

Fig. 1. A view of the  $[\text{Ni}(\text{NCCH}_3)_6]^{2+}$  entity.

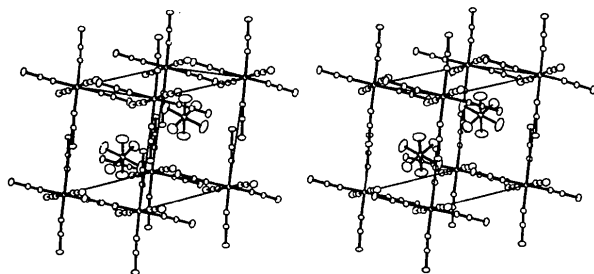


Fig. 2. A stereoview (Johnson, 1965) showing the crystal packing. H atoms were omitted for clarity.

respectively. The angles Ni–N–C(2) [ $175.5(3)^\circ$ ] and N–C(2)–C(1) [ $179.5(4)^\circ$ ] are also very close to the ideal value of  $180^\circ$ .

The  $[\text{SbF}_6]^-$  octahedra exhibit  $C_3$  symmetry with three equivalent Sb–F(1) and Sb–F(2) distances of 1.825 (4) and 1.827 (4) Å respectively. The angles F–Sb–F vary from  $93.3(3)$  to  $87.9(3)^\circ$ . This distortion is probably due to ionic interactions between the structural units.

No significant intermolecular contacts were observed.

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## Coordination of Thioether to the Hard Metals $\text{Ti}^{\text{IV}}$ and $\text{Pb}^{\text{II}}$

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**Abstract.** Trichloro(1,5-dithiacyclooctan-3-olato-*O,S,S'*)titanium(IV), (1),  $[\text{Ti}(\text{C}_6\text{H}_{11}\text{OS}_2)\text{Cl}_3]$ ,  $M_r = 317.53$ ,  $Pn2_1a$ ,  $a = 12.852(4)$ ,  $b = 12.177(5)$ ,  $c = 7.584(3)$  Å,  $V = 1187(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m(298\text{ K}) =$

1.73,  $D_x(130\text{ K}) = 1.78\text{ g cm}^{-3}$ ,  $\text{Mo K}\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 17.0\text{ cm}^{-1}$ ,  $F(000) = 640$ ,  $T = 130\text{ K}$ ,  $R = 0.028$ , 1094 unique reflections. Bis(1,5-dithiacyclooctan-3-ol-*O,S,S'*)dinitratolead(II), (2),  $[\text{Pb}(\text{C}_6\text{H}_{12}\text{OS}_2)_2(\text{NO}_3)_2]$ ,  $M_r = 659.78$ ,  $P2_1/a$ ,  $a = 13.550(2)$ ,  $b = 10.732(1)$ ,  $c = 14.073(1)$  Å,  $\beta = 96.49(1)^\circ$ ,  $V$

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= 2033.3 (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x(130\text{ K}) = 2.15\text{ g cm}^{-3}$ ,  $\text{Cu } K\alpha$ ,  $\lambda = 1.54178\text{ Å}$ ,  $\mu = 203.0\text{ cm}^{-1}$ ,  $F(000) = 1280$ ,  $T = 130\text{ K}$ ,  $R = 0.084$ , 3375 unique reflections. In the titanium complex the anionic dithioether ligand is coordinated in a tridentate manner through two S atoms and one O atom. The coordination of titanium is approximately octahedral. Bond lengths for the two Ti–S bonds and one Ti–O bond are 2.595 (1), 2.607 (2) and 1.791 (4) Å, respectively. The Ti–Cl bond lengths are 2.260 (1), 2.276 (2) and 2.332 (2) Å; the long bond is *trans* to the coordinated O atom. The lead complex has a coordination number of ten that results from two tridentate neutral dithioether ligands and two bidentate nitrates. Average distances and deviations from the average are: Pb–S, 3.183 (25) Å; Pb–O(hydroxyl), 2.612 (28) Å, Pb–O(nitrate), 2.797 (49) Å.

**Introduction.** We report the structures of some unusual complexes of 1,5-dithiacyclooctan-3-ol. The hydroxyl group of this tridentate ligand is able to induce hard-metal ions, which normally exhibit a reluctance to bind to sulfur donors, to bind to a thioether group. We have already reported complexes of this ligand with softer metal ions  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Fe}^{\text{II}}$  (Musker, Olmstead & Kessler, 1984; Olmstead, Musker & Kessler, 1984), but we now have isolated crystalline complexes of both  $\text{Ti}^{\text{IV}}$  and  $\text{Pb}^{\text{II}}$ . To our knowledge, no crystal structure of complexes having a thioether group bonded to  $\text{Ti}^{\text{IV}}$  or  $\text{Pb}^{\text{II}}$  has been reported. Even more unusual is that the Pb atom has a coordination number of ten. Only two other ten-coordinated complexes of lead are known. One is a kryptofix 222 complex in which thiocyanate anions are also bound to the Pb atom (Metz & Weiss, 1974), and the other is a highly symmetrical complex of a planar hexadentate ligand with two bidentate nitrates (Aghaborzorg, Palenik & Palenik, 1986).

**Experimental.**  $[\text{Ti}(\text{C}_6\text{H}_{11}\text{OS}_2)\text{Cl}_3]$  obtained as orange tetrahedra from acetone, crystal dimensions  $0.05 \times 0.20 \times 0.26\text{ mm}$ ; Syntex  $P2_1$  diffractometer, locally modified LT-1 apparatus,  $T = 130\text{ K}$ ,  $\text{Mo } K\alpha$  radiation, graphite monochromator; cell dimensions from least-squares fit of 10 reflections with  $12 < 2\theta < 18^\circ$ ; space group  $Pn2_1a$  (*acb* setting of  $Pna2_1$ , No. 33) based on conditions  $0kl$ ,  $k + l = 2n$ ,  $hk0$ ,  $h = 2n$ , range of absorption correction factors 1.07–1.36; data collected to  $2\theta_{\text{max}} = 50^\circ$  with  $hkl$  ranges 0 to 14, 0 to 14, 0 to 8, respectively;  $\omega$  scans,  $1.2^\circ$  range,  $8^\circ\text{ min}^{-1}$  speed,  $1^\circ$  offset for background; two check reflections monitored every 200 reflections displayed no decay; 1241 reflections measured, 1094 unique data,  $R_{\text{int}} = 0.028$ , 1012 observed [ $I > 3\sigma(I)$ ] used in the solution and refinement (based on  $F$ ); structure solved by Patterson methods; absorption correction (program *XABS*, a method which obtains an absorption tensor from

$F_o - F_c$  differences, H. Hope & B. Moezzi) applied, blocked-cascade least-squares refinement, 117 parameters; all non-H atoms with anisotropic thermal parameters, isotropic thermal parameters of H atoms set equal to 1.2 times the equivalent isotropic thermal parameter of the bonded C atom. H atoms included using a riding model with C–H 0.96 Å;  $R = 0.028$ ,  $wR = 0.027$ ,  $w = 1/[\sigma^2(F_o)]$ ,  $S = 1.045$ ;  $(\Delta/\sigma)_{\text{max}} = 0.15$  for x of Cl (1),  $(\Delta/\sigma)_{\text{av}} = 0.006$ ;  $\Delta\rho$  excursions 0.32 and  $-0.34\text{ e Å}^{-3}$ .

$[\text{Pb}(\text{C}_6\text{H}_{12}\text{OS}_2)_2(\text{NO}_3)_2]$  obtained as colorless parallelepipeds from methanol/water, crystal dimensions  $0.05 \times 0.08 \times 0.10\text{ mm}$ ;  $\text{Cu } K\alpha$  radiation, graphite monochromator; cell dimensions from least-squares fit of 16 reflections with  $45 < 2\theta < 94^\circ$ ; space group  $P2_1/a$  (alternate setting of  $P2_1/c$ , No. 14) based on conditions  $0k0$ ,  $k = 2n$ ,  $h0l$ ,  $h = 2n$ , range of absorption correction factors 2.3–4.8; data collected to  $2\theta_{\text{max}} = 130^\circ$  with  $hkl$  ranges 0 to 15, 0 to 12,  $-16$  to 16, respectively;  $\omega$  scans,  $1.0^\circ$  range,  $15^\circ\text{ min}^{-1}$  speed,  $1^\circ$  offset for background; two check reflections monitored every 200 reflections displayed no decay; 3738 reflections measured, 3375 unique data,  $R_{\text{int}} = 0.039$ , 3215 observed [ $I > 3\sigma(I)$ ] used in the solution and refinement (based on  $F$ ); structure solved by Patterson methods; absorption correction applied (program *XABS*), blocked-cascade least-squares refinement, 134 parameters; Pb and S atoms with anisotropic thermal parameters, isotropic thermal parameters of H atoms set equal to 1.2 times the isotropic thermal parameter of the bonded C atom. H atoms included using a riding model with C–H 1.00 Å;  $R = 0.084$ ,  $wR = 0.090$ ,  $w = 1/[\sigma^2(F_o)]$ ,  $S = 1.483$ ;  $(\Delta/\sigma)_{\text{max}} = 0.028$  for y of O(2),  $(\Delta/\sigma)_{\text{av}} = 0.005$ ;  $\Delta\rho$  excursions 5.7 and  $-5.6\text{ e Å}^{-3}$ ; large peaks, all in the vicinity of Pb, and large  $R$  value ascribed to inability to correct adequately for absorption effects (the function used becomes less appropriate with simultaneous high absorption and high  $2\theta$ ); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs from the *SHELXTL* (version 3) package (Sheldrick, 1981). The final atomic coordinates and isotropic thermal parameters for compounds (1) and (2) are given in Tables 1 and 2.\*

**Discussion.** Bond lengths and angles for the titanium complex (1) are given in Table 3. The structure of the complex (Fig. 1) reveals that the ligand, the 1,5-dithiacyclooctan-3-olate anion, is coordinated to the Ti atom in a tridentate manner using an  $\text{S}_2\text{O}$  donor set.

\* Lists of structure factors, anisotropic thermal parameters and calculated H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44097 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for [Ti(C<sub>6</sub>H<sub>11</sub>OS<sub>2</sub>)Cl<sub>3</sub>]

	x	y	z	$U_{eq}^*$
Ti	1763 (1)	4230	10797 (1)	14 (1)
Cl(1)	3399 (1)	4114 (2)	11874 (2)	25 (1)
Cl(2)	2107 (1)	5535 (1)	8624 (2)	23 (1)
Cl(3)	1053 (1)	5361 (1)	12861 (2)	20 (1)
S(1)	-28 (1)	4064 (1)	9242 (2)	18 (1)
S(2)	2286 (1)	2821 (2)	8364 (2)	19 (1)
O(1)	1253 (3)	2957 (3)	11605 (4)	18 (1)
C(1)	-255 (4)	2648 (4)	9869 (8)	22 (2)
C(2)	735 (4)	2128 (5)	10594 (7)	23 (2)
C(3)	1525 (4)	1694 (4)	9238 (7)	25 (2)
C(4)	1774 (4)	3066 (5)	6170 (6)	23 (2)
C(5)	589 (4)	3123 (5)	5951 (7)	24 (2)
C(6)	39 (4)	4072 (6)	6842 (6)	24 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for [Pb(C<sub>6</sub>H<sub>12</sub>OS<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]

	x	y	z	$U_{eq}^*$
Pb	4868 (1)	-149 (1)	2403 (1)	14 (1)
S(1)	7154 (2)	564 (3)	2302 (2)	18 (1)
S(2)	5158 (2)	2759 (3)	2231 (2)	19 (1)
S(3)	6545 (2)	-2089 (3)	3169 (2)	18 (1)
S(4)	4065 (2)	-2828 (3)	2507 (2)	19 (1)
O(1)	5680 (6)	1112 (8)	3903 (5)	19 (2)
O(2)	5258 (6)	-1705 (8)	1095 (5)	19 (2)
O(3)	3061 (9)	-168 (9)	1229 (8)	30 (2)
O(4)	4209 (6)	817 (9)	588 (5)	24 (2)
O(5)	2737 (6)	655 (9)	-181 (5)	24 (2)
O(6)	3317 (7)	825 (10)	3199 (6)	30 (2)
O(7)	4061 (6)	-513 (9)	4195 (5)	21 (2)
O(8)	3001 (7)	789 (9)	4678 (6)	29 (2)
N(1)	3323 (7)	435 (10)	533 (6)	17 (2)
N(2)	3461 (8)	388 (10)	4023 (7)	17 (2)
C(1)	6453 (8)	1973 (11)	3818 (7)	14 (2)
C(2)	7354 (8)	1312 (12)	3462 (7)	20 (2)
C(3)	7357 (9)	1799 (12)	1466 (7)	21 (2)
C(4)	6429 (8)	2197 (11)	791 (7)	18 (2)
C(5)	5805 (9)	3176 (12)	1204 (8)	22 (2)
C(6)	6051 (8)	3092 (11)	3271 (7)	19 (2)
C(7)	5640 (9)	-2935 (12)	1344 (8)	24 (3)
C(8)	6588 (9)	-2854 (12)	2036 (8)	22 (2)
C(9)	6242 (9)	-3342 (12)	3949 (8)	23 (2)
C(10)	5219 (9)	-3255 (12)	4317 (7)	23 (3)
C(11)	4337 (9)	-3677 (13)	3625 (8)	26 (3)
C(12)	4764 (9)	-3655 (12)	1686 (8)	23 (2)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Three Cl ions complete the approximately octahedral coordination. There are no short intermolecular contacts. The eight-membered ring of the coordinated dithioether group is in the boat-chair conformation. The Ti-O bond is short [1.791 (4) Å] while the Ti-S bonds are long [2.595 (1), 2.607 (2) Å], suggesting that the thioether groups only reluctantly bind to the Ti<sup>IV</sup> atom while the O atom is strongly bound. The Ti-Cl (2) bond *trans* to the coordinated O atom is longer than the other two at 2.332 (2) Å, again reflecting the strong bonding of the O atom. The Ti-Cl bonds *trans* to the S atoms are 2.260 (1) and 2.276 (2) Å.

Table 3. Bond lengths (Å) and angles (°) for [Ti(C<sub>6</sub>H<sub>11</sub>OS<sub>2</sub>)Cl<sub>3</sub>]

Ti-Cl(1)	2.260 (1)	Ti-Cl(2)	2.332 (2)
Ti-Cl(3)	2.276 (2)	Ti-S(1)	2.595 (1)
Ti-S(2)	2.607 (2)	Ti-O(1)	1.791 (4)
S(1)-C(1)	1.812 (6)	S(1)-C(6)	1.822 (5)
S(2)-C(3)	1.811 (6)	S(2)-C(4)	1.814 (5)
O(1)-C(2)	1.432 (7)	C(1)-C(2)	1.524 (8)
C(2)-C(3)	1.539 (8)	C(4)-C(5)	1.534 (8)
C(5)-C(6)	1.514 (9)		
Cl(1)-Ti-Cl(2)	97.0 (1)	Cl(1)-Ti-Cl(3)	99.3 (1)
Cl(2)-Ti-Cl(3)	98.6 (1)	Cl(1)-Ti-S(1)	170.0 (1)
Cl(2)-Ti-S(1)	84.3 (1)	Cl(3)-Ti-S(1)	90.2 (1)
Cl(1)-Ti-S(2)	88.5 (1)	Cl(2)-Ti-S(2)	84.2 (1)
Cl(3)-Ti-S(2)	171.2 (1)	S(1)-Ti-S(2)	81.7 (1)
Cl(1)-Ti-O(1)	99.4 (1)	Cl(2)-Ti-O(1)	154.3 (1)
Cl(3)-Ti-O(1)	98.1 (1)	S(1)-Ti-O(1)	76.3 (1)
S(2)-Ti-O(1)	76.5 (1)	Ti-S(1)-C(1)	95.6 (2)
Ti-S(1)-C(6)	114.3 (2)	C(1)-S(1)-C(6)	105.9 (3)
Ti-S(2)-C(3)	95.8 (2)	Ti-S(2)-C(4)	116.6 (2)
C(3)-S(2)-C(4)	105.3 (3)	Ti-O(1)-C(2)	126.7 (3)
S(1)-C(1)-C(2)	110.8 (4)	O(1)-C(2)-C(1)	106.8 (4)
O(1)-C(2)-C(3)	107.0 (4)	C(1)-C(2)-C(3)	116.9 (5)
S(2)-C(3)-C(2)	109.9 (4)	S(2)-C(4)-C(5)	117.8 (4)
C(4)-C(5)-C(6)	116.8 (5)	S(1)-C(6)-C(5)	117.7 (4)

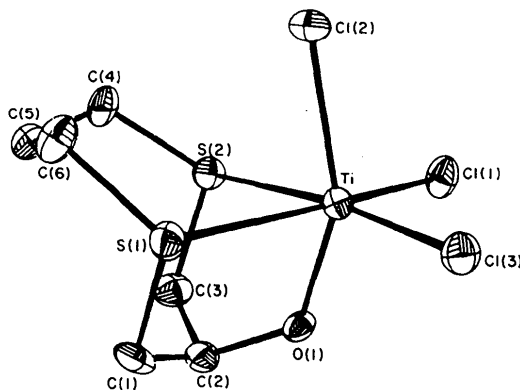
Fig. 1. A drawing of [Ti(C<sub>6</sub>H<sub>11</sub>OS<sub>2</sub>)Cl<sub>3</sub>] showing thermal ellipsoids at the 50% probability level and the atom-numbering scheme.

Table 4 summarizes the bond lengths and angles for the lead complex, (2). As can be seen in Fig. 2, the complex contains two tridentate neutral 1,5-dithiacyclooctan-3-ol ligands and two bidentate nitrate anions, giving the Pb atom a coordination number of ten. There appear to be no steric constraints which force the lead to assume such a high coordination number since each of the nitrate ions could have been monodentate rather than bidentate. Each hydroxyl group of the 1,5-dithiacyclooctane ligands is hydrogen bonded to a nitrate O atom of a neighboring molecule. These H atoms were not located, but the O...O distances are indicative of hydrogen bonding: O(4)...O(2<sup>i</sup>) [(i) = 1 - x, -y, -z] = 2.72 (1) Å and O(7)...O(1<sup>ii</sup>) [(ii) = 1 - x, -y, 1 - z] = 2.74 (1) Å.

Both rings adopt the chair-chair conformation. The complex is quite asymmetric with both 1,5-dithiacyclooctan-3-ol ligands on one side of the Pb atom and

Table 4. Bond lengths (Å) and angles (°) for  $[\text{Pb}(\text{C}_6\text{H}_{12}\text{OS}_2)_2(\text{NO}_3)_2]$ 

Pb-S(1)	3.208 (3)	Pb-S(2)	3.158 (3)
Pb-S(3)	3.179 (3)	Pb-S(4)	3.084 (3)
Pb-O(1)	2.640 (7)	Pb-O(2)	2.584 (8)
Pb-O(3)	2.795 (11)	Pb-O(4)	2.807 (8)
Pb-O(6)	2.701 (10)	Pb-O(7)	2.886 (8)
S(1)-C(2)	1.812 (11)	S(1)-C(3)	1.814 (12)
S(2)-C(5)	1.828 (12)	S(2)-C(6)	1.826 (10)
S(3)-C(8)	1.799 (12)	S(3)-C(9)	1.812 (13)
S(4)-C(11)	1.820 (12)	S(4)-C(12)	1.808 (13)
O(1)-C(1)	1.413 (14)	O(2)-C(7)	1.447 (16)
O(3)-N(1)	1.258 (15)	O(4)-N(1)	1.263 (13)
O(5)-N(1)	1.230 (12)	O(6)-N(2)	1.245 (13)
O(7)-N(2)	1.268 (14)	O(8)-N(2)	1.246 (14)
C(1)-C(2)	1.543 (16)	C(1)-C(6)	1.495 (16)
C(3)-C(4)	1.548 (15)	C(4)-C(5)	1.506 (17)
C(7)-C(8)	1.525 (16)	C(7)-C(12)	1.538 (18)
C(9)-C(10)	1.536 (17)	C(10)-C(11)	1.522 (16)
S(1)-Pb-S(2)	68.4 (1)	S(1)-Pb-S(3)	61.0 (1)
S(2)-Pb-S(3)	125.7 (1)	S(1)-Pb-S(4)	124.9 (1)
S(2)-Pb-S(4)	166.6 (1)	S(3)-Pb-S(4)	67.4 (1)
S(1)-Pb-O(1)	66.2 (2)	S(2)-Pb-O(1)	60.7 (2)
S(3)-Pb-O(1)	81.2 (2)	S(4)-Pb-O(1)	123.9 (2)
S(1)-Pb-O(2)	81.2 (2)	S(2)-Pb-O(2)	123.1 (2)
S(3)-Pb-O(2)	67.8 (2)	S(4)-Pb-O(2)	62.1 (2)
O(1)-Pb-O(2)	143.2 (2)	S(1)-Pb-O(3)	139.6 (2)
S(2)-Pb-O(3)	94.0 (2)	S(3)-Pb-O(3)	137.7 (2)
S(4)-Pb-O(3)	74.4 (2)	O(1)-Pb-O(3)	137.3 (3)
O(2)-Pb-O(3)	79.0 (3)	S(1)-Pb-O(4)	94.6 (2)
S(2)-Pb-O(4)	66.1 (2)	S(3)-Pb-O(4)	133.8 (2)
S(4)-Pb-O(4)	108.0 (2)	O(1)-Pb-O(4)	126.8 (3)
O(2)-Pb-O(4)	70.1 (3)	O(3)-Pb-O(4)	45.4 (3)
S(1)-Pb-O(6)	136.6 (2)	S(2)-Pb-O(6)	76.1 (2)
S(3)-Pb-O(6)	132.3 (2)	S(4)-Pb-O(6)	92.6 (2)
O(1)-Pb-O(6)	75.2 (3)	O(2)-Pb-O(6)	141.0 (3)
O(3)-Pb-O(6)	65.0 (3)	O(4)-Pb-O(6)	93.0 (3)
S(1)-Pb-O(7)	122.3 (2)	S(2)-Pb-O(7)	105.3 (2)
S(3)-Pb-O(7)	86.7 (2)	S(4)-Pb-O(7)	70.2 (2)
O(1)-Pb-O(7)	62.3 (2)	O(2)-Pb-O(7)	131.5 (3)
O(3)-Pb-O(7)	97.0 (3)	O(4)-Pb-O(7)	137.0 (2)
O(6)-Pb-O(7)	45.6 (3)	Pb-S(1)-C(2)	96.5 (4)
Pb-S(1)-C(3)	114.9 (4)	C(2)-S(1)-C(3)	104.0 (5)
Pb-S(2)-C(5)	112.2 (4)	Pb-S(2)-C(6)	102.1 (4)
C(5)-S(2)-C(6)	104.6 (5)	Pb-S(3)-C(8)	95.3 (4)
Pb-S(3)-C(9)	119.3 (4)	C(8)-S(3)-C(9)	103.4 (6)
Pb-S(4)-C(11)	118.0 (4)	Pb-S(4)-C(12)	102.4 (4)
C(11)-S(4)-C(12)	103.7 (6)	Pb-O(1)-C(1)	120.9 (6)
Pb-O(2)-C(7)	120.9 (6)	Pb-O(3)-N(1)	98.7 (7)
Pb-O(4)-N(1)	98.0 (6)	Pb-O(6)-N(2)	101.1 (7)
Pb-O(7)-N(2)	91.6 (6)	O(3)-N(1)-O(4)	118.0 (9)
O(3)-N(1)-O(5)	121.4 (10)	O(4)-N(1)-O(5)	120.6 (10)
O(6)-N(2)-O(7)	119.6 (10)	O(6)-N(2)-O(8)	121.3 (10)
O(7)-N(2)-O(8)	119.1 (9)	O(1)-C(1)-C(2)	110.3 (9)
O(1)-C(1)-C(6)	109.8 (8)	C(2)-C(1)-C(6)	117.3 (9)
S(1)-C(2)-C(1)	116.9 (7)	S(1)-C(3)-C(4)	115.3 (8)
C(3)-C(4)-C(5)	114.1 (9)	S(2)-C(5)-C(4)	118.3 (9)
S(2)-C(6)-C(1)	115.2 (8)	O(2)-C(7)-C(8)	110.8 (10)
O(2)-C(7)-C(12)	105.5 (10)	C(8)-C(7)-C(12)	116.9 (10)
S(3)-C(8)-C(7)	118.9 (9)	S(3)-C(9)-C(10)	115.7 (9)
C(9)-C(10)-C(11)	116.1 (9)	S(4)-C(11)-C(10)	118.2 (9)
S(4)-C(12)-C(7)	115.6 (9)		

both nitrate ions on the opposite side. That is, two of the S atoms on different 1,5-dithiacyclooctan-3-ol ligands are separated by an S(1)-Pb-S(3) angle of  $61.0(1)^\circ$ , whereas the other two S atoms are separated by an S(2)-Pb-S(4) angle of  $166.6(1)^\circ$ .

A comparison of the bond distances among the four known complexes of 1,5-dithiacyclooctan-3-ol, as well as with the titanium complex of the anionic form of the

ligand, reveals some interesting correlations. The revised Shannon (1976) ionic radii for the metal ions are subtracted from the average of the M-S and M-O bond distances for each complex to obtain the effective S and O atom radii given below. [The ionic radius for six-coordinate  $\text{Cu}^{\text{II}}$  is used for the Cu-S (equatorial) bond. The radius is adjusted by adding  $0.3 \text{ \AA}$  for the Cu-O bond (axial); this is a reasonable procedure to account of the tetragonal distortion of  $\text{Cu}^{\text{II}}$  coordination.]

Metal ion	Effective S radius (Å)	Effective O radius (Å)	M-O-C (°)
$\text{Ti}^{\text{IV}}$	2.00	1.19	126.7
$\text{Fe}^{\text{II}}$	1.76	1.28	112.7
$\text{Ni}^{\text{II}}$	1.71	1.36	108.4
$\text{Cu}^{\text{II}}$	1.60	1.34	101.3
$\text{Pb}^{\text{II}}$	1.76	1.21	120.9

As expected,  $\text{Ti}^{\text{IV}}$  shows a strong affinity for the hydroxyl O atom, and the effective O-atom radius is smaller than that found in complexes where the hydroxyl group is not deprotonated. However,  $\text{Ti}^{\text{IV}}$  repels the S atoms so strongly that the effective S-atom radius is appreciably larger in the  $\text{Ti}^{\text{IV}}$  complex than in the other complexes. The opening of the M-O-C angle in both the  $\text{Ti}^{\text{IV}}$  and  $\text{Pb}^{\text{II}}$  complexes also reflects the shortening of the M-O bond and lengthening of the M-S bond relative to the first-row transition metals.

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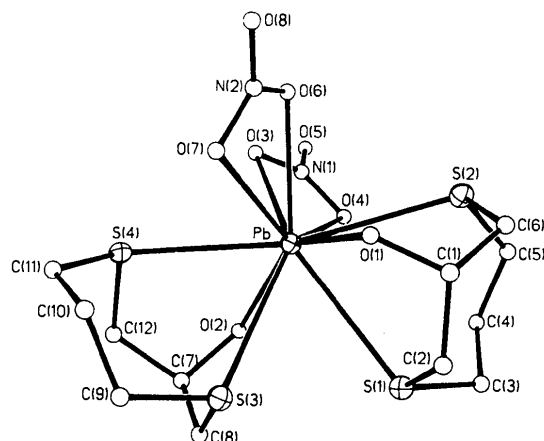


Fig. 2. A drawing of  $[\text{Pb}(\text{C}_6\text{H}_{12}\text{OS}_2)_2(\text{NO}_3)_2]$  showing the atom-numbering scheme. Anisotropic atoms are shown with thermal ellipsoids at the 50% level; other atoms are drawn an arbitrary size.

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## Structures of Ethylenediammonium Monohydrogentetraoxophosphate(V) and Ethylenediammonium Monohydrogentetraoxoarsenate(V)

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**Abstract.** (I): C<sub>2</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>.HPO<sub>4</sub><sup>2-</sup>, *M<sub>r</sub>* = 158.09, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 8.059 (3), *b* = 11.819 (5), *c* = 7.513 (3) Å, β = 110.12 (5)°, *V* = 672 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.562 Mg m<sup>-3</sup>, λ(Ag Kα) = 0.5608 Å, μ = 0.198 mm<sup>-1</sup>, *F*(000) = 336, *T* = 295 K, final *R* = 0.030 for 1286 unique reflexions. (II): C<sub>2</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>.HAsO<sub>4</sub><sup>2-</sup>, *M<sub>r</sub>* = 202.04, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.433 (9), *b* = 8.163 (6), *c* = 8.062 (6) Å, β = 90.33 (7)°, *V* = 687 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.953 Mg m<sup>-3</sup>, λ(Ag Kα) = 0.5608 Å, μ = 2.740 mm<sup>-1</sup>, *F*(000) = 408, *T* = 295 K, final *R* = 0.038 for 1499 unique reflexions. In both cases planes of XO<sub>4</sub>H<sup>2-</sup> tetrahedra alternate with planes of (CH<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> groups. In the first type of planes, XO<sub>4</sub>H tetrahedra are associated in pairs forming X<sub>2</sub>O<sub>8</sub>H<sub>2</sub><sup>+</sup> groups. (CH<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> groups are centrosymmetric for *X* = As, pseudocentrosymmetric for *X* = P.

**Introduction.** During investigations of interactions of ethylenediamine with various kinds of acidic monophosphates or monoarsenates we very often observed the formation of very stable compounds corresponding to the formula H<sub>3</sub>XO<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub> (*X* = P, As). These compounds appeared later to be interesting starting materials for further syntheses. The present work is devoted to a detailed structural investigation of these two species.

**Experimental.** (I) C<sub>2</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>.HPO<sub>4</sub><sup>2-</sup>. Single crystals are easily prepared by slow evaporation at room temperature of an aqueous solution of H<sub>3</sub>PO<sub>4</sub> and ethylenediamine in stoichiometric ratio. Crystals appear as stout, multifaceted, monoclinic prisms. Crystal size: 0.24 × 0.24 × 0.30 mm. Density not measured. Philips

PW 1100 diffractometer, graphite monochromator. Systematic absences: *h*0*l*: *h* = 2*n*; 0*k*0: *k* = 2*n*. 24 reflexions (10 < θ < 14°) for refining unit-cell dimensions. ω scan. 2229 non-zero unique reflexions collected (3 < θ < 30°), ±*h,k,l*, *h*<sub>max</sub> = 13, *k*<sub>max</sub> = 20, *l*<sub>max</sub> = 12. Scan width 1.40°, scan speed 0.03° s<sup>-1</sup>, total background measuring time 10 s. Two intensity and orientation reference reflexions ( $\bar{6}52$  and 652), no variation. Lorentz and polarization correction, no absorption correction. Structure solved by classical methods (Patterson and successive Fourier syntheses). H atoms from difference Fourier map. Anisotropic full-matrix least-squares refinement (on *F*), isotropic for H atoms. Unit weights. Final refinement cycles with 1286 reflexions corresponding to *I* > 6σ<sub>*I*</sub>. Final *R* = 0.030 (*ωR* = 0.035). *S* = 0.655. Max. Δ/σ = 0.00. Max. peak height in the final difference Fourier synthesis 0.39 e Å<sup>-3</sup>. No extinction correction. *R* = 0.054 for the complete set of 2229 reflexions. Scattering factors for neutral atoms and *f*', *f*'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) SDP employed for all calculations. Computer used: PDP 11/70.

(II) C<sub>2</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>.HAsO<sub>4</sub><sup>2-</sup>. The chemical preparation from H<sub>3</sub>AsO<sub>4</sub> and ethylenediamine is identical to that described for (I). The morphology of the crystals obtained is close to that of the phosphorus complex. Crystal size: 0.30 × 0.30 × 0.24 mm. Density not measured. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: *h*0*l*: *l* = 2*n*; 0*k*0: *k* = 2*n*. 18 reflexions (10 < θ < 12°) for refining unit-cell dimensions. ω scan. 2804 non-zero unique reflexions collected (3 < θ < 30°), ±*h,k,l*, *h*<sub>max</sub> = 16, *k*<sub>max</sub> = 14, *l*<sub>max</sub> = 14. Scan width 1.30°, scan speed