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Bis(μ-2-sulfonatobenzoato)-bis[(1,10-phenanthroline)lead(II)] dihydrate

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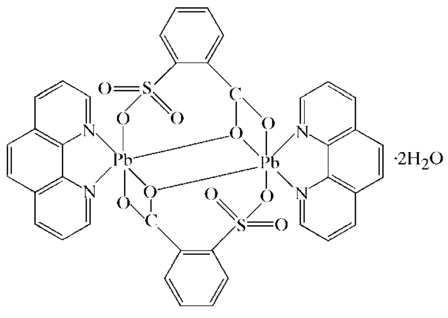
In the title centrosymmetric dimer, $[Pb_2(sbc)_2(phen)_2]\cdot 2H_2O$ [sbc is the 2-sulfonatobenzoate dianion ($C_7H_4O_5S$) and phen is 1,10-phenanthroline ($C_{12}H_8N_2$)], each Pb^{II} ion is six-coordinated by four O atoms, *viz*. carboxylate and sulfonate O atoms from two sbc anions, and two N atoms from a 1,10-phenanthroline ligand. One 1,10-phenanthroline ligand and the carboxylate group of one sbc ligand are chelated to each Pb^{II} cation, and the sulfonate group of the other sbc unit is monodentate. One O atom of the chelated carboxylate group also bridges to the other Pb^{II} cation, so that each pair of Pb^{II} ions is bridged by two sbc anions and has the same coordination environment, forming a dinuclear ring. Each pair of Pb^{II} ions is thus connected by two different kinds of bridges, namely a carboxylate short bridge and a carboxylate–sulfonate long bridge. There is also a special position of $\bar{1}$ site symmetry at the centre of the two Pb^{II} cations.

Comment

Lead(II) is capable of exhibiting a variable coordination number and geometry with or without a stereochemically active lone pair of electrons (Wang & Vittal, 2003). Among such compounds, a number of polymeric Pb^{II} compounds have been structurally characterized (Cecconi *et al.*, 2003; Bridgewater & Parkin, 2000; Ying *et al.*, 2003). The absence of crystal field-stabilization energy effects also allows Pb^{II} cations to adopt a range of different coordination geometries, not restricted to octahedral, tetrahedral or square-planar (Foreman *et al.*, 2000). 2-Sulfobenzoate (sbc) is a very interesting ligand, with both carboxylate and sulfonate as potential coordinating groups. It can form not only short bridges between metal ions *via* one carboxylate end or one sulfonate end, but also a long bridge *via* the benzene ring. Thus, we have selected the Pb–sbc system to extend this research and we present here the crystal structure of the title compound, namely $[Pb(sbc)(phen)]_2\cdot 2H_2O$, (I).

In (I), each Pb^{II} ion coordinates to three O atoms from two carboxylate groups of two sbc anions, with a typical range of Pb—O distances [2.574 (3)–2.595 (4) Å; Foreman *et al.*, 2000], to one sulfonate O atom from one sbc anion, with a Pb—O distance of 2.646 (4) Å, and to two N atoms from one 1,10-phenanthroline ligand, with Pb—N distances of 2.540 (4) and 2.569 (4) Å. The coordination numbers of the two Pb^{II} ions are equivalent, but although both Pb^{II} cations are six-coordinated, the coordination geometries of the Pb^{II} cations are not octahedral (Fig. 1), due to the absence of crystal field stabilization energy effects. The two N atoms of 1,10-phenanthroline and two carboxylate O atoms are chelated to each Pb^{II} cation, and the sulfonate group of the other sbc anion is monodentate. One O atom of the chelated carboxylate group also bridges to the other Pb^{II} cation, with a Pb—O distances of 2.734 (3) Å. Thus, each pair of Pb^{II} ions has the same coordination environment and is bridged by two sbc anions, forming a centrosymmetric dinuclear ring. Each pair of Pb^{II} ions is therefore connected by two different kinds of bridges, namely a carboxylate short bridge and a carboxylate–sulfonate long bridge. There is also a special position of $\bar{1}$ site symmetry at the centre of the two Pb^{II} cations.



(I)

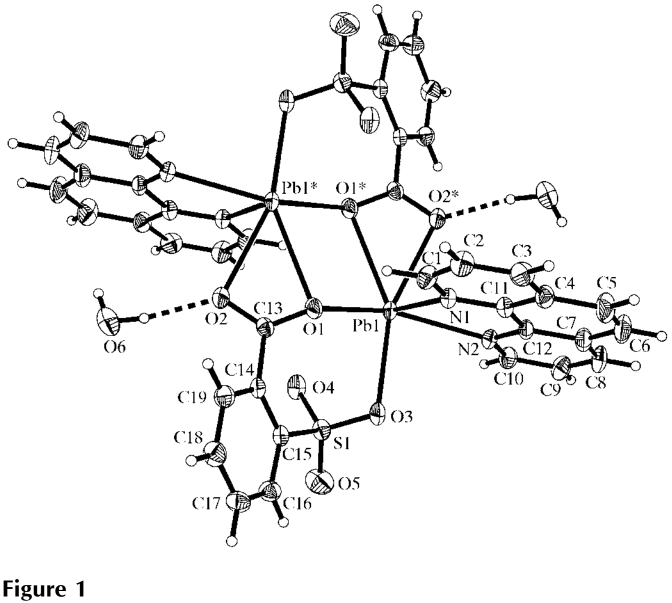


Figure 1
The coordination environment of the Pb^{II} ion in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with an asterisk (*) are at the symmetry position $(2 - x, 1 - y, 1 - z)$.

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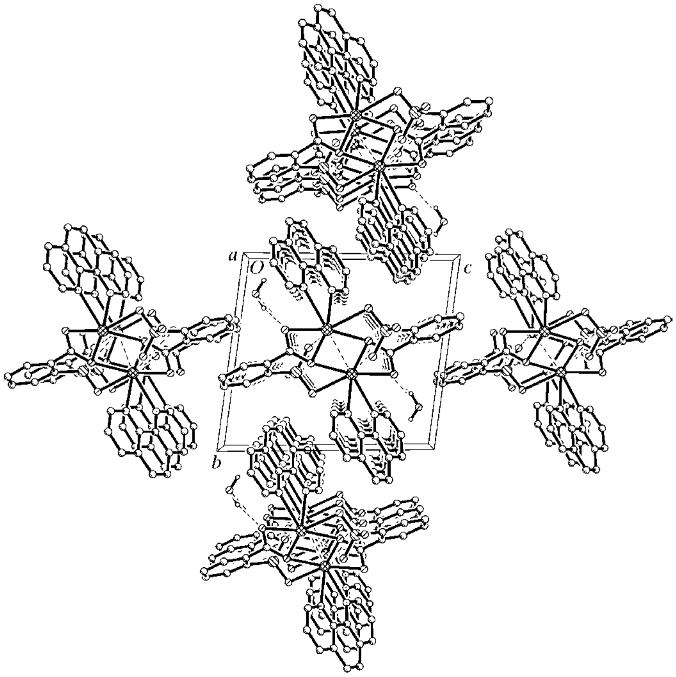

Figure 2
A perspective view of the molecular packing of (I) along the *a* axis, illustrating the hydrogen-bonding and π–π interactions. Hydrogen-bonding interactions are shown as dashed lines and H atoms not involved in hydrogen bonds have been omitted for clarity.

The S1—O3, S1—O4 and S1—O5 distances are 1.469 (4), 1.465 (4) and 1.428 (4) Å, respectively, and all fall within the typical range of S—O bond distances in the sulfonate anion (1.40–1.49 Å; Onoda *et al.*, 2001). The similarity of the three S—O bond distances suggests that strong conjugation of the sulfonate is predominant in (I). In addition, each sbc anion acts as a tetradentate ligand, connecting two Pb^{II} ions through its bridging and chelating carboxylate group and its monodentate sulfonate group. This coordination mode is quite different from that in the above-mentioned polymeric Pb^{II} compounds, in which the carboxylate groups are either bidentate chelating or monodentate bridging.

It should be noted that hydrogen-bonding interactions and π–π interactions play an important role in the solid-state structure of (I), as shown in Fig. 2. Adjacent units are connected by hydrogen bonds and π–π stacking, resulting in a packing framework stucture.

Experimental

The title compound was synthesized by adding a solution of 1,10-phenanthroline (0.04 g, 0.2 mmol), 2-sulfobenzenecarboxylic acid (0.04 g, 0.2 mmol) and 2,2′-dithiosalicylic acid (0.06 g, 0.2 mmol) in dimethylformamide (10 ml) dropwise to a stirred solution of lead nitrate (0.07 g, 0.2 mmol) in water (10 ml) at 298 K. The reaction mixture was filtered and the filtrate allowed to stand for about six weeks until colourless prismatic crystals of (I) were obtained. Crystals suitable for X-ray diffraction were collected by filtration, washed with water and ethanol, and dried in air.

Crystal data

$[Pb_2(C_7H_4O_5S)_2(C_{12}H_8N_2)_2]\cdot 2H_2O$
$M_r = 605.57$
Triclinic, $P\overline{1}$
$a = 7.3232$ (7) Å
$b = 10.8613$ (10) Å
$c = 12.0558$ (11) Å
$\alpha = 97.2800$ (10)°
$\beta = 100.320$ (2)°
$\gamma = 91.1500$ (10)°
$V = 934.89$ (15) Å^3
$Z = 2$
$D_x = 2.151$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3352 reflections
$\theta = 2.3$–25.3°
$\mu = 9.18$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2002)
$T_{min} = 0.034$, $T_{max} = 0.227$
6867 measured reflections
3352 independent reflections
3162 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.3°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.062$
$S = 1.05$
3352 reflections
270 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.2266P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

The water H atoms were refined subject to the restraint O—H = 0.82 (2) Å. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances of 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve

Table 1
Selected geometric parameters (Å, °).

Pb1—N1	2.540 (4)	Pb1—O1^i	2.734 (3)
Pb1—N2	2.569 (4)	S1—O5	1.428 (4)
Pb1—O1	2.574 (3)	S1—O4	1.465 (4)
Pb1—O2^i	2.595 (4)	S1—O3	1.469 (4)
Pb1—O3	2.646 (4)		
N1—Pb1—N2	65.03 (12)	O1—Pb1—O3	73.54 (11)
N1—Pb1—O1	77.52 (12)	O2^i—Pb1—O3	156.80 (12)
N2—Pb1—O1	137.24 (12)	N1—Pb1—O1^i	95.32 (12)
N1—Pb1—O2^i	74.86 (12)	N2—Pb1—O1^i	127.26 (11)
N2—Pb1—O2^i	78.37 (12)	O1—Pb1—O1^i	74.01 (12)
O1—Pb1—O2^i	111.94 (12)	O2^i—Pb1—O1^i	48.91 (11)
N1—Pb1—O3	84.87 (12)	O3—Pb1—O1^i	146.69 (10)
N2—Pb1—O3	82.95 (11)		
N1—Pb1—O1—Pb1^i	99.33 (14)	O3—Pb1—O1—Pb1^i	−172.39 (15)
N2—Pb1—O1—Pb1^i	128.15 (15)	O1^i—Pb1—O1—Pb1^i	0.0
O2^i—Pb1—O1—Pb1^i	31.51 (16)		

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H6$A\cdots$O2	0.92 (12)	1.88 (12)	2.770 (7)	163 (10)

structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1191). Services for accessing these data are described at the back of the journal.

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