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Anhydrous lead(II) heptanoate

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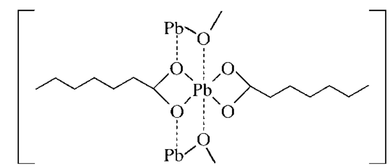
The title compound, *catena*-poly[[(heptanoato-O,O')lead(II)]-μ-heptanoato-O,O':O:O'], $[Pb(C_7H_{13}O_2)_2]$, is a metallic soap which can be used as a corrosion inhibitor since it forms a passive film at the Pb surface. Its structure is characterized by two-dimensional layers parallel to the *bc* plane. The layers are packed through van der Waals interactions along the *a* direction and form blocks parallel to (001). The $6s^2$ lone pair of electrons on Pb^{II} is stereochemically active in this compound, which leads to a hemidirected octahedral geometry for the O-environment around the Pb atoms.

Comment

Electrochemical studies have shown that aliphatic sodium carboxylate inhibits the corrosion of lead in aqueous solution (Rocca & Steinmetz, 2001). Particularly, the efficiency of this inhibition by these compounds, with the general formula $CH_3(CH_2)_{n-2}COONa$ (n = 7–11), was found to depend on the chain length of the aliphatic group. The passivation of the metal was attributed to the growth of passive layers containing metallic soap, $[Pb(C_nH_{2n-1}O_2)_2]$. Metals such as Cu, Zn, Mg and Fe, the corrosion/passivation behaviour of which is under study in our laboratory, can be protected by their corresponding metallic soaps. The general aim of these studies concerns new protective treatments, which would be less polluting than the phosphatation or chromatation often currently used in metal protection. To optimize the treatments, for example by varying the chain length of the aliphatic carboxylate group, it is necessary to understand better the interactions between the surface of the metal, oxidized or not, and the metallic soap, which requires knowledge of the crystallographic structure formed by the hydrophobic and protecting metallic soap.

Crystallographic structures for two short linear-chain carboxylates are known, namely lead formate, $[Pb(CHO_2)_2]$, and lead acetate trihydrate, $[Pb(C_2H_3O_2)_2]\cdot 3H_2O$ (Harrison & Steel, 1982). The former has a three-dimensional polymeric structure, while the latter is built up of parallel sheets and so adopts a two-dimensional character. The structure of the title compound, (I), is characterized by a lamellar building of sheets, formed by Pb—O bonds, parallel to the *bc* plane. The sheets are packed along the *a* direction by van der Waals interactions and consequently form blocks parallel to (001), as shown in Fig. 1. The Pb atoms are disposed on a zigzag chain through the middle of the sheets, running along the *b* direction.



(I)

Fig. 2 shows the environment around Pb. Each Pb atom is surrounded by six O atoms, which form a very distorted polyhedron. The six O atoms belong to four different bidentate carboxylate groups. Carboxylate O11/O12 is chelating [Pb—O11^{i} 2.583 (8) and Pb—O12^{i} 2.735 (8) Å; symmetry code: (i) $-x$, $-y$, $-z$] and also bridges the adjacent Pb atoms along the *b* direction [Pb—O11 2.567 (7) and Pb—O12^{ii} 2.620 (7) Å, and O11—Pb—O12^{ii} 166.6 (3)°; symmetry code: (ii) x, $1 + y$, z]. Carboxylate O21/O22 is only chelating and leads to the shortest Pb—O distances in the structure [Pb—O21 2.451 (8) and Pb—O22 2.410 (9) Å]. The average Pb—O distance is 2.56 Å, which is slightly shorter than the sum of the ionic radii (ionic radii: Pb^{II} = 1.19 Å when the coordination number is 6, and O = 1.40 Å; Shannon, 1976). The six Pb—O bonds are directed on the same side of a globe surrounding the Pb atom, so that the coordination can be qualified as 'hemidirected octahedral coordination' (Shimoni-Livny *et al.*, 1998). This type of coordination arises for Pb^{II} when the $6s^2$ lone pair is stereochemically active. There are voids in the Pb—O bonding distribution which make the lone-pair position identifiable; the lone pair is approximately situated in the direction of the relatively short Pb—O21 bond.

The absence of structural water, contrary to the case of the equivalent acetate compound, which is the trihydrate, was confirmed by thermogravimetric analysis measurements (no

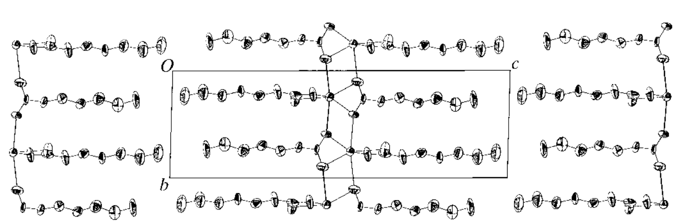


Figure 1
Projection of the structure of (I) along [100]. Displacement ellipsoids are drawn at the 70% probability level and H atoms have been omitted for clarity.

weight loss was observed between room temperature and 448 K) and micro-Raman spectroscopy (no signal due to water-molecule vibration was recorded in the wave-number range 3100–3500 cm^{-1}). The structures of both (I) and lead acetate have a two-dimensional character. The building of the sheets is similar, but the main differences in lead acetate are the existence of hydrogen bonds formed by water molecules and the coordination number for the Pb atoms, which is increased to eight by the O atoms of the water molecules.

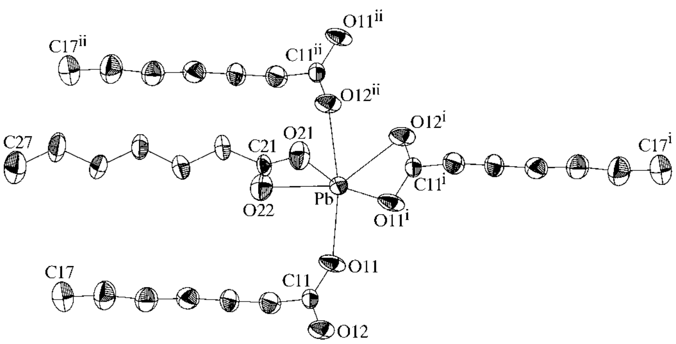


Figure 2
The environment of the Pb^{II} ion in (I) showing the orientation of the linear heptanoate chains. Displacement ellipsoids are drawn at the 70% probability level and H atoms have been omitted for clarity (symmetry codes are as in Table 1).

Experimental

Crystals of the title compound were prepared by the reaction of a solution of lead nitrate with sodium heptanoate. The precipitates obtained were washed with distilled water and dried. A small quantity of the product was recrystallized from ethanol for one month at room temperature. The colourless crystals were small plates with the (001) face well developed.

Crystal data

$[Pb(C_7H_{13}O_2)_2]$	$Z = 2$
$M_r = 465.2$	$D_x = 1.890$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 4.8574$ (10) Å	Cell parameters from 41 187 reflections
$b = 7.3046$ (10) Å	$\theta = 1$–31°
$c = 23.1846$ (10) Å	$\mu = 10.318$ mm^{-1}
$\alpha = 91.61$ (1)°	$T = 293$ (2) K
$\beta = 95.66$ (1)°	Plate, colourless
$\gamma = 90.99$ (1)°	0.15 × 0.13 × 0.01 mm
$V = 818.1$ (2) $Å^3$	

Data collection

Nonius KappaCCD area-detector diffractometer	16 127 measured reflections
CCD scans	2820 independent reflections
Absorption correction: empirical, fitted by spherical harmonic functions (*SORTAV*; Blessing, 1995)	2419 reflections with $I > 2\sigma(I)$
$T_{min} = 0.22$, $T_{max} = 0.90$	$R_{int} = 0.078$
	$\theta_{max} = 24.84°$
	$h = -5 \rightarrow 5$
	$k = -8 \rightarrow 8$
	$l = 0 \rightarrow 27$

Table 1
Selected geometric parameters (Å, °).

Pb—O22	2.410 (9)	Pb—$O12^{ii}$	2.620 (7)
Pb—O21	2.451 (8)	Pb—$O12^{i}$	2.735 (8)
Pb—O11	2.567 (7)	O11—C11	1.270 (12)
Pb—$O11^{i}$	2.583 (8)	O12—C11	1.239 (12)
O22—Pb—O21	52.4 (3)	O11—Pb—$O12^{ii}$	166.6 (3)
O22—Pb—O11	81.3 (3)	$O11^{i}$—Pb—$O12^{ii}$	117.4 (3)
O21—Pb—O11	91.1 (3)	O22—Pb—$O12^{i}$	129.2 (3)
O22—Pb—$O11^{i}$	118.7 (3)	O21—Pb—$O12^{i}$	78.1 (3)
O21—Pb—$O11^{i}$	77.6 (3)	O11—Pb—$O12^{i}$	113.4 (2)
O11—Pb—$O11^{i}$	65.2 (3)	$O11^{i}$—Pb—$O12^{i}$	48.3 (2)
O22—Pb—$O12^{ii}$	86.4 (3)	$O12^{ii}$—Pb—$O12^{i}$	70.9 (3)
O21—Pb—$O12^{ii}$	77.2 (3)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, 1+y, z$.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0852P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.034$	$\Delta\rho_{max} = 1.12$ e $Å^{-3}$
2820 reflections	$\Delta\rho_{min} = -2.15$ e $Å^{-3}$
172 parameters	

H atoms were placed geometrically (C—H = 0.95–0.97 Å) but their parameters were not refined and their individual isotropic displacement parameters were fixed at $U_{iso} = 1.2U_{eq}$(C).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* in *HKL* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* in *HKL*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SIR*97 (Altomare *et al.*, 1998); molecular graphics: *ATOMS* (Dowty, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1131). Services for accessing these data are described at the back of the journal.

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