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Acta Cryst. (1976). **B32**, 3063

Carbonato(1,4,7,10-tetraazacyclododecane)cobalt(III) Perchlorate Monohydrate

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(Received 16 January 1976; accepted 21 May 1976)

$\text{Co}(\text{C}_8\text{H}_{20}\text{N}_4)\text{CO}_3\text{ClO}_4 \cdot \text{H}_2\text{O}$, orthorhombic, $P2_12_12$, $Z=4$; $a=13.68$ (3), $b=13.32$ (3), $c=8.92$ (2) Å; $\rho_{\text{obs}}=1.69$ (1), $\rho_{\text{calc}}=1.669$ (7) g cm^{-3} . The tetradentate amine ligand occurs in the less symmetric of the two sterically-reasonable configurations and utilizes adjacent octahedral sites on the Co. The other two *cis* sites are occupied by the bidentate carbonate ligand. The cations are linked *via* a hydrogen-bond network and the solvent molecules also hydrogen-bond with each other and with the perchlorate anion.

Introduction

Deep-red crystals of this compound were obtained from J. P. Collman. The crystal chosen for data collection was an almost perfect cube, 0.20 mm on a side. It was mounted along the *c* axis, perpendicular to one of the faces. A similar crystal was used for determination of the lattice constants.

The cell dimensions were determined with a manual General Electric XRD-2 diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation. Least-squares analysis of 2 θ measurements from 27 independent reflections with $\lambda=1.5418$ Å gave the lattice constants and their standard deviations.

The intensity data were collected with a Philips linear diffractometer fitted with a graphite monochromator and $\text{Mo K}\alpha$ radiation. No degradation of the crystal diffraction was apparent from measurements on a monitor peak. The calculated absorption coefficient is $\mu=13.12$ cm^{-2} . No correction was made for absorption, which in this case would cause a maximum error in the intensities of about $\pm 5\%$ from the mean.

Intensity measurements were carried out to $\theta=29^\circ$ ($\sin \theta/\lambda=0.685$); this thus includes a little more than the $\text{Cu K}\alpha$ sphere. Lorentz and polarization corrections were made on all data. Atomic scattering factors used were those of Hanson, Herman, Lea & Skillman (1964). Of the 1360 reflections measured, 420 were zero or classified as insignificant on the basis of counting statistics; this left 940 reflections which were used in the structure determination and early stages of refinement.

Systematic extinctions were observed for $h00$ with h odd and for $0k0$ with k odd. Reflections with non-zero l and either $h0l$ with h odd (39 measured) or $0kl$ with k odd (37 measured) were generally fairly weak or insignificant. These $0kl$ reflections were all zero or insignificant, but four of the $h0l$ reflections had significant intensities. Space group $Pb\bar{3}m$ was considered but $P2_12_12$ was chosen because of these non-extinct reflections and the less reasonable atom parameters and R value in the $Pb\bar{3}m$ refinement. The positions of the Co and Cl atoms were determined by the heavy-atom method and the remaining atoms, other than H,

were found from successive least-squares cycles and electron density syntheses.

Some initial correlation problems in the refinement resulting from a pseudo-mirror through the tetramine ring were overcome by allowing only one of each pair of related atoms to refine in any given least-squares cycle. After a few initial refinement cycles, all atoms except hydrogens were allowed to refine at once without difficulty. In the final stages of refinement the atoms in the perchlorate anion and the Co atom were refined anisotropically. All others were left isotropic; this gave a total of 123 parameters varied. The positions and thermal parameters of the H atoms were not refined. Before each of the final least-squares cycles, H atoms on the cation were inserted in calculated positions with all C-H distances 1.08 Å, N-H distances 0.99 Å, and angles chosen to be as close to tetrahedral as permitted by the bonds to other atoms, and with $B = 4.0 \text{ \AA}^2$. No attempt was made to include the hydrogens of the water molecule.

In the final two least-squares cycles a weighting scheme was introduced where weight = XY with $X = 1$ for $\sin \theta > 0.285$, otherwise $X = \sin \theta / 0.285$; and $Y = 1$ for $F_{\text{obs}} > 30$, and $30/F_{\text{obs}}$ for larger values of F_{obs} . At this stage all reflections with $F_{\text{obs}} < 10.9$ were also considered 'less-than' and not used in computing final shifts. The weighted and unweighted R values for the 881 reflections omitting the 'less-thans' were 0.053 and 0.063 respectively. The unweighted R for the initial

940 observed reflections was 0.067 and for all 1360 measured reflections was 0.069.*

The average shift/error in the final cycle was 0.138 with only the x coordinate of the solvent O having a shift/error greater than 0.75 (1.73). The highest peak in the electron density difference map had a value of 0.46 e \AA^{-3} .

All refinements were by full-matrix least squares using various versions of the *ORFLS* program of Busing, Martin & Levy (1962). Early calculations were carried out on the University of Chicago computer system; the later ones were with the CDC-6600 version of the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970).

The atomic coordinates and thermal parameters are shown in Table 1. The calculated bond lengths and angles are shown in Table 2. Fig. 1 shows the projection on (001) of a portion of the unit cell and indicates the numbering system used.

Discussion

Collman & Schneider (1966) synthesized a series of transition-metal complexes with the cyclic, tetra-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31907 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional parameters and temperature factors for one asymmetric unit

Positional parameters are in fractions of the unit-cell vectors $\times 10^4$. Thermal parameters are in \AA^2 for atoms refined isotropically and of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ for Co and the atoms of the perchlorate anion ($\beta \times 10^4$). All e.s.d.'s are in units of the last given digit. H-atom parameters are in calculated positions before the last refinement with B fixed at 4.0 \AA^2 and were not refined.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	3093 (1)	5212 (1)	5004 (6)	23 (1)	18 (1)	114 (3)	0 (1)	18 (3)	8 (5)
Cl	3559 (4)	3256 (3)	17 (14)	86 (3)	44 (2)	161 (9)	-2 (2)	32 (10)	35 (9)
O(4)	2767 (20)	3112 (35)	787 (59)	95 (20)	250 (49)	795 (206)	33 (23)	121 (45)	169 (71)
O(5)	3209 (47)	3232 (17)	-1453 (31)	631 (95)	53 (12)	135 (41)	-70 (29)	-164 (49)	21 (17)
O(6)	3960 (18)	4209 (11)	76 (58)	164 (19)	60 (9)	413 (60)	-21 (11)	-94 (49)	-38 (39)
O(7)	4200 (23)	2489 (18)	324 (82)	188 (26)	90 (14)	679 (171)	49 (16)	68 (61)	88 (55)
	x	y	z	B		x	y	z	
O(1)	2669 (7)	3838 (7)	4854 (22)	3.2 (2)	H(1)	1812	6488	5110	
O(2)	4175 (6)	4315 (6)	4836 (18)	2.3 (2)	H(2)	1229	4546	3906	
C(9)	3578 (9)	3534 (9)	4881 (32)	2.4 (3)	H(3)	574	5678	3730	
O(3)	3852 (7)	2670 (6)	4730 (14)	2.3 (2)	H(4)	1882	6451	2363	
N(1)	1789 (8)	5747 (8)	5180 (24)	2.8 (2)	H(5)	1694	5265	1539	
N(2)	2944 (13)	5372 (17)	2878 (24)	3.1 (4)	H(6)	3095	4728	2387	
N(3)	3893 (7)	6400 (7)	4952 (31)	2.4 (2)	H(7)	4369	5815	2235	
N(4)	3142 (14)	5349 (17)	7254 (23)	3.3 (4)	H(8)	3420	6455	1304	
C(1)	1290 (15)	5353 (16)	3856 (27)	3.6 (4)	H(9)	2966	7322	3647	
C(2)	1928 (22)	5647 (22)	2537 (33)	4.7 (6)	H(10)	4225	7506	3333	
C(3)	3649 (18)	6144 (22)	2354 (30)	3.9 (6)	H(11)	4575	6165	4860	
C(4)	3665 (22)	6948 (24)	3562 (36)	4.5 (7)	H(12)	4450	7464	6516	
C(5)	3842 (17)	6954 (17)	6405 (24)	2.2 (4)	H(13)	3166	7367	6496	
C(6)	3894 (19)	6138 (21)	7587 (29)	3.7 (5)	H(14)	3751	6461	8686	
C(7)	2110 (20)	5650 (24)	7779 (35)	5.0 (7)	H(15)	4612	5803	7595	
C(8)	1387 (16)	5419 (16)	6675 (27)	3.2 (4)	H(16)	3328	4701	7716	
					H(17)	2098	6446	8009	
O(8)	591 (36)	3948 (37)	676 (65)	18 (2)	H(18)	1940	5247	8806	
					H(19)	724	5819	6930	
					H(20)	1248	4623	6681	

dentate ligand 1,4,7,10-tetraazacyclododecane (cyclen). By comparison of the visible absorption spectra with those of known tetramine complexes, they inferred that the cyclen ligand occupied four adjacent octa-

Table 2. Bond lengths and angles

(a) Bond lengths (Å) with e.s.d.'s in units of last digit given in parentheses

Co—O(1)	1.925 (11)	C(3)—C(4)	1.520 (43)
Co—O(2)	1.909 (9)	C(4)—N(3)	1.472 (40)
O(1)—C(9)	1.308 (16)	N(3)—C(5)	1.493 (33)
O(2)—C(9)	1.324 (15)	C(5)—C(6)	1.517 (35)
C(9)—O(3)	1.219 (16)	C(6)—N(4)	1.501 (34)
Co—N(1)	1.927 (12)	N(4)—C(7)	1.540 (34)
Co—N(2)	1.920 (22)	C(7)—C(8)	1.429 (38)
Co—N(3)	1.925 (11)	C(8)—N(1)	1.508 (31)
Co—N(4)	2.016 (22)	Cl—O(4)	1.297 (38)
N(1)—C(1)	1.462 (29)	Cl—O(5)	1.397 (36)
C(1)—C(2)	1.517 (37)	Cl—O(6)	1.384 (18)
C(2)—N(2)	1.470 (35)	Cl—O(7)	1.374 (31)
N(2)—C(3)	1.485 (34)		

(b) Bond angles (°) with e.s.d.'s in tenths of degrees in parentheses

O(1)—Co—O(2)	68.4 (4)	Co—N(2)—C(2)	109.4 (16)
O(1)—Co—N(1)	94.5 (5)	Co—N(2)—C(3)	108.6 (15)
O(1)—Co—N(2)	90.2 (9)	C(2)—N(2)—C(3)	112.1 (21)
O(1)—Co—N(4)	99.5 (9)	N(2)—C(3)—C(4)	105.9 (22)
O(2)—Co—N(2)	94.2 (8)	C(3)—C(4)—N(3)	104.5 (23)
O(2)—Co—N(3)	94.1 (4)	Co—N(3)—C(4)	107.9 (16)
O(2)—Co—N(4)	96.3 (8)	Co—N(3)—C(5)	111.0 (15)
N(1)—Co—N(2)	86.6 (9)	C(4)—N(3)—C(5)	118.4 (17)
N(1)—Co—N(3)	103.0 (5)	N(3)—C(5)—C(6)	104.3 (18)
N(1)—Co—N(4)	85.2 (8)	C(5)—C(6)—N(4)	109.4 (20)
N(2)—Co—N(3)	86.8 (10)	Co—N(4)—C(6)	106.5 (15)
N(3)—Co—N(4)	86.0 (10)	Co—N(4)—C(7)	107.2 (16)
Co—O(1)—C(9)	90.4 (8)	C(6)—N(4)—C(7)	112.7 (21)
Co—O(2)—C(9)	90.6 (7)	N(4)—C(7)—C(8)	111.6 (23)
O(1)—C(9)—O(2)	110.0 (11)	C(7)—C(8)—N(1)	107.2 (19)
O(1)—C(9)—O(3)	125.7 (12)	O(4)—Cl—O(5)	102.0 (33)
O(2)—C(9)—O(3)	123.3 (12)	O(4)—Cl—O(6)	116.5 (26)
Co—N(1)—C(1)	103.5 (12)	O(4)—Cl—O(7)	108.5 (30)
Co—N(1)—C(8)	107.6 (12)	O(5)—Cl—O(6)	101.1 (25)
C(1)—N(1)—C(8)	116.2 (14)	O(5)—Cl—O(7)	112.9 (34)
N(1)—C(1)—C(2)	105.4 (18)	O(6)—Cl—O(7)	114.9 (17)
C(1)—C(2)—N(2)	108.6 (22)		

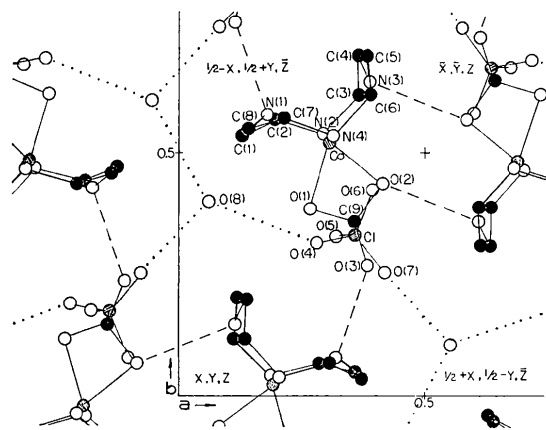


Fig. 1. A portion of the unit cell projected on (001). The C atoms are black; the Co and Cl are shaded. Solvent-anion hydrogen bonds are indicated by dotted lines, and the cation-cation hydrogen bonds by dashed lines.

hedral coordination sites, with the other two sites *cis* to one another. The *cis*-cyclen complexes differed markedly from the majority of synthetic and natural cyclic tetramine complexes, which form a planar structure with the two remaining ligand positions *trans* (Fleischer, 1970; Bosnich, Mason, Pauling, Robertson & Tobe, 1965). Studies with molecular models show that the ethylenediamine linkages in cyclen are too short to allow the planar configuration to be sterically likely. With the *cis*-cyclen arrangement one can construct models with two different ring configurations. One of the structures has approximate point symmetry $2mm$, while the other has only point symmetry m .

In the actual structure the cyclen ligand is present in the less symmetric configuration with approximate symmetry m . The Co atom, carbonate ligand atoms, and two of the cyclen nitrogens, N(1) and N(3), all lie within 0.071 Å of a plane whose normal makes an angle of about 4.5° with the c axis. The proximity of this pseudo-mirror plane to the $z=0.5$ plane in the unit cell results in a structure which differs only slightly from one with space group $Pbam$, and led to early correlation problems in the refinement. The CO_3 group is tilted relative to (001) in conjunction with the asymmetric orientation of the perchlorate ion, which has one of its oxygens pointed away from the tilt. Each of the cations is linked by four hydrogen bonds to its neighboring cations, using the H atoms on the N atoms lying near the $z=0.5$ plane to bond to carbonate oxygens of adjacent cations. The two N—O hydrogen-bond distances are 2.71 [N(1)—H(1)···O(3ⁱⁱⁱ)] and 2.81 Å [N(3)—H(11)···O(2ⁱ)]. The hydrogen bonds belonging to this network are shown by dashed lines in Fig. 1.

The solvent water molecules participate in hydrogen bonding with each other and with O atoms on the perchlorate ions. The O—O distance between water molecules is 3.24 Å. The solvent-perchlorate ion O—O distances are: to O(4), 3.18; to O(7ⁱⁱ), 2.84 Å. Because of the number of H atoms, only four of the five bonds can be occupied. Occupancy of the water-water bond requires disorder of the water molecules and may be partially responsible for the abnormally large temperature factor of the water O atom, O(8). The difference map shows some residual electron density consistent with these bonds but no attempt was made to include these H atoms in the refinement. Anion-solvent hydrogen bonds are shown as dotted lines in Fig. 1.

All bond lengths appear to be normal except for C(7)—C(8), which is about 0.1 Å shorter than usual for a C—C single bond. The Cl—O bonds in the perchlorate appear somewhat shorter than the usual value of 1.43 Å found in other perchlorates (Lee & Carpenter, 1969). The 1.36 Å found here may be a result of the fact that it is the distance to the center of an anisotropic thermal ellipsoid rather than the radius of a thermal librational spherical cap which should more accurately model the motion of the anion oxygens.

We gratefully acknowledge support for this work from the National Science Foundation, ARPA, and Wellesley's Faculty Awards Program and Shell Assist Gift. The early portion of the work was carried out in the Department of Chemistry at the University of Chicago.

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Acta Cryst. (1976). B32, 3066

The Hydrogen-Bond System in a Water-Rich Crystalline Hydrate: A Neutron Diffraction Study of Trisodium Tris(oxydiacetato)cerate(III) Nonahydrate

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(Received 7 April 1976; accepted 15 May 1976)

To obtain information on the hydrogen-bond system in solid $\text{Na}_3[\text{Ce}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 9\text{H}_2\text{O}$ the structure of this triclinic (space group $P\bar{1}$) compound has been studied by single-crystal neutron diffractometry. The structure was refined to $R=0.063$. The unit cell has $a=10.3597$ (7), $b=11.6189$ (12), $c=12.7957$ (9) Å, $\alpha=113.001$ (4), $\beta=90.227$ (4), $\gamma=92.065$ (7)°, $Z=2$. The positions of the heavy atoms agree with the earlier X-ray study. The structure is built up of layers, parallel to the ab plane, containing tris(oxydiacetato)cerate(III) ions connected by partly hydrated Na^+ ions. The layers are held together in the c direction by van der Waals and hydrogen bonds, the latter *via* water molecules. Pairs of identical non-coordinated water molecules are located in a disordered state within the layers. Hydrogen bonds transfer the disorder to a second non-coordinated water molecule in the structure. One of the water molecules, coordinated to Na^+ , is located in such a large cavity that it can occupy two sites, one of which is energetically slightly less favourable than the other. Because of crystal-packing considerations all the hydrogen bonds are bent and rather weak.

Introduction

When salts of oxoanions are precipitated from water, the ability of the water molecule to form hydrogen bonds normally causes 'water of crystallization' to be incorporated in the solid phase. The effect is often further increased by the O lone-pair orbitals which make water an excellent ligand for many cations. The building blocks of such crystalline hydrates are thus hydrated ions, and the crystal packing may be determined by hydrogen bonds donated and accepted by the water molecules.

In a structural study of nine-coordinate, mononuclear lanthanoid complexes with the tridentate ligands oxydiacetate (or diglycolate) and pyridine-2,6-dicarboxylate (dipicolinate) several water-rich crystalline hydrates were encountered (Albertsson, 1972). Four dipicolinate structures were investigated: triclinic $\text{Na}_3[\text{ML}_3] \cdot 15\text{H}_2\text{O}$, $M=\text{Ce}-\text{Dy}$, monoclinic $\text{Na}_3[\text{ML}_3] \cdot 13\text{H}_2\text{O}$, $M=\text{Ho}-\text{Yb}$, orthorhombic $\text{Na}_3[\text{ML}_3] \cdot 14\text{H}_2\text{O}$, $M=\text{Yb}-\text{Lu}$, and

hexagonal $\text{Na}_3[\text{ML}_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$, $M=\text{Ho}-\text{Lu}$, $L^{2-}=\text{C}_7\text{H}_3\text{NO}_4^{2-}$. In the triclinic, monoclinic, and hexagonal compounds several of the water molecules appeared to be dynamically disordered. In the oxydiacetate compounds $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $M=\text{Ce}-\text{Lu}$, the water content is fairly low, and the molecules are confined to one set of equivalent positions in the structure. As X-ray diffraction was used in all cases, only some of the crystal-packing considerations could be revealed. Both the outer and the inner, *i.e.* coordinated, carboxylate O atoms of the mononuclear complexes can act as acceptors of hydrogen bonds, donated by the water molecules. Without knowledge of the locations of the water H atoms it is impossible to establish the hydrogen-bond schemes.

In a study of Ce compounds with very low magnetic heat capacities (Doran, Erich & Wolf, 1972; Albertsson, Chen & Wolf, 1975) large crystals of a new triclinic phase of trisodium tris(oxydiacetato)cerate(III) nonahydrate (TCDG) were obtained. The X-ray structure has been reported (Elding, 1976). The crystal data