Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1335). Services for accessing these data are described at the back of the journal.

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Triethylenetetraminehexaacetic Acid Complex of Lead

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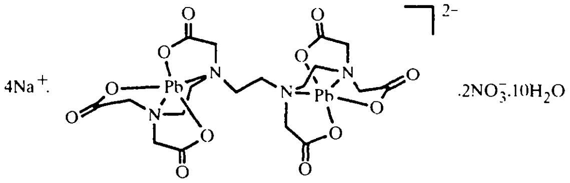
Abstract

In the title compound, tetrasodium μ-[3,6,9,12-tetrakis(carboxymethyl)-3,6,9,12-tetraazatetradecanedioato-$1\kappa^5O^1,N^3,O^3,N^6,O^6:2\kappa^5N^9,O^9,N^{12},O^{12},O^{14}$]dilead dinitrate decahydrate, $Na_4[Pb_2(C_{18}H_{24}N_4O_{12})](NO_3)_2\cdot10H_2O$, the Pb^{2+} ions have highly distorted bonding geometry, with a primary coordination number of five and two secondary intermolecular contacts. The Pb—N bond distances range from 2.505 (4) to 2.641 (4) Å, and the Pb—O bond distances range from 2.454 (3) to 2.559 (3) Å. The binuclear lead complexes sit on inversion centers and are bridged to form polymeric structures. The polymers are linked into sheets *via* N···O contacts.

Comment

The use of metal-ion chelation for remediation of soils and waters contaminated with toxic metal ions (Pb, Cd, Hg) is finding increasing application. Extractants such as nitrilotriacetic acid, H_3NTA, ethylenediaminetetraacetic acid, H_4EDTA, and diethylenetriaminepentaacetic acid, H_5DTPA, have commonly been used for extraction of lead (Barbarick & Workman, 1987; Elliott & Brown, 1989; Raghavan *et al.*, 1989). Polymeric aminocarboxylate systems with multiple metal-binding sites are also of interest for waste-water treatment (Geckeler & Volchek, 1996). Surprisingly, only a few structural studies of this class of molecules with heavy metals have been reported in the literature (Harrison & Steel, 1982; Solans *et al.*, 1985). Characterization of metal-ion binding in these simple yet effective molecular extractants will enhance our ability to design new chelator systems based on this functional group. We report herein the structure of a triethylenetetraminehexaacetic acid (H_6TTHA) complex of lead, (1).



(1)

Tetrasodium triethylenetetraminehexaacetatodilead dinitrate decahydrate, (1), contains a binuclear complex that forms weak dibridged polymeric structures. Further weak intermolecular bonding leads to a sheet-like structure. As shown in Fig. 1, all ten donor atoms of the TTHA ligand are utilized in binding the two Pb^{2+} ions, and the ligand has an inversion center at the midpoint of the central ethylene bridge (C9—C9′). The ligand bond distances and angles are typical (Fallon & Gatehouse, 1974, 1976; Leverett, 1974). The other four reported TTHA–metal complexes (*M* = VO, Cr, Cu, Sb) are discrete molecules with very similar ligand geometries (Allen & Kennard, 1993; Fallon & Gatehouse, 1974, 1976; Leverett, 1974). The lead salt reported here has a polymeric structure and the ligand geometry differs from that reported in other M_2TTHA complexes in that

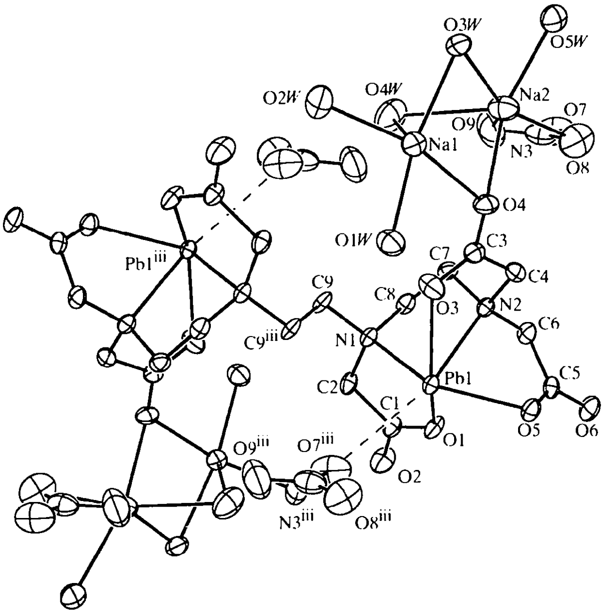


Fig. 1. View of (1) showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (iii) $-x$, $1-y$, $1-z$.]

the orientation of the C7—C8 ethylene bridge relative to the C9—C9′ ethylene bridge is shifted by approximately 90°. This structural change enlarges the binding site to accommodate the larger Pb^{2+} ion.

In the $[Pb_2TTHA]^{2-}$ complex, the Pb^{2+} ions have five primary bonds to the TTHA ligand. The Pb—N distances range from 2.505 (4) to 2.641 (4) Å, and the Pb—O distances range from 2.454 (3) to 2.559 (3) Å; these distances are within the sums of the ionic radii. It has been proposed that the change from an active lone pair to an inactive lone pair in lead–amine complexes is accompanied by a lengthening of the Pb—N bonds (Hancock *et al.*, 1988). The Pb—N distances are intermediate between those reportedly associated with complexes with a stereochemically active lone pair and those with an inactive lone pair. Inversion-related dibridged lead complexes form weakly bound linear polymers, with $Pb\cdots O5^{i}$ [symmetry code: (i) $-x, 1-y, -z$] bond distances of 2.822 (3) Å and $Pb\cdots Pb$ distances of 4.468 (1) Å. The Pb^{2+} ions are weakly coordinated to the nitrate anions [$Pb\cdots O7^{ii}$ 3.088 (6) Å; symmetry code: (ii) $1+x, y, z$], which are also coordinated to the Na^+ cations to form a sheet-like structure. These sheets are connected through extensive hydrogen bonding.

The primary coordination environment of the Pb^{2+} ions is five-coordinate. The coordination environment is very distorted, with the Pb lone pair presumably occupying the sixth coordination site. To complete the coordination sphere of Pb, a dibridged dimeric polymer is formed. This type of dimer formation is not uncommon in lead–carboxylate structures (Harrison & Steel, 1982). Even with the inclusion of the secondary $Pb\cdots O$ bonds in the coordination sphere, there is space available for a stereochemically active Pb lone pair.

Harrison & Steel (1982) reported the structures of four lead(II)–carboxylate complexes: formate, acetate, pentafluorobenzoate and EDTA. They found that lead tended towards a coordination number of eight except in the Pb–EDTA structure. The structural types varied from isolated monomers and dimers to three-dimensional structures. The Pb–EDTA structure consists of seven-coordinate monomeric and eight-coordinate dimeric complexes. The coordination environment around the Pb^{2+} ion in the Pb–EDTA monomer is formed through five primary bonds [two Pb—N bonds (2.518 and 2.604 Å) and three Pb—O bonds (2.494–2.567 Å)] and two secondary bonds. The fourth carboxylate has a longer bond distance (2.735 Å) and a water molecule is weakly bound (2.967 Å). Based on the coordination number and bond distances, this coordination environment is similar to that found for the $[Pb_2TTHA]^{2-}$ anion. The authors report that the Pb lone pair is stereochemically active in the case of the Pb–EDTA monomer.

Experimental

Aqueous solutions of $Pb(NO_3)_2$ (0.404 g in 10 ml) and H_6TTHA (0.305 g in 10 ml) were combined, and the pH of the resulting solution was adjusted to 7 using NaOH. The solution was allowed to evaporate slowly to give colorless crystals of (1).

Crystal data

$Na_4[Pb_2(C_{18}H_{24}N_4O_{12})]\text{-}(NO_3)_2.10H_2O$
$M_r = 1298.9$
Triclinic
$P\overline{1}$
$a = 10.200\,(1)$ Å
$b = 10.243\,(1)$ Å
$c = 11.230\,(1)$ Å
$\alpha = 63.70\,(1)°$
$\beta = 87.54\,(1)°$
$\gamma = 69.45\,(1)°$
$V = 976.0\,(2)$ Å^3
$Z = 1$
$D_x = 2.210$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 13\text{–}25°$
$\mu = 8.76$ mm^{-1}
$T = 293\,(2)$ K
Square plate
0.37 × 0.33 × 0.16 mm
Colorless

Data collection

Siemens *P*4/PC diffractometer
ω scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1990)
$T_{min} = 0.095$, $T_{max} = 0.246$
6084 measured reflections
5243 independent reflections

4805 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30°$
$h = -1 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 3.21%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.079$
$S = 1.079$
5243 reflections
262 parameters
H atoms constrained (see below)
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.4283P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.58$ e Å^{-3}
$\Delta\rho_{\min} = -2.04$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pb1—O1	2.455 (3)	Pb1—N1	2.641 (4)
Pb1—O3	2.559 (3)	Pb1—N2	2.505 (4)
Pb1—O5	2.454 (3)		
O5—Pb1—O1	73.06 (11)	C1—O1—Pb1	118.4 (3)
O5—Pb1—N2	66.35 (12)	C3—O3—Pb1	116.7 (3)
O1—Pb1—N2	83.84 (12)	C5—O5—Pb1	116.7 (3)
O5—Pb1—O3	106.49 (12)	C8—N1—Pb1	106.8 (2)
O1—Pb1—O3	145.63 (13)	C2—N1—Pb1	105.1 (2)
N2—Pb1—O3	65.84 (12)	C9—N1—Pb1	112.8 (3)
O5—Pb1—N1	121.86 (12)	C6—N2—Pb1	109.1 (3)
O1—Pb1—N1	64.57 (11)	C4—N2—Pb1	106.8 (3)
N2—Pb1—N1	71.10 (12)	C7—N2—Pb1	110.8 (3)
O3—Pb1—N1	89.47 (13)		

All methylene H atoms were fixed and refined using the *HFIX* and *AFIX* facilities in *SHELXL*93 (Sheldrick, 1993). A riding model was used to refine the H atoms and the isotropic displacement parameters were fixed at $1.2U_{\rm eq}$(C). The protons for two of the water molecules were found in the difference map and coordinates, occupancy and isotropic displacement parameters (0.08 Å^2) were fixed. Protons on the other water molecules were not included. All peaks with residual densities greater than 1 e Å^{-3} were within 1 Å of the Pb position.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Bis(pyridinium) Pentachloro(pyridine-*N*)-molybdate(III)

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Abstract

The title complex, $(C_5H_6N)_2[MoCl_5(C_5H_5N)]$, belongs to a group of halo(pyridine)molybdenum(III) octahedral complexes. The pyridinium cations and pentachloro(pyridine-*N*)molybdate(III) anions are held together by N—H···Cl hydrogen bonds which affect the distances within the $[MoCl_5(py)]^{2-}$ anion. The anion displays a previously unobserved orientation of the coordinated pyridine, which lies in almost the same plane as two *trans*-positioned equatorial chlorines.

Comment

We report here the structure of $(pyH)_2[MoCl_5(py)]$, (I), as part of our research on halo(pyridine)molybdenum(III) coordination compounds with the formula $[MoX_{6-n}(py)_n]^{n-3}$, where n = 1, 2, 3, 4 (X = Cl$^-$, Br$^-$; py = pyridine, C_5H_5N). $(pyH)_2[MoX_5(py)]$ is the first product of the stepwise substitution of halides in