

Crystal Structures of Ethylenediaminetetraacetato Metal Complexes. II.
catena-2,2,2,2-Tetraqua- μ -ethylenediaminetetraacetato-cadmiummanganese
Dihydrate, $[\text{Cd}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)\text{Mn}(\text{OH}_2)_4]_n \cdot 2n\text{H}_2\text{O}$

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Abstract. $M_r = 563.65$, triclinic, $P\bar{1}$, $a = 10.852$ (3), $b = 10.535$ (3), $c = 9.233$ (2) Å, $\alpha = 96.44$ (4), $\beta = 103.35$ (3), $\gamma = 102.83$ (3)°, $V = 986.4$ (5) Å³, $Z = 2$, $D_x = 1.90$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.757$ mm⁻¹, $F(000) = 566$, room temperature, $R = 0.059$ for 3368 observed reflections. The crystal structure consists of infinite chains of Mn and Cd coordination polyhedra, running parallel to the x axis. The Mn atom displays octahedral coordination being linked to four water molecules and two oxygen atoms of two ethylenediaminetetraacetato ligands, while the Cd atom is heptacoordinated, being linked to four oxygen and two nitrogen atoms of one ethylenediaminetetraacetato ligand and to an O atom of a second ligand. These ligands act as bridges between Mn...Cd and Cd...Cd metal ions. Each Cd coordination polyhedron is bridged to a Cd and two Mn coordination polyhedra, while the two Mn atoms act as bridges between two Cd coordination polyhedra. The different chains are linked by hydrogen bonds.

Introduction. A systematic study on metal complexes with the ethylenediaminetetraacetato (edta) ligand is being carried out by the Departments of Crystallography and Mineralogy, Faculty of Geology and Inorganic Chemistry and Faculty of Pharmacy of the University of Barcelona (Solans, Font-Altaba, Oliva & Herrera, 1983).

Generally, as can be observed from the literature, the crystal structure of compounds with formula $[(\text{H}_2\text{O})_4X(\text{edta})Y]_n \cdot p\text{H}_2\text{O}$ consists of infinite chains of X and Y coordination polyhedra, where the edta ligand acts as a bridge between X and Y metals ($X = \text{Co}, \text{Mg}, \text{Mn}, \text{Y} = \text{Cu}, \text{Co}, \text{Ni}, \text{Zn}$) (Candlish, Michael, Neal, Lingafelter & Rose, 1978; Pozhidaev, Polynova, Porai-Koshits & Neronova, 1973; Solans, Font-Altaba, Oliva & Herrera, 1983). The title compound has the same metal/ H_2O ratio as the preceding compounds, where the Y metal displays six coordination, while seven

coordination for Cd was expected according to its ionic radius. In order to elucidate the coordination of Mn and Cd in the title complex, an X-ray analysis was undertaken.

Experimental. Colourless prisms ($0.1 \times 0.1 \times 0.2$ mm), Philips PW 1100 diffractometer, Mo $K\alpha$, graphite monochromator, cell parameters from 25 reflections ($5 \leq \theta \leq 12^\circ$), ω -scan technique, scan width 0.8° , scan speed $0.03^\circ \text{ s}^{-1}$, 3373 independent reflections with $\theta \leq 25^\circ$, 3368 with $I \geq 2.5\sigma(I)$, $hkl = \pm 12, \pm 12, 10$. Three standard reflections measured every two hours, significant intensity variation not observed. Lp correction, absorption ignored; direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), anisotropic full-matrix least squares on F (SHELX76; Sheldrick, 1976), $w||F_o| - |F_c||^2$ minimized, anomalous-scattering factors for all atoms (International Tables for X-ray Crystallography, 1974); H of edta ligand computed and refined with constrained bond distances; non-coordinated water molecule [O(W6)] is disordered into two positions [O(W6) and O(W7)] with an occupancy factor very close to 0.5 which were refined anisotropically; final $R = 0.059$, $wR = 0.078$, $w = [\sigma^2(F_o) + 0.0666F_o^2]^{-1}$; max. $\Delta/\sigma = 1.1$ in U_{12} of O(W1), max. and min. peaks of final ΔF synthesis $0.2 \text{ e } \text{Å}^{-3}$ at 0.51 Å from O(W5) and $-0.3 \text{ e } \text{Å}^{-3}$, respectively. Digital VAX-750 and IBM 4341 computers.

Discussion. Final atomic coordinates are given in Table 1 and principal bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a full list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42102 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Mn atom displays a distorted octahedral coordination being linked to four water molecules and two oxygen atoms of two edta ligands in *trans* positions. These oxygen atoms are in *cis* positions in

Table 1. Atomic coordinates ($\times 10^4$, Cd $\times 10^5$) and equivalent isotropic temperature coefficients

$$B_{eq} = 8\pi^2/3 \sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
Mn	6777 (1)	1933 (1)	3091 (1)	1.56 (6)
O(W1)	6286 (6)	1901 (10)	5225 (10)	3.3 (3)
O(W2)	7599 (6)	2109 (7)	1067 (7)	2.7 (2)
O(W3)	5099 (7)	275 (7)	1680 (9)	3.7 (3)
O(W4)	8441 (7)	3600 (7)	4211 (8)	3.0 (2)
O(W5)	3611 (9)	1610 (10)	5029 (10)	5.4 (5)
O(W6)†	5407 (13)	2482 (9)	-1442 (15)	4.8 (4)
O(W7)†	4008 (15)	4510 (8)	5434 (13)	7.2 (6)
Cd	14271 (4)	15533 (4)	3011 (5)	1.58 (4)
N(8)	2495 (6)	3879 (6)	665 (7)	1.8 (2)
C(9)	1948 (7)	4419 (8)	-697 (8)	1.8 (3)
C(10)	1693 (8)	3438 (8)	-2159 (10)	2.6 (3)
N(11)	797 (6)	2159 (6)	-2169 (7)	1.7 (2)
O(12)	3517 (6)	2032 (5)	2013 (6)	2.5 (2)
C(13)	4369 (6)	3022 (7)	1839 (8)	1.6 (2)
O(14)	5579 (6)	3249 (6)	2357 (7)	2.7 (2)
C(15)	3903 (7)	3986 (7)	899 (8)	1.7 (3)
O(16)	259 (6)	2787 (7)	1458 (7)	2.9 (2)
C(17)	889 (7)	3916 (8)	2182 (8)	2.0 (3)
O(18)	509 (5)	4568 (6)	3109 (7)	2.8 (2)
C(19)	2235 (7)	4527 (9)	2008 (10)	2.7 (3)
O(20)	2432 (6)	545 (6)	-1270 (6)	2.8 (2)
C(21)	1917 (8)	395 (8)	-2668 (8)	1.9 (3)
O(22)	2169 (6)	-416 (6)	-3661 (6)	3.0 (2)
C(23)	928 (7)	1117 (8)	-3288 (8)	1.9 (3)
O(24)	-823 (6)	337 (5)	-1165 (6)	2.2 (2)
C(25)	-1408 (7)	1005 (8)	-2025 (8)	1.9 (3)
O(26)	-2631 (6)	783 (7)	-2479 (8)	3.4 (2)
C(27)	-560 (7)	2195 (7)	-2447 (8)	1.7 (3)

† Indicates occupancy factor 0.5.

Table 2. Main bond distances (\AA) and angles ($^\circ$)

O(W1)—Mn	2.159 (6)	N(8)—Cd	2.416 (5)
O(W2)—Mn	2.257 (5)	N(11)—Cd	2.423 (4)
O(W3)—Mn	2.246 (5)	O(12)—Cd	2.357 (4)
O(W4)—Mn	2.176 (5)	O(16)—Cd	2.341 (4)
O(14)—Mn	2.163 (4)	O(20)—Cd	2.307 (4)
O(22 ^b)—Mn	2.205 (4)	O(24)—Cd	2.476 (4)
		O(24 ^v)—Cd	2.247 (4)
O(W2)—Mn—O(W1)	171.5 (2)	O(16)—Cd—N(8)	70.4 (1)
O(W3)—Mn—O(W1)	98.4 (2)	O(16)—Cd—N(11)	96.1 (2)
O(W3)—Mn—O(W2)	89.4 (2)	O(16)—Cd—O(12)	105.0 (1)
O(W4)—Mn—O(W1)	88.0 (2)	O(20)—Cd—N(8)	104.6 (2)
O(W4)—Mn—O(W2)	84.3 (2)	O(20)—Cd—N(11)	71.8 (1)
O(W4)—Mn—O(W3)	173.3 (2)	O(20)—Cd—O(12)	82.7 (1)
O(14)—Mn—O(W)	94.1 (2)	O(20)—Cd—O(16)	167.9 (2)
O(14)—Mn—O(W2)	89.7 (2)	O(24)—Cd—O(12)	160.5 (1)
O(14)—Mn—O(W3)	86.7 (2)	O(24)—Cd—O(16)	81.2 (1)
O(14)—Mn—O(W4)	91.2 (2)	O(24)—Cd—O(20)	94.5 (1)
O(22 ^b)—Mn—O(W1)	87.6 (2)	O(24 ^v)—Co—N(8)	152.4 (2)
O(22 ^b)—Mn—O(W2)	89.4 (2)	O(24 ^v)—Co—N(11)	131.9 (2)
O(22 ^b)—Mn—O(W4)	94.9 (2)	O(24 ^v)—Cd—O(12)	90.3 (2)
O(22 ^b)—Mn—O(14)	173.7 (2)	O(24 ^v)—Cd—O(16)	98.3 (2)
N(11)—Co—N(8)	75.4 (2)	O(24 ^v)—Co—O(20)	90.9 (2)
O(12)—Cd—N(8)	69.7 (1)	O(24 ^v)—Cd—O(24)	70.4 (2)
O(12)—Cd—N(11)	129.3 (1)		

Symmetry code: (ii) $1-x, -y, -z$; (v) $-x, -y, -z$.

$[(\text{H}_2\text{O})_4\text{Mn}(\text{edta})\text{Y}]_n \cdot 2n\text{H}_2\text{O}$ ($Y = \text{Cu}, \text{Co}, \text{Ni}$ and Zn) (Solans, Font-Altaba, Oliva & Herrera, 1983). The Cd atom is linked to two nitrogen atoms and four oxygen atoms of one edta ligand and to an O atom of a second edta ligand. Heptacoordination for Mn, Fe or Mg is also present in other edta complexes of these metals (Richards, Pedersen, Silverton & Hoard, 1964; Lind, Hamor, Hamor & Hoard, 1964; Stezowski, Countryman & Hoard, 1973; Passer, White & Cheng, 1977), where the seventh coordination site is occupied by a water molecule. The coordination polyhedron of the Cd atom is a distorted pentagonal bipyramid with O(16) and O(20) in apical positions.

A projection of the unit-cell contents down the *z* axis is shown in Fig. 1. The structure consists of infinite chains of Cd and Mn coordination polyhedra, bridged by the edta ligands; each Cd coordination polyhedron is linked to two Mn and one Cd coordination polyhedra, while the two Mn polyhedra act as bridges between Cd polyhedra. The possible interchain hydrogen bonds are O(W2)...O(16ⁱ) 2.742 (4); O(W2)...O(20ⁱⁱ) 2.816 (4); O(W3)...O(12) 2.827 (4) and O(W4)...O(18ⁱ) 2.718 (4) \AA [symmetry code: (i) $x+1, y, z$; (ii) $1-x, \bar{y}, \bar{z}$]. Different chains are linked by the following hydrogen bonds: O(W1)...O(26ⁱⁱⁱ) 2.700 (4) and O(W4)...O(18^{iv}) 2.792 (4) \AA [(iii) $x+1, y, z+1$; (iv) $1-x, 1-y, 1-z$]. O(W5) and the disordered O(W6) and O(W7) water molecules act as buffers between different chains through hydrogen bonds.

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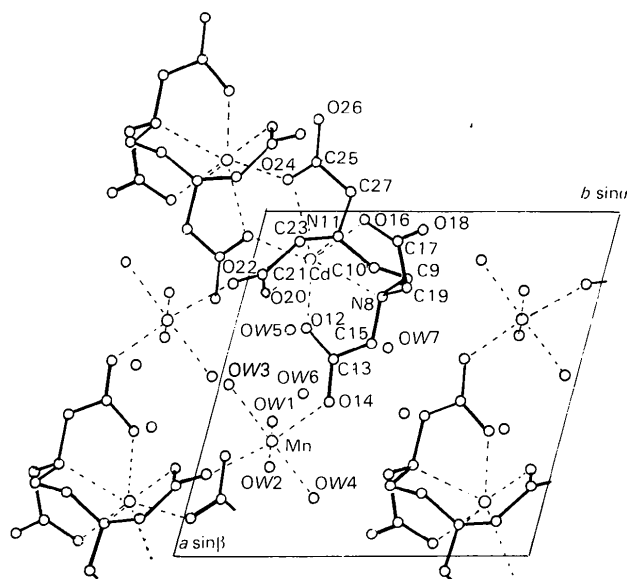


Fig. 1. Unit-cell contents, with the numbering of atoms.

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Tris(trimethylammonium) Nonachlorodiantimonate(III), [NH(CH₃)₃]₃[Sb₂Cl₉]

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Abstract. *M*_r = 742.94, monoclinic, *Pc*, *a* = 10.085 (3), *b* = 9.072 (4), *c* = 15.459 (6) Å, β = 90.17 (3)°, *V* = 1414 (2) Å³, *Z* = 2, *D*_x = 1.744 (2) g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 27.8 cm⁻¹, *F*(000) = 720, *T* = 296 K, final *R* = 0.034 for 2384 independent observed reflections. The structure contains SbCl₃ pyramids with Sb–Cl bonds ranging from 2.401 (3) to 2.473 (3) Å. The Cl⁻ anions interconnect the SbCl₃ groups into a two-dimensional network by forming bridges with Sb–Cl lengths ranging from 2.883 (3) to 3.316 (3) Å. The cations are connected by N–H...Cl hydrogen bonds to the Sb₂Cl₉ layers. One hydrogen bond is bifurcated and very weak.

Introduction. This work is part of our study of the crystal structures of alkylammonium metal halogenides. In the particular case of Sb^{III} chlorides and bromides the following ions can be obtained: [SbX₄]⁻, [SbX₅]²⁻, [SbX₆]³⁻ and the enneahalide [Sb₂X₉]³⁻. In these compounds the metal shows a tendency towards distorted octahedral coordination with some rather long Sb–X bonds, which is attributed to the aspherical distribution of lone-pair electrons at Sb^{III}. This work describes the crystal structure determination of [NH(CH₃)₃]₃[Sb₂Cl₉].

Experimental. Crystals by slow evaporation of an aqueous solution of [NH(CH₃)₃]Cl and SbCl₃. Crystal 0.2 × 0.2 × 0.6 mm. Precession photographs indicated monoclinic symmetry. Cell constants from setting angles of 15 reflections with 6 < θ < 10°. Syntex P2₁

diffractometer, Nb filter. Hemisphere up to 2θ = 50°, (sinθ/λ)_{max} = 0.59 Å⁻¹, range of *hkl*: *h* 0→11, *k* ±10, *l* ±18, ω/2θ scan. Total number of reflections 6757; 2465 independent. Three standard reflections every 60 reflections remained stable. Background corrections by profile analysis (Blessing, Coppens & Becker, 1974). Absorption correction, transmission range 0.57–0.62. Averaging of equivalent reflections, *R*_{int} = 0.035. 2384 reflections with *I* > 0 used. Weighting scheme *w*(*I*) = 1/[σ²(*I*) + (0.03*I*)²]. Structure determination by Patterson and Fourier methods. H atoms at N were calculated but not refined; those at C could not be determined. Refinement on *F*. Extinction coefficient *g* = 11.2 (2) × 10⁻³ (Larson, 1969). (Δ/σ)_{max} = 0.1. Final difference Fourier map peaks < 0.35 e Å⁻³. Final *R* = 0.034, *wR* = 0.029, *S* = 1.21. Scattering factors and *f*' from *International Tables for X-ray Crystallography* (1974); use of *f*' did not distinguish between enantiomorphs, consequently *f*' was not used in final refinement. Calculations with XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. The positional parameters are reported in Table 1, † bond lengths and angles in Table 2. A view of the structure is shown in Fig. 1. The structure contains SbCl₃ pyramids with Sb–Cl bond lengths ranging from 2.401 (3) to 2.473 (3) Å. The average Cl–Sb–Cl angle is 89.6 (1)°. The Cl⁻ anions form bridges with

† Lists of structure factors, anisotropic thermal parameters, and bond distances and angles in the cations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42133 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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