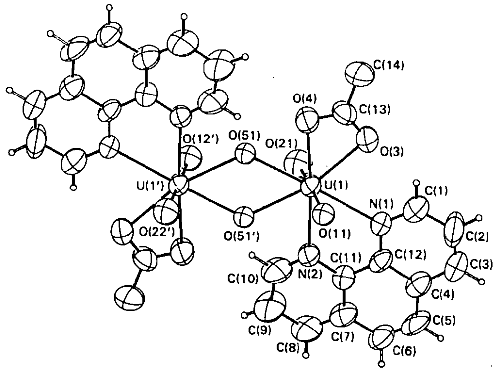

Fig. 3. View of (2), as an idealized non-centrosymmetric dimer, with O(11) and O(21) associated with U(1), and O(12) and O(22) [as the centrosymmetrically-related equivalents O(12′) and O(22′)] associated with U(1′); only O(51) and O(51′) are included as bridging hydroxide positions.

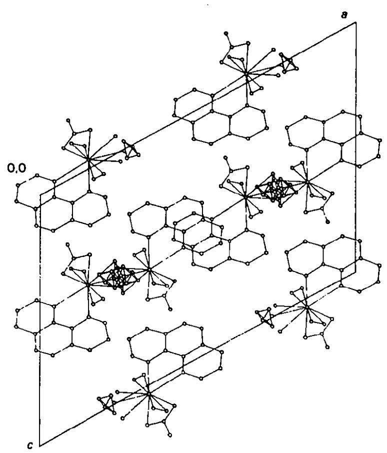

Fig. 4. Packing diagram for (2), viewed down **b**. The alternative positions for the uranyl and bridging oxygen atoms can be seen.

2·34 (5)–2·42 (4) and 2·46 (1)–2·47 (2) Å]. Again these are similar to values previously observed (Alcock, Flanders & Brown 1984), but there is a possible lengthening of the U—N(ligand) bonds to 2·65 (3) and 2·63 (2) Å compared with 2·56 (2) Å found in (1). The O···N (acetate–phenanthroline) contact [2·97 (2) Å] is slightly longer than the equivalent distance found in the 2,2′-bipyridyl complex [2·96 (1) Å]. This may be caused by the need to accommodate the more rigid ligand in the equatorial plane, but it should also be borne in mind that one complex has two nitrate ligands and the other has one acetate and two hydroxides. The atoms which form the equatorial plane are again puckered with deviations in the range −0·18 (5) to 0·15 (5) Å. The coordinating ligands are substantially displaced out of the equatorial plane [by up to 0·61 (5) Å] as seen in Table 4. The acetate group is displaced slightly out of the equatorial plane with a bite [2·20 (1) Å] similar to that found in the 2,2′-bipyridyl analogue [2·16 (1) and 2·17 (1) Å]. The packing diagram, Fig. 4, again indicates a face-to-face alignment of the aromatic rings.

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Polymeric Bis(*O*-methyldithiocarbonato)lead(II)

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Abstract. $[Pb(S_2COCH_3)_2]$, $M_r = 421{\cdot}5$, monoclinic, $C2$, $a = 12{\cdot}285\,(5)$, $b = 4{\cdot}2596\,(7)$, $c = 10{\cdot}060\,(3)$ Å, $\beta = 108{\cdot}04\,(3)°$, $V = 500\,(2)$ Å^3, $D_x = 2{\cdot}800$ Mg m^{-3} for $Z = 2$, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 17{\cdot}693$ mm^{-1}, $F(000) = 384$, $T = 295\,(2)$ K, $R = 0{\cdot}058$ for 455 observed reflections. The Pb atom in $Pb(S_2COCH_3)_2$ is

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situated on a crystallographic twofold axis and is chelated by two $^{-}S_2COCH_3$ ligands related to each other across this axis; Pb—S(1) 3·01 (2), Pb—S(2) 2·92 (1) Å and S(1)—Pb—S(2) 62·3 (2)°. The two S(1) atoms of one $Pb(S_2COCH_3)_2$ molecule also coordinate an adjacent Pb atom, S(1)—Pb′ 3·02 (2) Å, which generates a polymeric structure and has the result that each Pb atom is six-coordinate. The Pb atom exists in a distorted octahedral environment with the two non-bridging S atoms occupying approximate axial positions and the basal plane being defined by the four bridging S atoms.

Introduction. Recent crystallographic studies on non-transition-metal xanthate ($-S_2COR$) complexes have shown that the geometry adopted about a given central atom may depend markedly on the nature of the R substituent. Thus, in $Bi(S_2COCH_3)_3$ (Snow & Tiekink, 1987) the Bi atom is six coordinate with one of the asymmetrically chelating xanthate ligands defining an approximate mirror plane whereas in the $R = i\text{-}C_3H_7$ derivative the Bi atom is seven coordinate as a result of the presence of bridging xanthate ligands in the polymeric structure (Hoskins, Tiekink & Winter, 1985). Substantial differences in the central-atom geometries have also been found for the bis(xanthates) of Hg^{II}. In the $R = CH_2CH_3$ (Watanabe, 1977; Chieh & Moynihan, 1980) and $R = i\text{-}C_3H_7$ (Watanabe, 1981) compounds, the 16-membered rings, formed by bridging xanthate ligands, feature distorted tetrahedral Hg centres; however, in the $R = CH_3$ complex (Tiekink, 1987) the polymeric structure is based on a helical chain in which the Hg atoms exist in T-shaped geometries. These studies have now been extended to the Pb xanthates.

The Pb^{II} bis(xanthates) $R = CH_2CH_3$ (Hagihara & Yamashita, 1966) and $R = n\text{-}C_4H_9$ (Hagihara, Watanabe & Yamashita, 1968) show pyramidal environments about the Pb atoms and weak intermolecular Pb···S interactions (> 3·3 Å) in their respective crystal lattices (perhaps indicating a propensity for polymerization). The crystal structure of the title compound, $Pb(S_2COCH_3)_2$, has been determined in order to investigate the nature of the Pb-atom geometry when coordinated by the $-S_2COCH_3$ anion given the above observations.

Table 1. *Fractional atomic coordinates and* B_{eq} *values* (Å²)

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	B_{eq}
Pb	0·0	0·0	0·0	5·84
S(1)	−0·0262 (5)	0·4981 (55)	−0·2198 (6)	6·04
S(2)	−0·2294 (9)	0·2479 (33)	−0·1351 (9)	7·12
C(1)	−0·1755 (26)	0·3978 (52)	−0·2504 (25)	4·34
O(1)	−0·2336 (14)	0·4827 (80)	−0·3731 (16)	4·71
C(2)	−0·3593 (18)	0·4903 (92)	−0·4168 (26)	5·39

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Pb—S(1)	3·01 (2)	Pb—S(2)	2·92 (1)
S(1)—C(1)	1·82 (3)	S(2)—C(1)	1·63 (3)
C(1)—O(1)	1·27 (3)	O(1)—C(2)	1·47 (3)
Pb—S(1^{i})	3·02 (2)		
S(1)—Pb—S(2)	62·3 (2)	S(1)—Pb—S(1^{ii})	90·3 (2)
S(1)—Pb—S(2^{ii})	87·4 (2)	S(1)—Pb—S(1^{i})	89·9 (2)
S(1)—Pb—S(1^{iii})	179·8 (2)	S(2)—Pb—S(2^{ii})	137·6 (2)
S(2)—Pb—S(1^{i})	92·7 (2)	S(2)—Pb—S(1^{iii})	117·7 (2)
Pb—S(1)—C(1)	80 (1)	Pb—S(2)—C(1)	86 (1)
S(1)—C(1)—S(2)	126 (2)	S(1)—C(1)—O(1)	109 (2)
S(2)—C(1)—O(1)	125 (3)	C(1)—O(1)—C(2)	121 (2)
Pb—S(1)—Pb(^{i})	89·9 (2)		

Symmetry code: (i) $x, -1+y, z$; (ii) $\bar{x}, y, \bar{z}$; (iii) $\bar{x}, -1+y, \bar{z}$.

Experimental. The title compound was synthesized by reacting the potassium salt of $^{-}S_2COCH_3$ with lead nitrate in aqueous solution; the resultant precipitate was filtered off and recrystallized from acetone. The crystals thus obtained were fine needles elongated in the b-axis direction; attempts to cut the crystals were unsuccessful as they were easily cleaved. Enraf–Nonius CAD-4F diffractometer controlled by PDP8/A computer, graphite-monochromated Mo $K\bar{\alpha}$ radiation; ω:2θ scan technique. Cell parameters on crystal 0·015 × 0·015 × 0·75 mm from least-squares procedure on 25 reflections ($10 \leq \theta \leq 16°$). Analytical absorption correction applied (Sheldrick, 1976); max./min. transmission factors 0·6762 and 0·0790. Total of 1081 reflections ($1 \leq \theta \leq 25·0°$) measured in the range $-14 \leq h \leq 14$, $0 \leq k \leq 5$, $-11 \leq l \leq 11$; some high-angle Friedel pairs also included. No significant variation in the intensities of three reference reflections (220, 204, $2\bar{2}1$) measured every 7200 s. Space group from analysis. 573 unique reflections ($R_{int} = 0·043$), 455 satisfied $I \geq 2·5\sigma(I)$. Structure solved from interpretation of Patterson map, full-matrix least-squares refinement of 51 parameters based on F (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms, H atoms included in the model at their calculated positions. At convergence $R = 0·058$, $wR = 0·060$, $w = 2·13/[\sigma^2(F) + 0·0029F^2]$, $S = 1·96$, $(\Delta/\sigma)_{max} \leq 0·06$, $(\Delta\rho)_{max} = 1·33$, $(\Delta\rho)_{min} = -2·61$ e Å^{-3}; no extinction correction. Scattering factors for H,C,O and S given in *SHELX*76 (Sheldrick, 1976) and those for neutral Pb corrected for f' and f'' (Hamilton & Ibers, 1974). All calculations on VAX11/785 computer system. Atomic parameters are given in Table 1, bond distances and angles in Table 2;* the numbering scheme used is shown in Fig. 1.

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* Lists of structure factors, thermal parameters, H-atom parameters and mean-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44457 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The Pb atom in $Pb(S_2COCH_3)_2$ is situated on a crystallographic site of symmetry 2, located at (0,0,0), and thus only half of the $Pb(S_2COCH_3)_2$ molecule constitutes the asymmetric unit. The $^-S_2COCH_3$ anion chelates the Pb atom with relatively long Pb—S bonds of Pb—S(1) 3·01 (2) and Pb—S(2) 2·92 (1) Å and subtends an angle at the Pb centre of 62·3 (2)° [S(1)—Pb—S(2)]. The two S(1) atoms of each $Pb(S_2COCH_3)_2$ unit also coordinate a neighbouring Pb atom thereby generating a linear polymer situated about the twofold axis and parallel to the *b* axis (*i.e.* the needle axis); there are no significant interchain interactions. The Pb···Pb separations correspond to the unit-cell length of the *b* axis, *i.e.* 4·2596 (7) Å, and are not indicative of significant Pb···Pb interactions; the Pb atom is thus six-coordinate. As illustrated in Fig. 1, the Pb atom is coplanar with the four symmetry-related S(1) atoms with the S(2) and S(2″) atoms above and below the basal plane respectively; the coordination environment may then be described as being based on a distorted octahedron. As the Pb atom is in the formal oxidation state of +II, it may be expected that the $6s^2$ lone-pair of electrons would occupy a coordination site, *i.e.* display stereochemical activity, in the Pb-atom coordination environment. If stereochemically active, the lone pair of electrons would, because of the crystallographically imposed symmetry, lie on the twofold axis, and be directed along the Pb···Pb vector between the bridging S(1) atoms. However, there is no significant distortion from 90° in the S—Pb—S angles, defining the basal plane, and thus it may be concluded that the lone pair of electrons is stereochemically inactive in this compound. The deviation of the S(2)—Pb—S(2″) angle of 137·6 (2)° from linearity can be related to the restricted bite distance of the xanthate ligand.

The structure found for $Pb(S_2COCH_3)_2$ contrasts with those found for $Pb(S_2COCH_2CH_3)_2$ (Hagihara & Yamashita, 1966) and $Pb(S_2CO\text{-}n\text{-}C_4H_9)_2$ (Hagihara, Watanabe & Yamashita, 1968). In the latter compounds the molecules are essentially discrete with the Pb atoms existing in pyramidal geometries. In $Pb(S_2COCH_2CH_3)_2$, the Pb atom is chelated by two xanthate ligands at Pb—S 2·74 (3), 2·84 (3) Å and 2·79 (3), 2·95 (3) Å respectively; there is some weak intermolecular association in this structure *via* Pb···S interactions of 3·32 (3), 3·37 (3), and 3·50 (3) Å but none that compare with those found in $Pb(S_2COCH_3)_2$. A similar situation exists in the structure of $Pb(S_2CO\text{-}n\text{-}C_4H_9)_2$ (Hagihara, Watanabe & Yamashita, 1968). It is noteworthy that unit-cell repeat distances of 4·301 (15) Å [$R = CH_2CH_3$] and 4·58 (11) Å [$R = n\text{-}C_4H_9$] for the *b* axes, which correspond to the direction of the intermolecular Pb···S association, although longer in these compounds, are comparable to that found for polymeric $Pb(S_2COCH_3)_2$ of 4·2596 (7) Å.

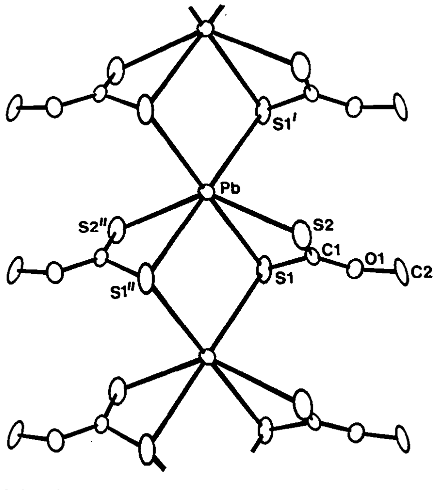

Fig. 1. Molecular structure and numbering scheme for polymeric $Pb(S_2COCH_3)_2$ (Johnson, 1971).

The structure found for $Pb(S_2COCH_3)_2$ can be seen to be derived from $Pb(S_2COCH_2CH_3)_2$ if the S atoms involved in the weaker interactions to the Pb atom in $Pb(S_2COCH_2CH_3)_2$ are considered equivalent to the S atoms forming the shorter Pb—S bonds in $Pb(S_2COCH_3)_2$. Assuming this relationship, the S atoms forming the stronger Pb—S bonds in $Pb(S_2COCH_2CH_3)_2$ now bridge two Pb atoms in $Pb(S_2COCH_3)_2$ with a concomitant lengthening of these Pb—S bonds.

Similar pyramidal Pb-atom environments and intermolecular association as found in $Pb(S_2COCH_2CH_3)_2$ (Hagihara & Yamashita, 1966) and $Pb(S_2CO\text{-}n\text{-}C_4H_9)_2$ (Hagihara, Watanabe & Yamashita, 1968) have been reported for the related dithiocarbamate compounds, $Pb(S_2CNR_2)_2$ [$R = CH_3$ (Iwasaki, 1980); $R = CH_2CH_3$ (Iwasaki & Hagihara, 1972); $R = i\text{-}C_3H_7$ (Ito & Iwasaki, 1980)]. A different structural type has been reported for the dithiophosphate derivative, $Pb[S_2P(i\text{-}OC_3H_7)_2]_2$ (Lawton & Kokotailo, 1972), in which, like that found for $Pb(S_2COCH_3)_2$, the Pb atom is six coordinate. The bridging mode of coordination of the dithiophosphate ligands is similar to that found for the xanthate ligands in $Pb(S_2COCH_3)_2$; however, in $Pb[S_2P(i\text{-}OC_3H_7)_2]_2$ each dithiophosphate ligand bridges a different Pb atom which leads to a polymeric structure. In the latter compound (Lawton & Kokotailo, 1972) the lone pair of electrons is stereochemically active so that the Pb-atom geometry is based on a distorted pentagonal bipyramid with the lone pair of electrons occupying a position in the basal plane. The structure reported here for $Pb(S_2COCH_3)_2$ represents a third structural type for Pb(1,1-dithiolate)$_2$ compounds.

In contrast with the $Hg(S_2COCH_3)_2$ (Tiekink, 1987) and $Bi(S_2COCH_3)_3$ (Snow & Tiekink, 1987) compounds (in which the coordination number of the central atom is less than those found in the $R = CH_2CH_3$ and $i\text{-}C_3H_7$ homologues) there is an increase in the formal coordination number of the Pb atom in $Pb(S_2COCH_3)_2$ compared with the higher homologues. The structure determination reported herein provides another example of a different coordination environment in a metal xanthate compound when the nature of the *R* substituent in the ^-S_2COR anion is changed.

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Structures of Dibromobis(tetrahydroselenophene)mercury(II) and Diiodobis(tetrahydroselenophene)mercury(II)

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Abstract. $[HgBr_2(C_4H_8Se)_2]$, $M_r = 630·53$, monoclinic, $C2/c$, $a = 23·551\ (3)$, $b = 5·1288\ (5)$, $c = 14·596\ (2)$ Å, $\beta = 128·14\ (1)°$, $V = 1386·6\ (2)$ Å^3, $Z = 4$, $D_x = 3·02$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 220$ cm^{-1}, $F(000) = 1000$, $T = 295$ K, $R = 0·025$ for 1083 observed unique reflections. $[HgI_2(C_4H_8Se)_2]$, $M_r = 724·53$, triclinic, $P\bar{1}$, $a = 5·1653\ (8)$, $b = 9·0009\ (12)$, $c = 16·884\ (4)$ Å, $\alpha = 92·21\ (2)$, $\beta = 91·29\ (2)$, $\gamma = 101·75\ (2)°$, $V = 767·6\ (2)$ Å^3, $Z = 2$, $D_x = 3·13$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 187$ cm^{-1}, $F(000) = 572$, $T = 295$ K, $R = 0·031$ for 2122 observed unique reflections. Both compounds consist of monomeric species with the Hg atoms four-coordinated by two halogen atoms and two tetrahydroselenophene ligands. The Hg coordination polyhedron is a distorted tetrahedron with [I]Br–Hg–Br[I] and Se–Hg–Se bond angles of 110·06 (4) [120·79 (3)] and 114·79 (4)° [109·62 (4)°]. The Hg–Br[I] and Hg–Se distances are 2·604 (1) [2·730 (1), 2·755 (1)] and 2·648 (1) Å [2·688 (1), 2·718 (1) Å].

Introduction. Compounds of mercury(II) halides with neutral organic sulfur, selenium or tellurium ligands show a remarkable variety in composition, structure and spectroscopic properties. The composition of thioether complexes ($L = RSR'$) can, for example, range from $(HgX_2)_2.L$ to $HgX_2.2L$ with $3HgX_2.2L$ and $HgX_2.L$ being the common forms between the extremes.

As has been confirmed by numerous crystallographic investigations, monomeric as well as halogen-bridged dimeric and polymeric structures occur. Brändén (1964) reported the crystal structures of $(HgCl_2)_2.SEt_2$ and $HgCl_2.THT$ (THT = tetrahydrothiophene), both consisting of polymeric chains built up by halogen bridges. Sandström & Persson (in preparation) have investigated the structures of $HgX_2.2THT$ (X = Cl, Br) in the solid state and, together with Goggin (Sandström, Persson & Goggin, 1986), the bromide and iodide in THT solution. They found, both in the solid compounds and in the THT solutions, a distorted tetrahedral arrangement around Hg with two halogens and two THT S atoms.

Experimental. Summary of experiments and refinements are given in Table 1. Crystals were grown from a solution of mercury(II) bromide (iodide) in warm acetonitrile on addition of excess of tetrahydroselenophene (THSe), followed by slow cooling to room temperature. Single crystals of the two compounds were

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