metal-organic compounds

A one-dimensional mixed-anion lead(II) coordination polymer: *catena*-poly[[(1,10-phenanthroline)lead(II)]-*μ*-benzoato-*μ*-nitrato-[(1,10-phenanthroline)lead(II)]-di-*μ*-benzoato]

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In the title polymeric compound, $[Pb_2(C_7H_5O_2)_3(NO_3)(C_{12}H_8N_2)_2]_n$, both independent Pb atoms adopt an eight-coordinate geometry formed by one nitrate, three benzoate and one 1,10-phenanthroline ligand. The one-dimensional polymer consists of dimeric $[Pb_2(C_7H_5O_2)_3(NO_3)(C_{12}H_8N_2)_2]$ units, in which all nitrate and benzoate ligands act in a bridging–chelating coordination mode.

Comment

4-Carboxybenzeneboronic acid (Hcbba) has so far not been reported to take part in metal coordination compounds, and only a few organic complexes of Hcbba have been documented in the Cambridge Structural Database (CSD; May 2006 update; Allen, 2002). Zhu & Hu (2006) describe how this ligand can be converted into a benzoate ligand under hydrothermal conditions. In order to understand the coordination chemistry of Hcbba with heavy metal ions, the Pb^{2+} ion was selected for exploring the assembly of novel structures. The Pb^{2+} ion can exhibit a variety of coordination modes and possesses a stereochemically active lone pair of electrons, which is important for structural assembly, electron-charge transfer, and physical and chemical properties (Hancock *et al.*, 2004; Nordell *et al.*, 2004; Esteban-Gomez *et al.*, 2005; Panda *et al.*, 2004). Moreover, removing this toxic metal ion through the formation of insoluble complexes is a field of increasing importance (Kurtarun *et al.*, 2005; Magyar *et al.*, 2005). Therefore, the Pb^{2+}/Hcbba/1,10-phenanthroline system was investigated by hydrothermal synthesis and the mixed-anion coordination polymer *catena*-poly[[(1,10-phenanthroline)-lead(II)]-*μ*-nitrato-*μ*-benzoato-[(1,10-phenanthroline)lead(II)]-di-*μ*-benzoato], (I), which is reported here, was obtained.

The structure consists of a one-dimensional chain in which dimeric units formulated as $[Pb_2(NO_3)(ba)_3(phen)_2]$ (ba is

benzoate and phen is 1,10-phenanthroline) are linked by benzoate bridges. In the dimeric unit, each of the two independent Pb atoms is eight-coordinated by one nitrate, three benzoate and one 1,10-phenanthroline ligand in a PbN_2O_6 chromophore (Fig. 1 and Table 1). However, these two Pb atoms in fact adopt somewhat different coordination environments, *i.e.* atom Pb1 is coordinated by two N-atom donors from one 1,10-phenanthroline ligand, five O atoms from three benzoate ligands and one O atom from one nitrate ligand, while atom Pb2 is coordinated by two N donors from one 1,10-phenanthroline ligand, four O atoms from three benzoate ligands and two O atoms from one nitrate ligand. Three four-membered Pb_2O_2 rings (where usually weak Pb···Pb interactions build up) are formed within (and between) dimeric units. There are a variety of Pb···Pb separation distances: Pb1···Pb2, bridged by both nitrate and benzoate ligands, is 4.7420 (4) Å, which is longer than that in *catena*-poly-[tetraaquabis(μ_2-nitrato)bis(μ_6-pyrazole-3,5-dicarboxylato)-trilead(II)] [4.425 (1) Å; Bentiss *et al.*, 2004]. On the other hand, the Pb1···Pb1 and Pb2···Pb2 separations, bridged by benzoate ligands between dimeric units, are 4.2639 (5) and 4.6083 (6) Å, respectively. The Pb···Pb separation in the three Pb_2O_2 units is longer than the commonly accepted limit for a weak interaction (4.10 Å; Magyar *et al.*, 2005; Morsali & Mahjoub, 2004*a*), suggesting that the number and type of ligands present in (I) may not favour the Pb···Pb interaction in the Pb_2O_2 loops.

(I)
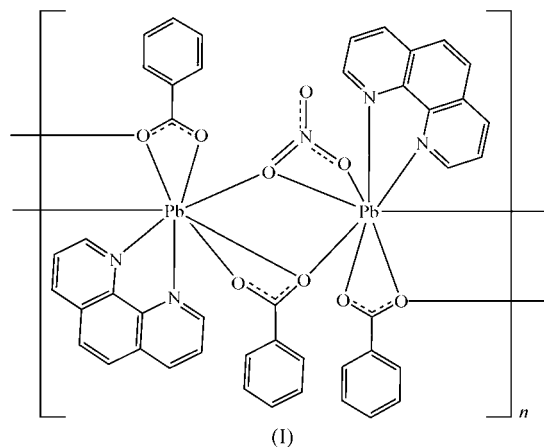
The Pb1—N bonds are slightly longer than the Pb2—N bonds, but all are in the normal range. The chelating Pb1—O (except Pb1—O8) distances are significantly shorter than those of Pb2—O. Such coordination geometries around Pb atoms indicate that the lone pair of electrons on atom Pb1 is inactive, while that on Pb2 is active; a very similar case is found in $\{[Pb_3\{N(CH_2COO)_2\}_3]_2(H_2O)_5\}_n$ (Chow & Mak, 1993). Oddly, only two Pb^{II}–benzoate complexes can be found in the CSD, and the carboxylates in these two complexes act in a chelating mode (Yonemura *et al.*, 1997; Hamilton *et al.*, 2004) and with rather similar Pb—O(COO) bond lengths, in contrast to the benzoate ligands in (I), which are converted from 4-carboxybenzeneboronic acid and adopt a bridging–chelating mode with a broad span of Pb—O coordination distances (Table 1).
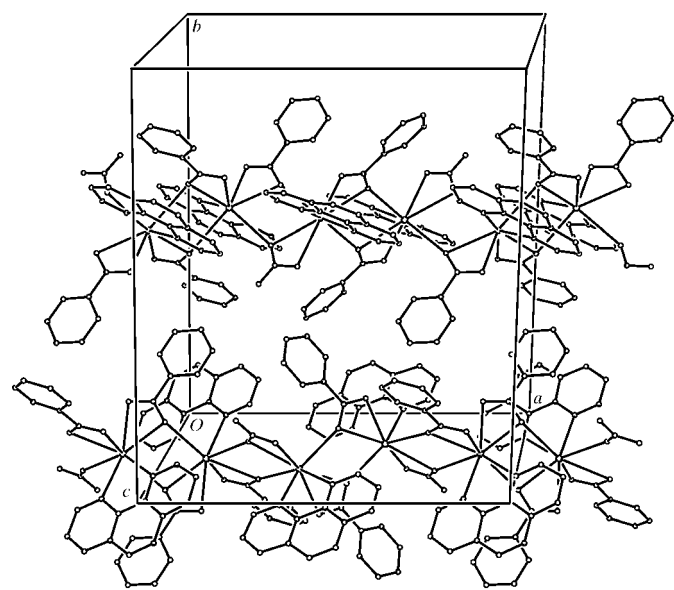
The nitrate anion is a versatile ligand, which may coordinate to metal atoms using one, two or three O atoms. In the present case, it acts as a two-atom chelate to Pb2, while also bridging the dimer (Fig. 1), a situation that is rare in lead(II) complexes, and only two examples, *viz.* tetrakis(1,2-ethylenediamine)-(μ_2-nitrato-$\kappa^3 O$:O,O')(μ_2-nitrato-$\kappa^2 O$:O')dilead(II) dinitrate and bis(μ_2-nitrato)(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane)(nitrato)lead(II), have been reported (Harrowfield, Miyamae, Skelton *et al.*, 1996; Harrowfield, Miyamae, Shand *et al.*, 1996). The co-existence of both nitrate and carboxylate bridges is also interesting, the former acting as a dimeric linker, while the latter extend these dimeric units into one-dimensional chains (Fig. 2). Only one other example containing both types of bridges has been previously reported (Bentiss *et al.*, 2004).

In general, lone-pair activity of lead(II) and π–π stacking interactions can play a significant role in the structural assembly of the solid state (Morsali & Mahjoub, 2004b). Both factors can be found in the title complex. The former has already been discussed above; regarding the latter, abundant ba–ba, ba–phen and phen–phen stacking interactions occur in neighbouring chains, with a centroid-to-centroid distance range of 3.544 (5)–3.885 (5) Å. These π–π interactions are not perfect face-to-face contacts but rather correspond to the offset type.
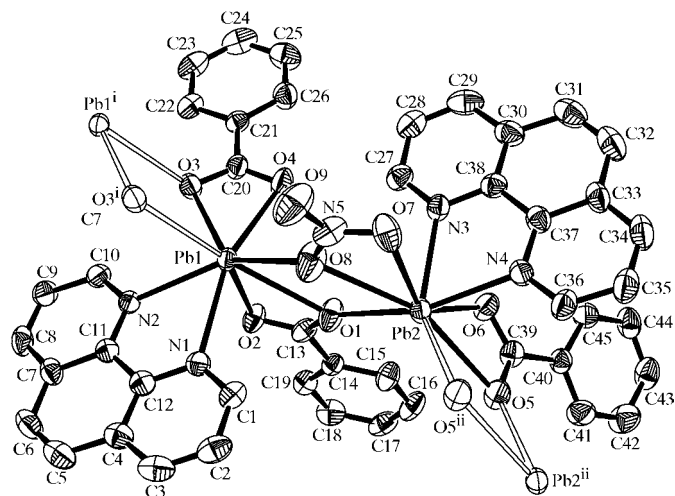
Figure 1
Part of the polymeric structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms are not shown for clarity. [Symmetry codes: (i) $-x$, $-y + 1$, $-z + 2$; (ii) $-x + 1$, $-y + 1$, $-z + 2$.]

Experimental

A mixture of lead(II) nitrate (0.165 g, 0.49 mmol), 4-carboxy-benzeneboronic acid (0.079 g, 0.48 mmol), 1,10-phenanthroline monohydrate (0.090 g, 0.45 mmol) and water (15 ml) was sealed in a 30 ml Teflon-lined stainless steel autoclave and heated at 423 K for 4 d. After cooling of the autoclave, a solution with some powdered solid was obtained, and this residue was filtered off. The filtrate was allowed to evaporate and, after one week, pale-yellow crystals in the form of blocks were obtained by filtration.

Crystal data

[Pb2(C7H5O2)3(NO3)(C12H8N2)2]	$Z = 4$
$M_r = 1200.13$	$D_x = 1.975$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 17.2481$ (10) Å	$\mu = 8.40$ mm^{-1}
$b = 20.6393$ (12) Å	$T = 295$ (2) K
$c = 11.5549$ (6) Å	Block, pale yellow
$\beta = 101.167$ (1)°	$0.13 \times 0.09 \times 0.08$ mm
$V = 4035.5$ (4) Å^3	

Data collection

Bruker APEX area-detector diffractometer	20990 measured reflections
φ and ω scans	7182 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	5090 reflections with $I > 2\sigma(I)$
$T_{min} = 0.417$, $T_{max} = 0.521$	$R_{int} = 0.031$
	$\theta_{max} = 25.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 4.7224P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.02$	$\Delta\rho_{max} = 2.23$ e Å^{-3}
7182 reflections	$\Delta\rho_{min} = -0.75$ e Å^{-3}
550 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Pb1—O2	2.363 (5)	Pb2—N3	2.454 (6)
Pb1—O3	2.531 (5)	Pb2—O6	2.470 (5)
Pb1—N2	2.585 (5)	Pb2—N4	2.497 (6)
Pb1—N1	2.666 (6)	Pb2—O5^{ii}	2.720 (5)
Pb1—O4	2.677 (5)	Pb2—O1	2.793 (5)
Pb1—O1	2.802 (5)	Pb2—O7	2.802 (6)
Pb1—O8	2.929 (6)	Pb2—O8	2.827 (6)
Pb1—O3^i	3.019 (5)	Pb2—O5	2.837 (5)

Symmetry codes: (i) $-x$, $-y + 1$, $-z + 2$; (ii) $-x + 1$, $-y + 1$, $-z + 2$.

Figure 2
A view of the one-dimensional chain of (I). H atoms are not shown for clarity.

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All H atoms were placed in calculated positions and treated as riding, with C—H distances of 0.93 Å and U_{iso}(H) values of $1.2U_{eq}$(C). The highest peak in the final difference Fourier map lies 0.99 Å from atom Pb2.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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