

LEAD(II) CARBOXYLATE STRUCTURES *

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Summary

The structures of four lead(II) carboxylate complexes, lead(II) formate, lead(II) acetate trihydrate, lead(II) pentafluorobenzoate bis(methanol) solvate, and the lead(II)-EDTA hydrate, $\text{Pb}_2(\text{EDTA})_2 \cdot 3\text{H}_2\text{O}$, are described. Lead(II) formate has a three-dimensional polymeric structure, lead(II) acetate trihydrate a chain structure linked by hydrogen-bonding to form parallel sheets, lead(II) pentafluorobenzoate bis(methanol) solvate a linear chain structure, and the lead(II)-EDTA hydrate, a structure comprising both isolated monomeric and dimeric units. In each case, the lead atom is eight-coordinated although with vastly differing stereochemistries, except for the monomeric units in the lead(II)-EDTA complex, which contain seven-coordinated lead.

There is a relative paucity of structural data for lead(II) complexes. The brief reports of the structures of both lead(II) formate [1] and lead(II) acetate trihydrate [2] are only approximate and are totally inadequate. However, a few more sophisticated complexes have been examined in detail. D-Penicillamine-lead(II), $\text{Pb}[\text{O}_2\text{CCH}(\text{NH}_2)\text{CMe}_2\text{S}]$, has a structure in which the amino acid residue functions as a terdentate ligand towards the metal, forming three strong bonds to oxygen, nitrogen and sulphur. Additional weak Pb—S and Pb—O interactions complete pseudo-pentagonal bipyramidal geometry in which one of the equatorial positions is occupied by the stereochemically-active lone pair of electrons of the lead [3]. The first coordination sphere of lead in the lead(II) formate-thiourea complex, $\text{Pb}(\text{O}_2\text{CH})_2 \cdot 2\text{SC}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$, has three sulphur and five oxygen atoms in a distorted dodecahedral arrangement. Adjacent lead atoms are bridged by sulphur atoms from the thiourea molecules forming $[-\text{S}-\text{Pb}-\text{S}-]$ chains extending along the [001] direction, and by unidentate bridging formate ions. The remaining thiourea molecule, water molecule, and formate ion are uni-

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coordinatively bonded to the same lead [4]. The analogous lead(II) acetate-thiourea complex, $\text{Pb}(\text{O}_2\text{CCH}_3)_2 \cdot \text{SC}(\text{NH}_2)_2$, also has a chain structure, in which adjacent lead ions are linked by bridging sulphur atoms. Three sulphur and four oxygen atoms make up the distorted pentagonal bipyramidal coordination polyhedron about the metal [5,6]. No lead-oxygen interactions occur in either of the thiourea-rich complexes, $\frac{3}{2} \text{Pb}(\text{O}_2\text{CH})_2 \cdot 4 \text{SC}(\text{NH}_2)_2$ [7] and $\text{Pb}(\text{picrate})_2 \cdot 4 \text{SC}(\text{NH}_2)_2$ [8]. In the former, the lead is eight-coordinated by sulphur atoms from eight different thiourea molecules giving a twisted prismatic geometry, whilst the latter complex contains polymeric chains of edge-sharing distorted $\{\text{Pb}[\text{SC}(\text{NH}_2)_2]_6\}$ octahedra.

In order to somewhat rectify the obvious deficiency in this area, we here describe the structures of four lead(II) carboxylate complexes, lead(II) formate, lead(II) acetate trihydrate, lead(II) pentafluorobenzoate bis(methanol) solvate, and the lead(II)-EDTA complex, $\text{Pb}_2(\text{EDTA})_2 \cdot 3 \text{H}_2\text{O}$. Pertinent crystallographic data for the four complexes are listed in Tables 1–4.

Lead(II) formate

Crystals of lead(II) formate comprise a three-dimensional polymeric network in which adjacent lead atoms are bridged by formate groups (Fig. 1). Both oxygen atoms of each ligand each form bonds to two different lead atoms, and therefore each formate group links four neighbouring lead atoms. The resulting

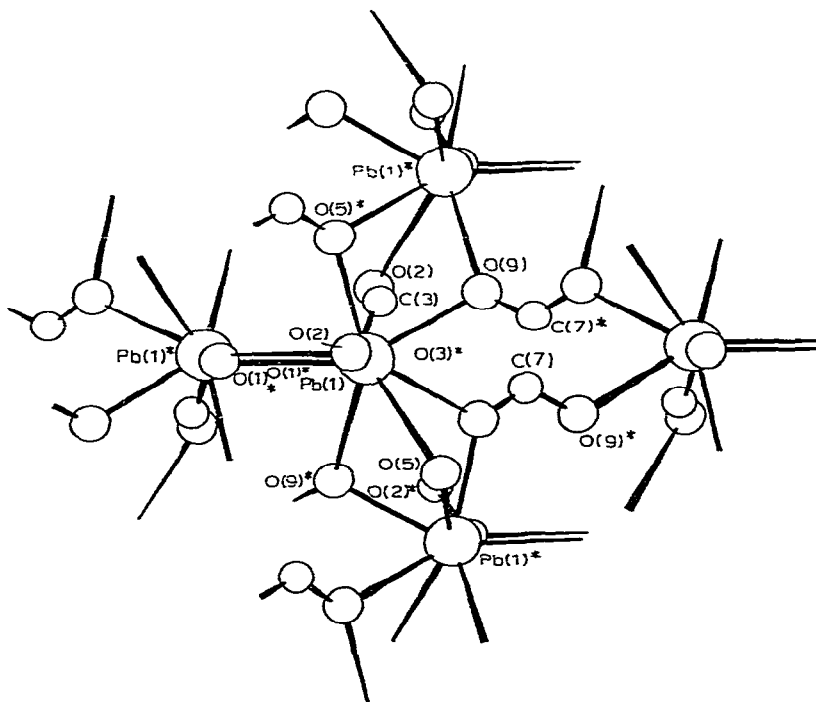


Fig. 1. View of the three-dimensional structure of lead(II) formate.

TABLE 1
CRYSTAL DATA FOR LEAD(II) FORMATE

Formula	C ₂ H ₂ O ₄ Pb
Formula weight	297.17
Crystal class	Orthorhombic
Space group	<i>Pnma</i>
Dimensions, <i>a</i> (Å)	6.5125
<i>b</i> (Å)	7.3961
<i>c</i> (Å)	8.7522
Volume, <i>U</i> (Å ³)	421.57
<i>Z</i>	2
<i>F</i> (000)	256
λ(Mo-Kα), (Å)	0.7107
No. of observed data	387
Final 'R'-value (%)	5.49

eight-coordination polyhedron of the lead is rather unusual, and is illustrated in Fig. 2 together with pertinent bond distance data. The coordination polyhedron is best regarded as a distorted octahedron in which one position is occupied by a 'tripod' of three oxygen atoms. This view is somewhat substantiated by an examination of the valence bond angles [angles between the apical oxygen atom and the four equatorial oxygen atoms: 67.5, 74.8, 80.6, 68.3°; angles between the apical oxygen atom and the three 'tripod' oxygen atoms: 132.8, 141.8, 148.8°; angles between the three 'tripod' oxygen atoms: 60.4, 61.7, 68.0°]. The lead atom is displaced below the plane of the four equatorial oxygen atoms towards the 'tripod' of oxygen atoms [angles between *trans* oxygen atoms in equatorial positions: 142.0, 148.2₅°; angles subtended by equatorial oxygen atoms at lead: 79.0, 82.0, 83.5, 96.3°, total 340.8°]. No vacancy in the coordination polyhedron is apparent, and hence the lone pair of the bivalent lead is

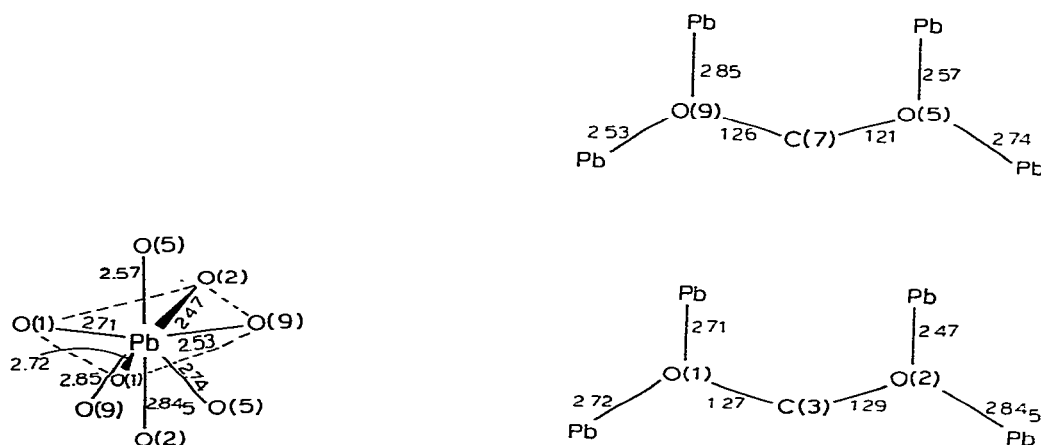


Fig. 2. Local stereochemistry about lead in lead(II) formate.

Fig. 3. Comparison of bond distance data for the two formate groups in lead(II) formate.

not stereochemically active and is confined to the metal 6s orbital. Typically for bivalent lead, the lead atom forms three short bonds to oxygen atoms (2.47, 2.53, 2.57 Å). The other five contacts to oxygen are significantly longer (2.71, 2.72, 2.74, 2.84₅, 2.85 Å).

The two formate groups are dissimilar, and bond data for these are summarised in Fig. 3. In one, the two carbon—oxygen distances are equal within experimental error (1.27, 1.29 Å), with only one short contact to lead. In the other, the carbon—oxygen distances are shorter and unequal (1.21, 1.26 Å), and each oxygen forms one short and one longer contact to lead.

Lead(II) acetate trihydrate

Changing the carboxylate group from formate to acetate has a profound effect on the solid-state structure. In lead(II) acetate trihydrate, only one acetate group participates in bridging, and crystals consist of chains extending parallel to the *b* axis (Fig. 4). Both acetate groups chelate the lead; one, which also bridges adjacent lead atoms within the chain, chelates the metal symmetrically (Pb—O 2.58 Å), whilst the other exhibits anisobidentate chelation (Pb—O 2.44, 2.75 Å). Not surprisingly, the carbon—oxygen distances within the two acetate groups are identical in the former (1.25 Å), but differ in the latter (1.19, 1.31 Å), the longer distance being associated with the shorter lead—oxygen distance and vice versa. The coordination at lead is completed by two water molecules at a distance of 2.95 Å.

Although also eight-coordinated, the coordination polyhedron at lead is different to that exhibited in lead(II) formate. In the case of lead(II) acetate trihydrate, the polyhedron can be considered as being based on a very distorted pentagonal bipyramid in which one apical position is occupied by the symmetrically chelating acetate group. A diagrammatic representation of the polyhedron is shown in Fig. 5 together with pertinent bond distance data, and illustrating the relation of the coordination polyhedron to the chain direction. The five oxygen atoms occupying equatorial sites in the polyhedron are coplanar (sum of the angles at lead 359.6°). The non-bridging acetate group

TABLE 2
CRYSTAL DATA FOR LEAD(II) ACETATE TRIHYDRATE

Formula	C ₄ H ₁₂ O ₇ Pb
Formula weight	379.5
Crystal class	Monoclinic
Space group	C2 or C2/m (Refinement in C2/m)
Dimensions, <i>a</i> (Å)	15.7397
<i>b</i> (Å)	7.2388
<i>c</i> (Å)	9.0198
β (deg.)	109.6057
Volume, <i>U</i> (Å ³)	968.18
<i>Z</i>	4
<i>F</i> (000)	696
λ(Mo-K _α) (Å)	0.7107
No. of observed data	925
Final 'R'-value	5.81

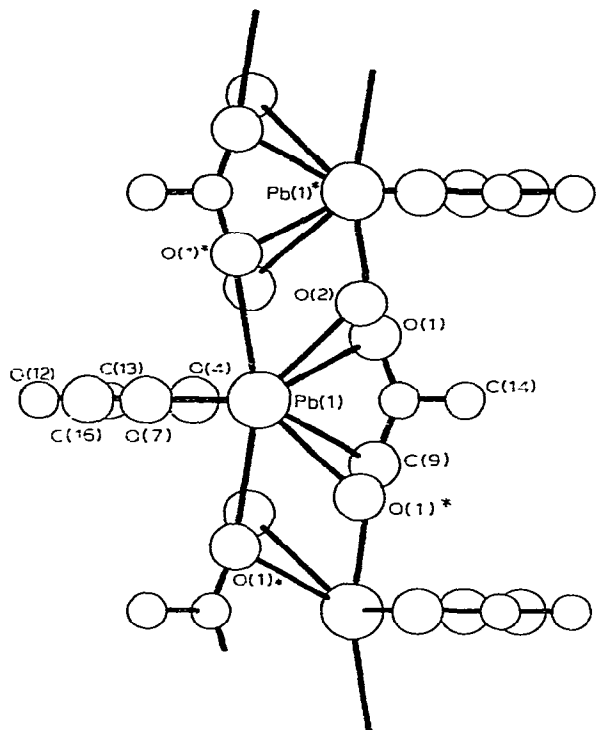


Fig. 4. View of the linear chain in lead(II) acetate trihydrate showing both bridging and non-bridging acetate groups.

spans an equatorial and the remaining axial site subtending an angle of only 50.1° at lead, thus leaving a large vacancy in the coordination polyhedron in which the lead lone pair may exhibit stereochemical activity (Fig. 5).

The third water molecule is not bonded directly to lead, but is hydrogen-bonded to the oxygen atom of the non-bridging acetate group occupying the apical site of the polyhedron, and in addition to both water molecules coordinated to a lead atom in a neighbouring chain. Adjacent chains are also

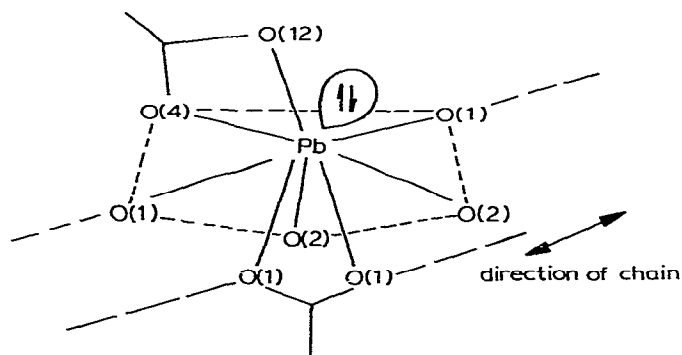


Fig. 5. Local stereochemistry about lead in lead(II) acetate trihydrate.

TABLE 3
CRYSTAL DATA FOR LEAD(II) PENTAFLUOROBENZOATE BIS(METHANOL) SOLVATE

Formula	$C_{16}H_8O_6F_{10}Pb$
Formula weight	683.41
Crystal class	Monoclinic
Space group	$C2/c$
Dimensions, a (Å)	21.4111
b (Å)	11.4641
c (Å)	8.1907
β (deg.)	95.7024
Volume, U (Å ³)	2013.3
Z	4
$F(000)$	1296
$\lambda(Mo-K\alpha)$ (Å)	0.7107
No. of observed data	1545
Final 'R'-value	3.31

linked by hydrogen-bonding between coordinated water molecules forming a 'sheet' structure.

Lead(II) pentafluorobenzoate bis(methanol) solvate

The coordination polyhedron of lead in lead(II) pentafluorobenzoate bis-(methanol) solvate differs from either of the two previous structures. Each lead atom is coordinated by two symmetrically chelating carboxylate groups (Pb—O 2.606, 2.591 Å) and two methanol molecules at a distance of 2.709 Å. One oxygen atom of each carboxylate group is also bonded to an adjacent lead atom at a distance of 2.659 Å, thus completing eight-coordination at the metal and forming a linear chain (Fig. 6). The resulting square antiprismatic stereochemistry (Fig. 7a) is distorted in such a way that the four upper oxygen atoms are more opened out than the lower four (*trans* valence angle of the four upper oxygen atoms 119.6, 165.9°; *trans* valence angles of the four lower oxygen atoms 77.2, 104.3°; sum of angles subtended at lead by the four upper oxygen atoms 345.8°), and again suggesting stereochemical activity for the lead lone pair as shown in Fig. 7b.

Dilead bis(ethylenediamine tetraacetate) trihydrate

Crystals of the complex comprise independent monomeric and dimeric units of composition $PbEDTA \cdot H_2O$ and $[PbEDTA \cdot H_2O]_2$, respectively (Fig. 8). In addition a further molecule of water of crystallisation is hydrogen bonded to carbonyl oxygen atoms of both monomer and dimer units (O...O 2.685, 2.687, 2.820 Å). In both units, the EDTA ligand functions as an hexadentate chelating ligand towards lead. Unusually however, the coordination at each crystallographically independent lead is quite different. The lead atom of the dimeric unit is eight-coordinated in a distorted square antiprismatic fashion by the hexadentate EDTA ligand, a water molecule, and a carbonyl oxygen atom from the EDTA ligand chelating the second lead atom of the dimer unit. Although the distances between the lead and the water molecule and bridging carboxyl

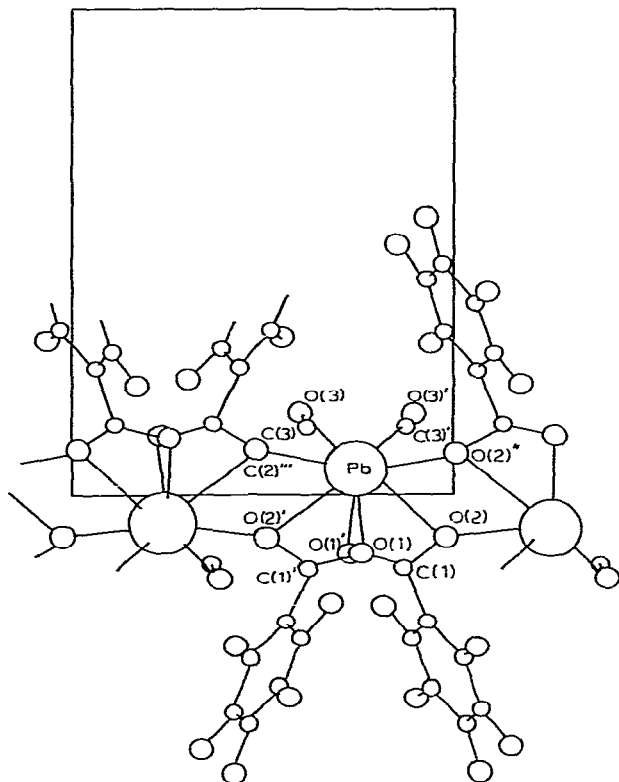


Fig. 6. View of the chain structure of lead(II) pentafluorobenzoate.

oxygen atoms are long (2.953 and 2.824 Å, respectively), the other Pb—O (2.540–2.645 Å) and Pb—N (2.624 and 2.572 Å) distances have typical values. The lone pair of electrons on lead appears to be stereochemically inactive, with no gross distortion of the basic square antiprismatic geometry or obvious vacancy in the first coordination sphere of the metal.

In contrast, the valence shell of the lead atom of the monomer unit exhibits a large space on the opposite side of the metal to the EDTA chelate, strongly

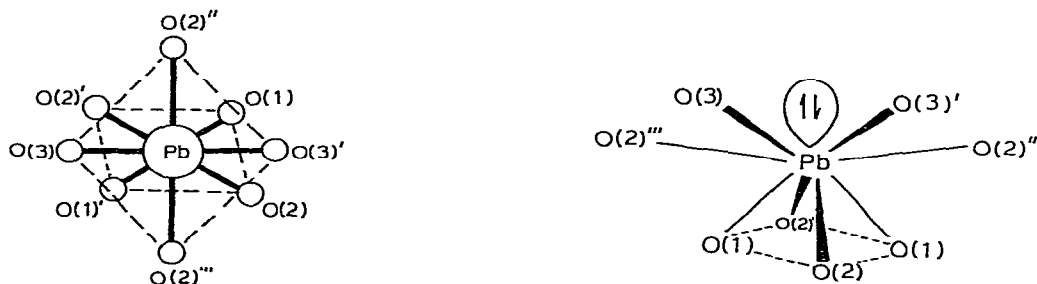


Fig. 7. Views of the local stereochemistry at lead in lead(II) pentafluorobenzoate from (a) above and (b) the side of the distorted square antiprism.

atom is replaced by the lone pair. The metal—ligand bond distances of the monomer (Pb—OH₂ 2.967 Å; Pb—O 2.494–2.735 Å; Pb—N 2.518, 2.604 Å) are, not unexpectedly, similar to the corresponding distances in the dimeric unit.

Conclusions

In its carboxylate derivatives, bivalent lead exhibits an overriding preponderance for eight-coordination (although seven-coordination has been observed in one case) with a variety of stereochemical arrangements. The overall structure of the lead(II) carboxylate depends greatly upon the size of the carboxylate group, and examples of polymeric (lead(II) formate), sheet (lead(II) acetate trihydrate), chain (lead(II) pentafluorobenzoate bis(methanol) solvate), and molecular (Pb₂(EDTA)₂·3H₂O) structures have been observed.

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