DALTON
FULL PAPER

Synthesis and characterisation of polymeric and oligomeric lead(II) carboxylates

Mark R. St J. Foreman,[*a] M. John Plater[b] and Janet M. S. Skakle[b]

[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY. Fax: Int. code + 44 207 5945801; E-mail: m.foreman@ic.ac.uk*
[b] *Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, UK AB24 3UE. Fax: Int. code + 44 1224 272921; E-mail: m.j.plater@abdn.ac.uk*

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The hydrothermal reactions of lead(II) acetate with carboxylic acids gave solids of composition $[Pb(C_4H_4O_4)]$ **1** ($C_4H_4O_4$ = succinate); $[Pb_6O_2(C_{14}H_9O_3)_8]$ **2** ($C_{14}H_9O_3$ = benzoylbenzoate), $[Pb(C_8H_4NO_4)_2(H_2O)]$ **4** ($C_8H_4NO_4$ = 2-nitrobenzoate) and $[Pb(C_8H_3N_2O_6)_2(H_2O)]$ **5** ($C_8H_3N_2O_6$ = 3,5-dinitrobenzoate). The reaction of lead monoxide with trichloroacetic acid in hot wet toluene followed by filtration and cooling gave a solid of composition $[Pb_3(C_2Cl_3O_2)_6(H_2O)_3]$ **3**. The compounds were characterised by X-ray single crystal structure determinations. Compounds **1**, **3**, **4** and **5** are polymeric whereas **2** is monomeric. The lead co-ordination number ranges from 5 to 8. Compound **2** is a novel hexanuclear lead(II) distorted octahedron containing two bridging oxide ligands.

Introduction

Lead has widely been used since ancient times in a range of applications such as roofing, fuel additives, batteries and solder and it is often present as a contaminant in the environment. The co-ordination chemistry of lead is the subject of ongoing research.[1] While in the crystallographic literature[2] many lead carboxylates with macrocyclic,[3,4] encapsulating[5] or bulky organometallic[6,7] ligands are reported, few monomeric homoleptic or hydrated lead(II) carboxylates are known.[8] Even the lead(II) salts of monobasic acids such as the acetic,[9] *p*-aminobenzoic[10] and pentafluorobenzoic[11] are polymeric structures containing bridging carboxylate oxygen atoms. While polybasic carboxylates offer even greater potential for polymer formation we and others have found that by hydrothermal synthesis good quality crystals of polymeric carboxylates may be obtained. For instance in this way zinc,[12,13] cobalt,[12,13] manganese,[13,14] copper,[15] lead,[16] cadmium,[17] calcium,[18] strontium,[18] and barium[18] salts of benzene-1,3,5-tricarboxylic acid were crystallised. Encouraged by the success of hydrothermal synthesis to obtain good crystals of these insoluble cross-linked polymeric solids, the method was applied to the crystallisation of more lead(II) salts.

Here we report the hydrothermal synthesis of lead(II) succinate, basic lead(II) 2-benzoylbenzoate, lead(II) 2-nitrobenzoate and lead(II) 3,5-nitrobenzoate from lead(II) acetate. Hydrated lead(II) trichloroacetate was synthesized at ambient pressure from lead monoxide and trichloroacetic acid. The five lead(II) carboxylates were characterised by single crystal structure determinations.

Results and discussion

Lead succinate $[Pb(C_4H_4O_4)]$ 1

In common with the other lead carboxylates **2**, **3**, **4**, and **5**, **1** was the only solid product of the reaction between lead(II) acetate trihydrate and succinic acid. The structure is shown in Fig. 1. In common with lead(II) oxalate,[19] malonate[20] and oxydiacetate,[21] lead(II) succinate has a polymeric structure containing Pb atoms linked into chains by carboxylate groups. At right angles to the chains of leads linked through the organic backbone of the succinates are two sets of chains of Pb_2O_2 rings so forming a three dimensional structure. Two oxygens bridge between each lead forming Pb_2O_2 rings which are similar to those we reported in the structure of the lead(II) salt of benzene-1,3,5-tricarboxylic acid.[16] Other polymeric succinates

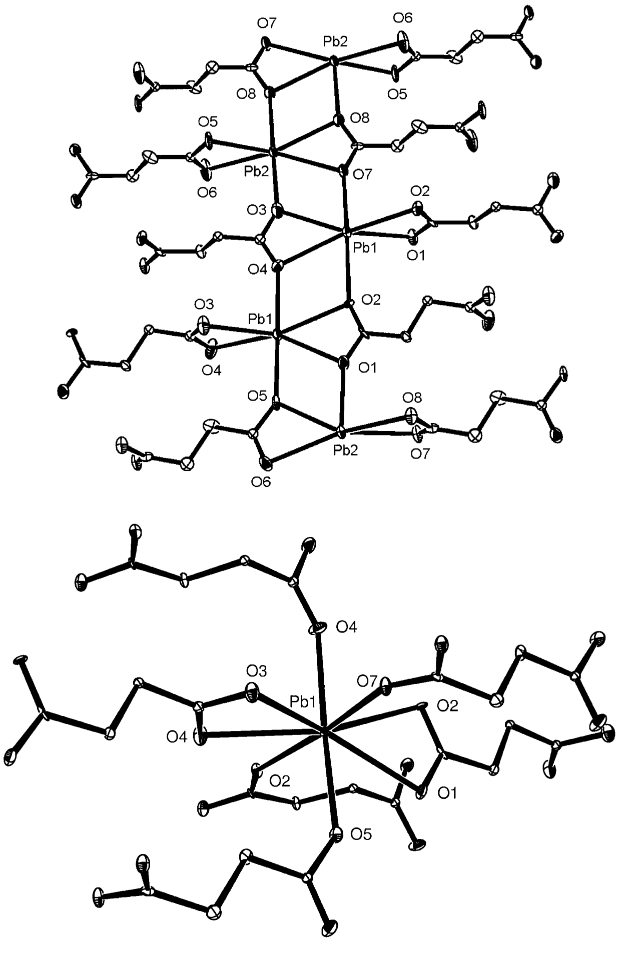

Fig. 1 Top: drawing of structure **1** showing a chain of Pb atoms linked by succinate ligands. Bottom: drawing of the co-ordination environment showing the binding of 6 succinates.

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Table 1 Selected bond lengths (Å) for **1**

Pb1–O4#4	2.57(1)	Pb2–O1	2.44(1)
Pb1–O5	2.54(1)	Pb2–O3	2.55(1)
Pb1–O7#1	2.47(1)	Pb2–O5	2.52(1)
		Pb2–O8#3	2.59(1)
Pb1–O1	2.66(1)	Pb2–O7	2.79(1)
Pb1–O2	2.75(1)	Pb2–O8	2.71(1)
Pb1–O3#3	2.67(1)	Pb2–O6#3	2.980(1)
Pb1–O4	2.79(1)		
Pb1–O2#4	2.91(1)		

Symmetry transformations used to generate equivalent atoms: #1 $x, y, z + 1$; #3 $x - 1, y, z - 1$; #4 $x + 1, y, z + 1$.

containing bridging oxygens atoms are known. Cadmium,[22] calcium,[23] silver,[24] manganese,[25] and copper[26] succinates are all polymeric. While bridging at oxygen atoms is present in the cadmium[22] and calcium[23] structures, it is absent in the others.[24–26]

Two slightly different lead environments are present in the structure. Ignoring any Pb–O bond longer than 2.58 Å, Pb1 has a T shaped geometry like that of chlorine trifluoride, suggesting that a stereochemically active lone pair is present on the lead. An analysis of bond valences[27] indicates that in these the co-ordination number is higher than three, as the valences associated with the three short bonds cover only 47% of the assumed oxidation state of the lead atom (2). By including Pb–O bonds of up to 2.8 Å the geometry changes to a grossly distorted pentagonal based bipyramid, with O4 and O7 in the axial sites. The axial oxygen (O4), which is far from the ideal position, is close to the location of the lone pair on the lead. At 2.914 Å (Table 1) is an oxygen (O2#4) which is *anti* to O7; this distant oxygen is in the same direction as the lead lone pair and it is not thought to be binding to the lead. In common with Pb2 the two most distant oxygens are close to the location of the lead lone pair. Including all 8 oxygens the calculated valence of Pb1 is now within 4% of the assumed value.

Ignoring any Pb–O bond longer than 2.58 Å, Pb2 has a distorted trigonal-based bipyramidal geometry like that of sulfur tetrafluoride, in which the stereochemically active lone pair occupies one equatorial site. An analysis of bond valences[27] indicates that in these the co-ordination number is higher than four, as the valences associated with the three short bonds cover only 65% of the assumed oxidation state of the lead atom. When oxygens within 2.80 Å are included the geometry becomes a distorted pentagonal based pyramid in which O1 occupies the axial site. Two further oxygen atoms are within 3.00 Å of Pb2; O6 can be thought of as the second axial atom in a pentagonal based bipyramid, which has been displaced far from the ideal axial position. The addition of the two most distant oxygens to the co-ordination environment changes the calculated valence of lead from within 16% of the ideal value to within 1%. The displacement of O6 is similar to that of O4 in the co-ordination environment of Pb1. O6#3 is *trans* to O1 and is close to the assumed location of the lead lone pair. If O6#3 were to be assumed to be in an axial site then O6 would be an edge-capping atom on a pentagonal based bipyramid. If any oxygen within 3.0 Å is considered as bonding to the lead then both Pb1 and Pb2 have essentially the same co-ordination environment: two carboxylates chelate to each lead, while four others bind through one oxygen to the lead.

Table 2 Co-ordination numbers and mean bond lengths for the bonds required for a lead bond valence of at least 1.8 in **1**–**5**

Compound	Lead atom	Co-ordination number required for bond valence of at least 1.8	Mean lead–oxygen distance/Å
1	Pb1	7	2.635
	Pb2	7	2.622
2	Pb1	5	2.494
	Pb2	6	2.545
	Pb3	6	2.571
3	Pb1	7	2.633
	Pb2	7	2.628
	Pb3	7	2.590
4	Pb1	7	2.611
5	Pb1	7	2.610

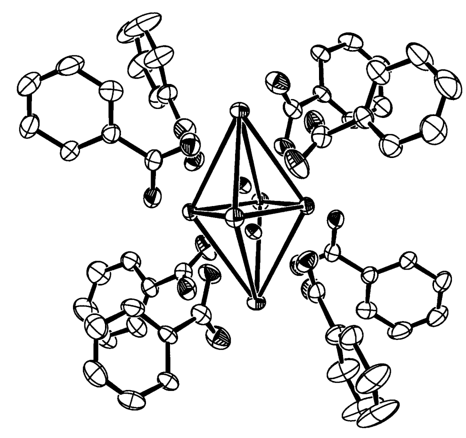

Fig. 2 Drawing of **2** showing the Pb_6O_2 lead core surrounded by 8 carboxylates. For clarity the benzoyl groups are omitted.

While it is conceivable that the distance and angle requirements for formation of a polymer might cause a distortion of the co-ordination geometry of a metal compound away from that which would be found for a molecular mononuclear complex, due to the fact that very few molecular mononuclear lead(II) carboxylates are known in the crystallographic literature which are either homoleptic or hydrated,[2] it is difficult to compare our polymeric lead carboxylates with mononuclear examples. It would be reasonable to assume that the lower the co-ordination number of lead the greater the bond valence for each ligand bonding to the metal would have to be. Forty co-ordination spheres of lead(II) carboxylates, in which only oxygen atoms were co-ordinating to the lead, were retrieved from the crystallographic literature[2,11,16] and examined. The co-ordination number was the minimum number of oxygen atoms required to calculate a bond valence of at least 1.80; the mean lead–oxygen distance for the co-ordinating oxygens was calculated. With the exception of Pb1 in 2 for all the lead atoms in our compounds the lowest co-ordination number, for which a valence of at least 1.8 is required, is 6 or 7 and the mean bond length falls within the literature ranges (Table 2). For 6- and 7-co-ordinate lead–carboxylates the literature mean lead–oxygen distances were in the ranges 2.520 to 2.580 and 2.585 to 2.707 Å respectively.

$[Pb_6O_2(C_{14}H_9O_3)_8]$ 2

The structure is shown in Figs. 2 and 3 (see also Table 3). It was expected that with the bulky *o*-benzoylphenyl group attached to the carboxylate a one-dimensional polymer like *catena*-[bis(μ_3-acetato)nonacarbonyltricobalt)lead(II)][28] would be formed. However a basic hexanuclear lead(II) carboxylate was obtained instead. The six lead atoms are arranged in a distorted octahedron. This can be redrawn as a pair of edge sharing tetrahedra, with an oxide ligand at the approximate centres of the tetrahedra. The distance between the oxide ligands in **2** is 2.830 Å, which is larger than the oxygen–oxygen distance in lead monoxide (2.791[29] and 2.800 Å[30]). The lead cluster in **2** could be thought of as a small fragment of lead oxide. Surrounding the 6 leads are 8 carboxylate ligands. These stabilise the group of leads by bridging between them. The group of lead carboxylates is encapsulated by the non-polar organic portion of the molecule. The benzoyl groups have been omitted for clarity.

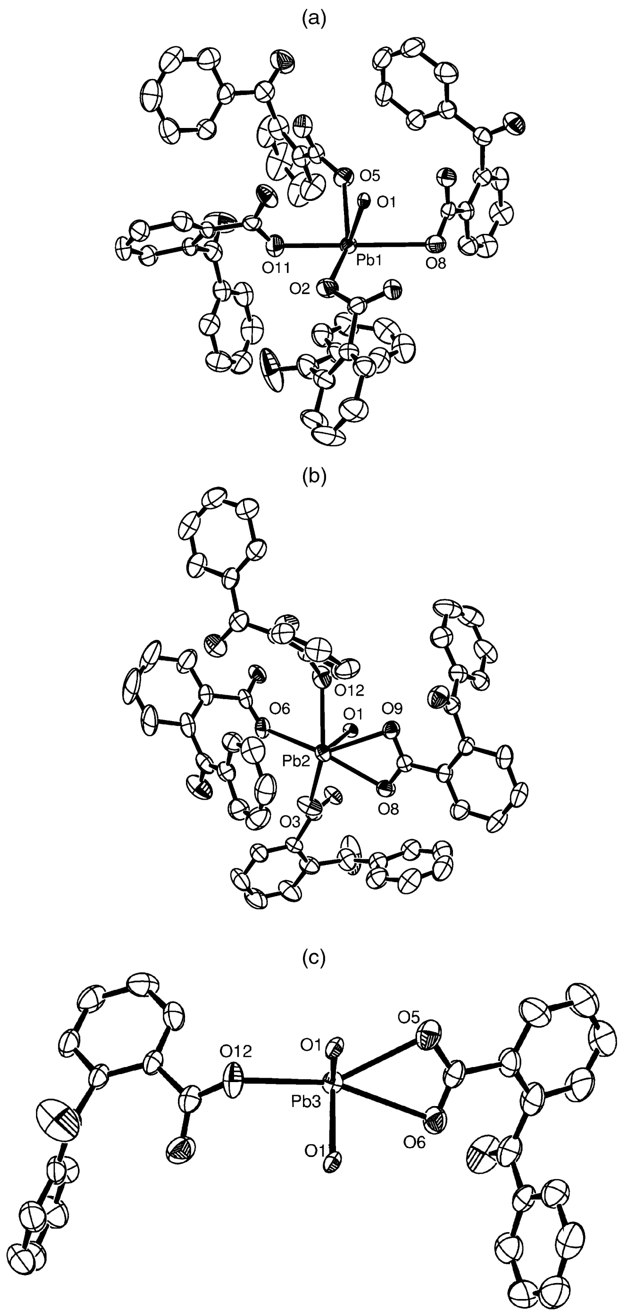

Fig. 3 Drawing showing the three different lead co-ordination environments in **2**.

Table 3 Selected bond lengths (Å) for **2**

Pb1–O1	2.292(3)	Pb2–O1	2.249(3)	Pb3–O1	2.319(3)
Pb1–O2	2.401(3)	Pb2–O3	2.483(4)	Pb3–O5	2.622(4)
Pb1–O5	2.513(3)	Pb2–O8	2.532(3)	Pb3–O6	2.720(3)
Pb1–O8	2.827(4)	Pb2–O9	2.643(3)	Pb3–O1#1	2.327(3)
Pb1–O11	2.435(4)	Pb2–O6#1	2.690(4)	Pb3–O12#1	2.519(4)
		Pb2–O12#1	2.673(4)		

Symmetry transformation used to generate equivalent atoms: #1 $-x$, $-y$, $z + 2$.

Ignoring any Pb–O bond longer than 2.58 Å, Pb1 (Fig. 3a) has a distorted square based pyramidal geometry, where the lead lone pair occupies the axial site. After adding a fifth oxygen (at 2.827 Å from the lead) the calculated valence only deviates by 9% from the ideal. By adding the sixth oxygen the co-ordination geometry of the lead changes to a grossly distorted square based pyramid in which the final oxygen occupies an axial site. The axial oxygen (O8) is the atom that is most distant from its position in an undistorted geometry. For Pb2 (Fig. 3b) and Pb3 (Fig. 3c) all weaker lead–oxygen bonds (up to 3.0 Å) must be included to satisfy the assumed valence state of the lead within 9 and 3% respectively. Pb2 has, ignoring any Pb–O bond longer than 2.58 Å, a trigonal pyramidal geometry, where the lead lone pair would occupy the axial site. By including three oxygens at distances of up to 2.70 Å the geometry changes to a pentagonal based pyramidal geometry. In the latter geometry the lead lone pair would be *trans* to the axial oxygen. The equatorial oxygens are in almost a perfect plane. If the co-ordination sphere of the lead is drawn such that the axial oxygen is pointing down, it is clear that the lead is above the equatorial plane of oxygens which is consistent with the presence of a stereochemicaly active lone pair on the lead *trans* to the axial oxygen. Ignoring any Pb–O bond longer than 2.58 Å, Pb3 would have a trigonal pyramidal geometry where the lead lone pair would occupy the axial site. When Pb–O bonds up to 2.9 Å are included the geometry changes to a distorted square based pyramid where the axial site is occupied by the lead lone pair, which is face capped by a carboxylate oxygen. A carboxylate oxygen is present at 2.918 Å from the lead, but as it is more distant than the other oxygen atoms it is not thought to be co-ordinating.

The presence of a bridging oxygen atom at the centre of a polyhedron formed by transition[31–34] and main group[35–38] block metals is well known, and includes hetero-polymetallic compounds containing lead with other metals.[39–42] However no lead carboxylate containing an oxide ligand bridging between the metal atoms in a homometallic polyhedron of lead atoms is present in the Cambridge Structural Database.[2] One explanation for the presence of the bridging oxygen in **2** is that owing to steric constraints sufficient carboxylate ligands cannot co-ordinate to the lead atoms to satisfy the positive charges of the lead ions.

$[Pb_3(C_2Cl_3O_2)_6(H_2O)_3]$ 3

As simple lead(II) salts of monobasic oxo acids such as acetic, nitric, perchloric and trichloroacetic are soluble in water, hydrothermal synthesis was rejected as a means of crystallising a trichloroacetate. Recrystallisation from hot toluene has been used to obtain lead(II) trimethylacetate,[43] and it was envisaged that the lipophilic trichloromethyl groups would surround the polar carboxylate groups to form a toluene soluble oligomer. As hoped a hydrated lead(II) carboxylate soluble in hot toluene was obtained. On cooling this lead salt forms a crystalline polymer **3** (Fig. 4). Compound **3** has a polymeric structure that consists of layers of lead carboxylates separated by trichloromethyl groups that form a series of layers. The layers consist of chains of lead atoms bridged together by carboxylate oxygen atoms; the two carboxylate oxygens bind to lead atoms in different chains. The chains are linked through carboxylate groups to adjacent chains. The formation of a 2-D layered structure contrasts with the structure of lead trimethylacetate.[44] The lipophilic *tert*-butyl groups form a honeycomb like network; the cavities are occupied by the lead atoms and the carboxylate groups. In this way 1-D chains are formed.

Ignoring any Pb–O bond longer than 2.58 Å Pb1 would have a trigonal pyramidal geometry where the lead lone pair occupies the axial site. The valences associated (1.07) with these three short bonds only cover 53% of the assumed oxidation state of the lead atom. By adding three lead oxygen bonds in the range 2.58 to 2.76 Å the geometry changes to a grossly distorted pentagonal based pyramid where the lead lone pair is approximately *anti* to the axial water oxygen (O1W). The addition of these three oxygens increases the calculated valence of the lead to 1.70. Oxygen atoms at 2.862 and 3.006 Å are binding weakly to the lead from positions which are in directions close to that of the lead lone pair. The sum of the valences associated with all eight oxygens is 1.97, and is within 2% of the assumed oxidation state of the lead. Pb1 is 8-co-ordinate (Pb–O contacts

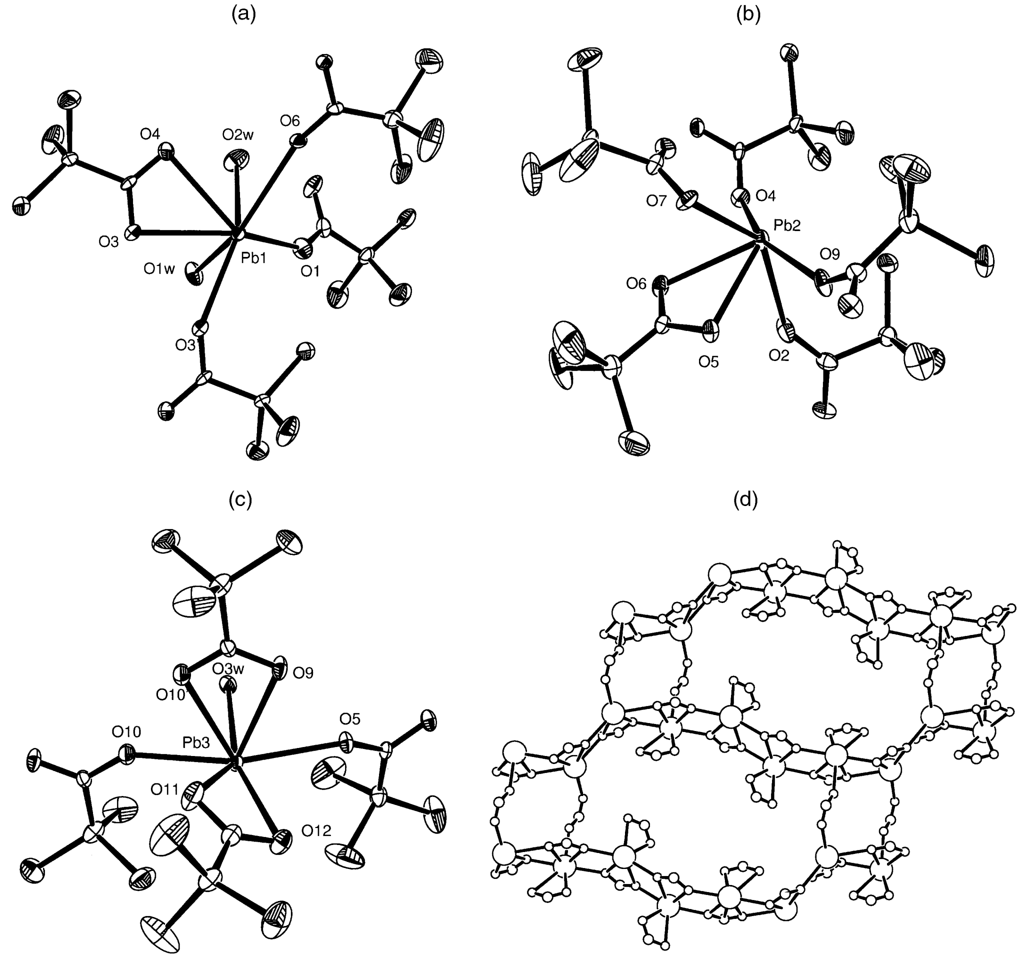

Fig. 4 Drawing showing the co-ordination environments of Pb1 (a), Pb2 (b) and Pb3 (c). Drawing showing the chains in **3** (d). The waters and trichloromethyl groups are omitted for clarity.

Table 4 Selected bond lengths (Å) for **3**

Pb1–O1W	2.379(9)	Pb2–O5	2.496(9)	Pb3–O11	2.443(12)
Pb1–O1	2.507(11)	Pb2–O7	2.543(9)	Pb3–O3W	2.527(10)
Pb1–O2W	2.529(12)	Pb2–O2#2	2.564(12)	Pb3–O10#3	2.550(10)
Pb1–O3	2.667(10)	Pb2–O6	2.568(9)	O10–Pb3	2.543(10)
Pb1–O3#1	2.735(10)	Pb2–O9	2.638(9)	O9–Pb3	2.649(10)
Pb1–O4	2.755(10)	O2–Pb2#2	2.564(12)	O5–Pb3	2.622(8)
				Pb3–O12	2.830(8)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, z + 1$; #2 $-x + 1, -y + 1, -z + 1$; #3 $-x + 1, -y, -z + 2$.

shorter than 3.1 Å) and has a grossly distorted face capped pentagonal bipyramidal geometry. Ignoring any Pb–O bond longer than 2.58 Å Pb2 would have geometry like that of a sulfur tetrafluoride molecule. The quasi-equatorial sites are occupied by two oxygens from a chelating carboxylate ligand. The addition of two oxygens at 2.633 and 2.638 Å (Table 4), changes the co-ordination geometry to a distorted pentagonal based bipyramid in which one of the equatorial sites is occupied by the lead lone pair. The site occupied by the lead lone pair is between the two more weakly bonded oxygens. A final oxygen atom, which is 2.956 Å from the lead, is attached. The addition of this oxygen raises the calculated valence of the lead to 1.83, which is 9% short of the assumed oxidation state. Ignoring any Pb–O bond longer than 2.58 Å Pb3 has a geometry like that of Pb2, except all four carboxylate oxygens are from different carboxylate groups. Addition of two oxygens at 2.622 and 2.649 Å alters the geometry to a distorted pentagonal based bipyramid in which one of the equatorial sites is occupied by the lead lone pair. Unlike Pb2, the site occupied by the lead lone pair is not between the two most weakly bound oxygen atoms. By including all oxygens, within 3.1 Å, the geometry changes to one like that of Pb2.

The hydrated erbium[45] and samarium[46] trichloroacetates have been characterised by crystallography, and in common with **3** they are polymeric. In common with lead(II) the lanthanides can form compounds with a high co-ordination number. In contrast to **3**, the lead(II) trichloroacetate in which the metal atom bears an 18-crown-6 ligand is monomeric.[4] This is because the crown ether prevents the approach of ligands from many directions. In this way by reducing the number of carboxylate oxygens that can bind to the lead the bridging at carboxylates is prevented. The formation of a lead(II) polymer containing monocarboxylates acting as bridging ligands has been observed before. For instance lead(II) crotonate,[47] phenoxyacetate,[48] and formate[11] are all polymeric with carboxylate oxygen atoms bridging between lead atoms.

$[Pb(C_8H_4NO_4)_2(H_2O)]$ 4 and $[Pb(C_8H_3N_2O_6)_2(H_2O)]$ 5

By heating lead acetate, *o*-nitrobenzoic acid and water under hydrothermal conditions a colourless solution was obtained. Only after this solution was concentrated by evaporation crystals of **4** formed. This contrasts with the formation of crystals of **5** when lead acetate, 3,5-dinitrobenzoic acid and water were heated and cooled in the same way. One explanation for this difference is that the dinitrobenzoate being a more symmetric ligand with a larger π system is able to pack better into the lattice.

In contrast with the structure of lead(II) *p*-nitrobenzoate[8] which is monomeric, structures **4** and **5** are similar 1-D coordination polymers in which carboxylate oxygens bridge between lead atoms. The structure of compound **4** is shown in

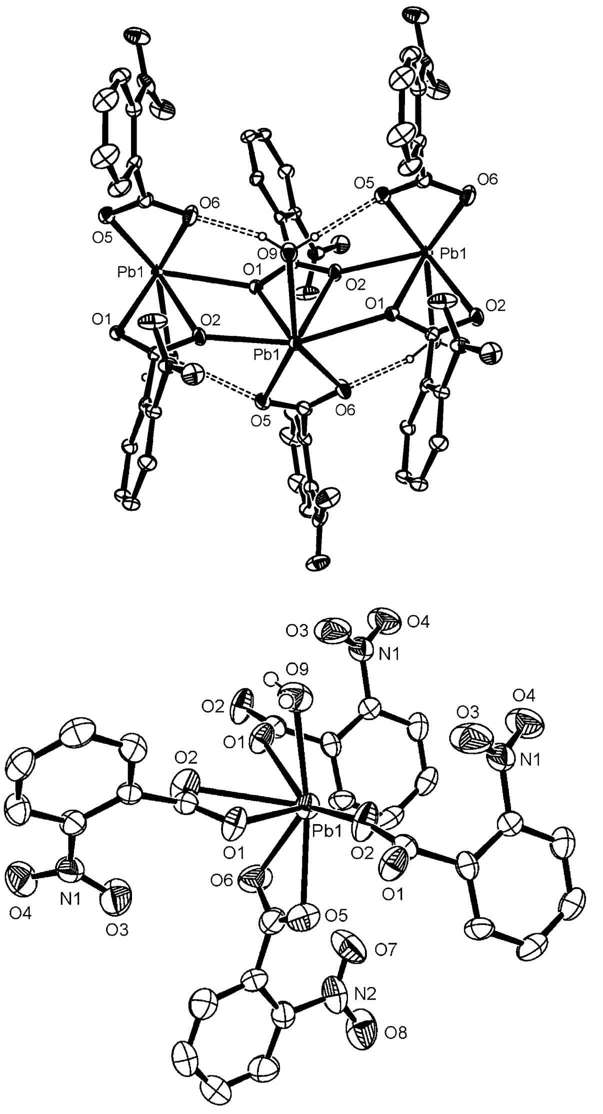

Fig. 5 Top: drawing of structure **4** showing a co-ordinative chain. Bottom: drawing of the Pb co-ordination environment.

Table 5 Selected bond lengths (Å) for **4**

Pb1–O1	2.421(4)	Pb1–O9	2.676(5)
Pb1–O5	2.531(5)	Pb1#1–O1	2.670(3)
Pb1–O2#1	2.558(4)	Pb1#2–O2	2.558(3)
Pb1–O6	2.631(5)		
Pb1–O1#2	2.670(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; #2 $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Fig. 5 (see also Tables 5–8). Within each asymmetric unit there is one lead and two carboxylate molecules. Both of the two carboxylates chelate to the lead. One carboxylate participates in a hydrogen bonding system while the other bridges between the leads forming Pb_2O_2 rings. The hydrogen bonding network is operating in the same direction as the chain of Pb_2O_2 rings that are linked at the lead atoms (Tables 4 and 7). While the methanol solvate of lead(II) pentafluorobenzoate consists of chains of Pb_2O_2 rings,[11] these rings are linked differently to those in **4** and **5**. In the pentafluorobenzoate each carboxylate binds to two lead atoms while in **4** and **5** a carboxylate either binds to one or three lead atoms.[11] Lead(II) *p*-aminobenzoate potentially has a similar hydrogen bonding system to that of **4** and **5**, but no hydrogen atoms were reported.[10] The amino group is so arranged that hydrogen bonds to two different carboxylate groups in a chain of Pb_2O_2 rings could form.[10]

Table 6 Hydrogen bonds for structure **4** [Å and °]

D–H···A	*d*(D–H	*d*(H···A)	*d*(D···A)	DHA
O(9)–H(9WA)···O(5)#2	0.78(6)	2.16(6)	2.94(1)	170(7)
O(9)–H(9WB)···O(6)#1	0.87(9)	1.99(9)	2.83(1)	162(9)

Symmetry transformations used to generate equivalent atoms as in Table 5.

Table 7 Selected bond lengths (Å) for **5**

Pb1–O1	2.358(2)	Pb1–O1#2	2.799(2)
Pb1–O7	2.520(3)	Pb1–O2	2.815(3)
Pb1–O8	2.543(3)	Pb1#1–O1	2.799(2)
Pb1–O2#1	2.577(2)	Pb1#2–O2	2.577(2)
Pb1–O1W	2.660(3)		

Symmetry transformations used to generate equivalent atoms: #1 $x - \frac{1}{2}, -y + \frac{1}{2}, -z$; #2 $x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

Table 8 Hydrogen bonds for **5** [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	DHA
O(1W)–H(1WA)···O(7)#2	0.80(7)	2.29(7)	2.96(1)	143(6)
O(1W)–H(1WB)···O(8)#1	0.72(4)	2.11(5)	2.82(1)	173(5)

Symmetry transformations used to generate equivalent atoms as in Table 7.

Ignoring all lead–oxygen bonds longer than 2.58 Å, the lead atom in **4** is 3-co-ordinate and has a pyramidal geometry, while the lead atom in **5** is 4-co-ordinate and has a square based pyramidal geometry where the axial site is occupied by the lead lone pair. By including Pb–O bonds of up to 3.0 Å the geometry of **4** changes to a grossly distorted edge capped pentagonal based pyramidal geometry where the axial sites are occupied by a carboxylate oxygen and the lead lone pair. The 7 oxygens are sufficient for a description of the lead co-ordination, as the sums of the valences of these 7 bonds deviate by only 6 and 3% from the assumed oxidation state of the lead for **4** and **5** respectively.

A stereochemicaly active lone pair is thought to be present on the lead *anti* to the non-bridging carboxylate oxygens. The equatorial sites are occupied by a water, the non-bridging carboxylate oxygens and the oxygens from bridging carboxylates in adjacent asymmetric units. The axial and capping sites are occupied by the bridging carboxylate oxygens from within the same asymmetric unit.

These studies exemplify the rich co-ordination chemistry of lead and its usefulness for the crystallisation of extended networks. The discovery of a discreet hexanuclear lead(II) cluster using benzoyl benzoate illustrates the scope for ligand design to control the formation of either discreet or polymeric networks.

Experimental

Lead(II) acetate trihydrate, lead monoxide, 3,5-dinitrobenzoic acid, 2-nitrobenzoic acid and 2-benzoylbenzoic acid from BDH, succinic acid and trichloroacetic acid from Aldrich. The equipment used for hydrothermal synthesis, thermal gravimetric analysis (TGA), thermal analysis with mass spectroscopy (TG-MS) and infrared spectroscopy has been described previously.[13]

Preparations

[$Pb(C_4H_4O_4)$] 1. Lead(II) acetate trihydrate (60.6 mg, 0.160 mmol), succinic acid (19.1 mg, 0.162 mmol) and water (20 ml) was placed inside a 45 ml bomb and was heated at 100 °C h^{-1} to 240 °C. After maintaining this temperature for 2 h the bomb

Table 9 Summary of crystal data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_4H_4O_4Pb$	$C_{56}H_{36}O_{13}Pb_3$	$C_{12}Cl_{18}O_{15}Pb_3$	$C_{14}H_{10}N_2O_9Pb$	$C_{14}H_8N_4O_{13}Pb$
M	323.26	1538.42	1643.79	557.43	647.43
T/K	293(2)	303(2)	293(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
Z	8	4	2	4	4
a/Å	6.883(1)	16.888(1)	11.292(2)	12.534(1)	7.286(1)
b/Å	20.951(1)	17.505(1)	11.971(2)	7.198(1)	11.039(1)
c/Å	7.535(1)	17.020(1)	16.051(2)	18.749(2)	23.201(2)
α/°			70.171(4)		
β/°	92.868(1)	93.8450(10)	75.406(5)	102.772(1)	
γ/°			74.713(2)		
V/Å^3	1085.3(1)	5020.3(4)	1937.0(4)	1649.6(2)	1866.20
μ/mm^{-1}	31.018	10.102	14.303	10.281	9.124
Reflections collected	5663	38963	17154	16278	19078
Independent reflections/R_{int}	1551/0.062	17968/0.066	11077/0.056	5907/0.070	6692/0.033
Data/restraints/parameters	1551/0/143	17968/0/649	11077/0/433	5907/0/243	6692/0/297
$R1/wR2$ [$F^2 > 2\sigma(F^2)$]	0.038/0.103	0.036/0.064	0.066/0.147	0.045/0.062	0.025/0.042
(all data)	0.052/0.108	0.079/0.074	0.140/0.173	0.111/0.074	0.035/0.043
Largest difference peak and hole/e Å^{-3}	3.06/−2.04	1.95/−1.15	4.83/−3.83	2.13/−1.99	1.26/−0.78

was cooled at 5 °C h^{-1} to 180 °C. After 6 h the bomb was cooled at 5 °C h^{-1} to 20 °C. A colourless solid (22.5 mg, 44%) was collected, washed with water and dried (Found: C, 14.9; H, 1.1; N, <0.3. $[Pb(C_4H_4O_4)]$ requires C, 14.9; H, 1.3; N, 0.0%); IR (KBr) 2923w, 1637m, 1617m, 1543s, 1508m, 1460w, 1406s, 1385s, 1319s, 1283m, 1233s, 1173m, 1057w, 1033m, 968w, 929w, 878w, 799m and 657s cm^{-1}.

$[Pb_6O_2(C_{14}H_9O_3)_8]$ 2. Lead(II) acetate trihydrate (268 mg, 0.707 mmol), 2-benzoylbenzoic acid (208 mg, 0.919 mmol), sodium acetate trihydrate (376 mg, 2.76 mmol) and water (10 ml) were placed in a 23 ml bomb and heated at 100 °C h^{-1} to 200 °C. After maintaining this temperature for 2 h the bomb was cooled at 5 °C h^{-1} to 180 °C. After 6 h the bomb was cooled at 4 °C h^{-1} to room temperature. The resulting crystals (274 mg, 77%) were collected by filtration, washed with water and air-dried (Found: C, 43.8; H, 2.1; N, <0.3. $[Pb_6O_2(C_{14}H_9O_3)_8]$ requires C, 43.7; H, 2.4; N, 0.0%); IR (KBr) 1671s, 1638w, 1617w, 1600w, 1579m, 1540s, 1517w, 1482w, 1448w, 1382s, 1314w, 1279m, 1251w, 1182w, 1160sh, 1092w, 1040w, 1026w, 999w, 934m, 910w, 890w, 879w, 848w, 799w, 769m, 730m, 717m, 700m, 688w, 669m and 636m cm^{-1}.

$[Pb_3(C_2Cl_3O_2)_6(H_2O)_3]$ 3. A mixture of lead monoxide (6.0 g, 26.9 mmol), trichloroacetic acid (8.4 g, 51.4 mmol), water (1 ml, 56 mmol) and toluene (220 ml) was heated under reflux for 40 min followed by hot filtration through a sintered glass disk. The filtrate was allowed to slowly cool forming colourless crystals, which were collected by filtration, washed with toluene, and dried (9.7 g, 69%) (Found: C, 9.1; H, 0.3; N, 0.3. $[Pb_3(C_2Cl_3O_2)_6(H_2O)_3]$ requires C, 8.7; H, 0.4; N, 0.0%); IR (KBr) 3466br, 1694s, 1666s, 1648vs, 1619s, 1594s, 1511m, 1476w, 1380sh, 1352s, 1235w, 833s, 750s, 714w and 688s cm^{-1}: TGA: between 60 and 110 °C an endothermic mass loss of 3.0% occurred (dehydration of the trihydrate would require a mass loss of 4.6%); above 170 °C a vigorous exothermic mass loss of 22.3% occurred during which the production of carbon dioxide was observed by TG-MS.

$[Pb(C_8H_4NO_4)_2(H_2O)]$ 4. 2-Nitrobenzoic acid (102 mg, 0.614 mmol), lead acetate trihydrate (143 mg, 0.377 mmol) and water (10 ml) were placed in a 23 ml Parr bomb and heated at 100 °C h^{-1} to 210 °C. After 2 h the bomb was cooled at 5 °C h^{-1} to 180 °C. After 6 h at 180 °C it was cooled at 5 °C h^{-1} to 20 °C then was opened and the clear solution placed in a vial and allowed slowly to evaporate. When the volume had decreased to approximately 5 ml white crystals were harvested (113 mg, 66%) (Found: C, 29.9; H, 1.7; N, 4.7. $[Pb(C_8H_4NO_4)_2(H_2O)]$ requires C, 30.2; H, 1.8; N, 5.0%); IR (KBr) 3425br, 1637m, 1616s, 1571m, 1525s, 1477w, 1464sh, 1439w, 1398s, 1351m, 1309w, 1265w, 1148w, 1075w, 963w, 865w, 841w, 788w, 748w, 701m, 669w, 649w and 426w cm^{-1}.

$[Pb(C_8H_3N_2O_6)_2(H_2O)]$ 5. 3,5-Dinitrobenzoic acid (122 mg, 0.575 mmol), lead(II) acetate trihydrate (111 mg, 0.293 mmol) and water (10 ml) were placed in a 23 ml Parr bomb and heated at 100 °C h^{-1} to 210 °C. After 2 h at 210 °C the bomb was cooled at 5 °C h^{-1} to 20 °C then opened, the solid was collected by filtration, washed with water and dried in air (115 mg, 61%) (Found: C, 26.0; H, 1.3; N, 8.5. $[Pb(C_8H_3N_2O_6)_2(H_2O)]$ requires C, 26.0; H, 1.3; N, 8.65%); IR (KBr) 3455br, 1628s, 1582m, 1458w, 1393m, 1346s, 1189w, 1083w, 926w, 898w, 796w, 732s, 718s and 639w cm^{-1}.

Structure determinations

Data were collected on a Bruker SMART 1000 CCD diffractometer using SMART[49] and reduced using SAINT.[49] Absorption correction was applied using SADABS.[49] Structures **1** and **4** were solved by Patterson methods using SHELXS 86,[50] the others by direct methods using SHELXS 97.[50] All were then refined by least squares methods using SHELXL 97,[50] smoothly to the values given. For structures **1**–**3** all H atoms were placed geometrically, whereas for structures **4** and **5** those for the water molecules were identified from the Fourier difference map. In structure **5** this approach resulted in one slightly short (0.71 Å) O–H bond. Structure **3** contained 3 water molecules but the H atoms could not be located satisfactorily. Problems were encountered with the structure of **5** for which the crystals were rather small and needle-shaped. In this case the Pb atoms dominated the scattering to such an extent that it was not possible to refine all of the non-H atoms anisotropically. In addition a strong pseudo-symmetry, mainly due to the two lead atoms in the asymmetric unit, was observed but most of the non-Pb atoms violated the pseudo-symmetry.[51] Thus the structure presented here gives the best fit to the data available. Ortep-3 was used as a graphics package in this work.[52] Crystal data are summarised in Table 9.

CCDC reference numbers 158365–158369.

See http://www.rsc.org/suppdata/dt/b1/b103519n/ for crystallographic data in CIF or other electronic format.

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