals of phase A, not more than 0.35 mm in cross-section ($\mu_{\text{M}_0} = 8.5 \text{ cm}^{-1}$) were examined under a microscope attached to a dry box (Crisler, 1964) and were sealed into capillaries. The crystals were found to be orthorhombic, with the cell dimensions in Table 1 and space group $P2_1cn$ or $Pm\bar{c}n$. Space group $P2_1cn$ ($x, y, z; \frac{1}{2} + x, \bar{y}, \bar{z}$;

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