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catena-Poly[[bis[aqua(1,10-phenanthroline)lead(II)]-di-μ_3-5-carboxy-3-sulfonatobenzoato] dihydrate]

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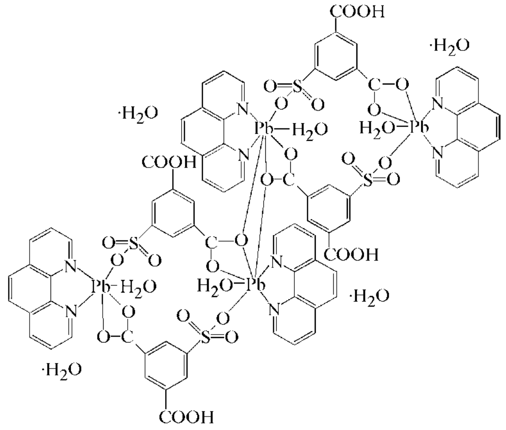
In the centrosymmetric title polymer, *catena*-poly[[bis[aqua(1,10-phenanthroline-κ^2N,N')lead(II)]-di-μ_3-5-carboxy-3-sulfonatobenzoato-1:2:1′κ^4O^3:O^1,$O^{1'}$:O^1;2′:1:2κ^4O^1:O^1,$O^{1'}$:-O^3] dihydrate], $\{[Pb(C_8H_4O_7S)(C_{12}H_8N_2)(H_2O)]\cdot H_2O\}_n$, each seven-coordinate lead(II) ion is bound by five O atoms from one water molecule and three 5-sulfoisophthalate (sip) anions, and by two N atoms from a 1,10-phenanthroline (phen) ligand. The sip sulfonate group is monodentate. One O atom of the sip carboxylate group is chelated to one Pb^{2+} cation, with the other also bridging an adjacent Pb^{2+} cation. The carboxyl group is uncoordinated. This unusual coordination results in a chain structure along the *b* axis, which is linked by strong intermolecular hydrogen bonds into a three-dimensional network.

Comment

The impact of the toxic heavy metal lead on the natural environment is reflected in the wealth of recent literature concerning the health hazards posed by lead to humans (Chiaradia *et al.*, 1997; Sauve *et al.*, 1997). In view of the steady increase in the amount of lead released into the environment by human activity, the removal of this toxic metal from the human body using chelating agents is a field of growing importance (Radecka-Paryzek & Gdaniec, 1997). Lead(II) exhibits variable coordination number and geometry with ligands, independent of the ability of these ligands to donate a lone pair of electrons (Wang & Vittal, 2003). 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 allows the Pb^{II} cations to adopt a range of different coordination geometries not restricted to octahedral, tetrahedral or square planar (Foreman *et al.*, 2000). The polytypic 5-sulfoisophthalate (sip) anion is an interesting ligand, with both carboxylate and sulfonate groups available as coordinating groups. This anion has the potential to form not only 'short-bridged' structures between metal ions *via* the carboxylate or sulfonate ends (Xiao *et al.*, 2004), but also 'longer-bridged' structures *via* the benzene ring (Foreman *et al.*, 2000). Against this background, we report here the structure of the title compound, (I).



(I)

In (I), each Pb^{2+} ion coordinates to three O atoms from two carboxylate groups of two sip anions, with a typical Pb—O(carboxylate) distance range (Foreman *et al.*, 2000), one sulfonate O atom from another sip anion, one water O atom, and two N atoms from one 1,10-phenanthroline (phen) ligand (Table 1). The Pb^{2+} cations are seven-coordinate, but their coordination geometry cannot be described as being close to a regular geometry, as expected by the absence of crystal field stabilization energy effects (Fig. 1). The two phen N atoms and one O atom of the sip carboxylate group are chelated to the Pb^{2+} cation, while the sulfonate group of another sip is monodentate. The other O atom of the chelated carboxylate bridges another Pb cation, with Pb—O distances of 2.831 (3) Å. In this way, two Pb^{II} ions are bridged by the sip carboxylate O atoms around a crystallographic centre of symmetry ('short bridging'). In addition, pairs of Pb^{II} ions are connected by two carboxylate and sulfonate 'long' bridges,

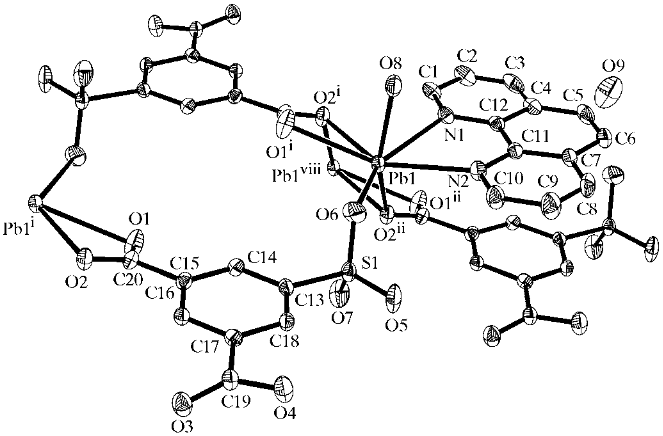


Figure 1
A view of (I), showing the contents of the asymmetric unit and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms bound to Pb1 and adjacent Pb atoms are labelled. H atoms have been omitted for clarity. [Symmetry codes: (i) $2 - x, 2 - y, 2 - z$; (ii) $x, y - 1, z$; (viii) $2 - x, 1 - y, 2 - z$.]

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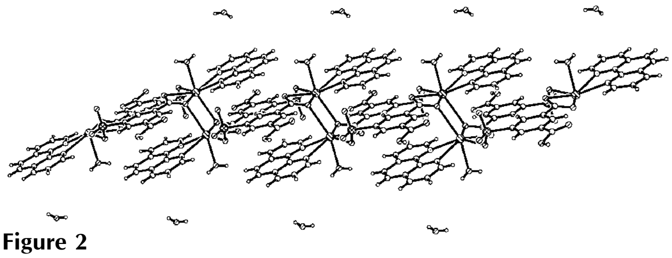

Figure 2
One chain of the polymeric structure of (I), showing the bridging of the sip anions. Pb and non-C atoms are striated.

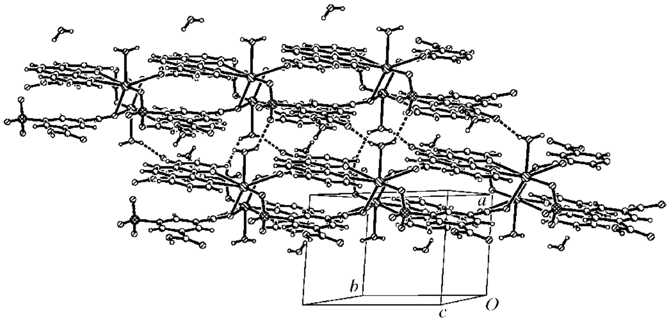

Figure 3
A perspective view of the molecular packing of (I). Hydrogen bonds are shown by dashed lines (see Table 2).

around another centre of symmetry. These two kinds of dinuclear ring are connected alternately, forming a chain structure along the *b* axis (Fig. 2).

The S—O distances fall within the typical range for the sulfonate anion (1.40–1.49 Å; Onoda *et al.*, 2001), while their similarity suggests that strong conjugation of the sulfonate group is predominant in (I). Each sip anion acts as a tetradentate ligand, connecting two Pb^{2+} ions through its one bridging and chelating carboxylate group and one monodentate sulfonate group. This coordination mode is quite different from other compounds containing this ligand, where the carboxylate groups are either in bidentate chelating or monodentate bridging mode, *e.g.* polymeric disodium (μ-*trans*-4,4′-ethylenedipyridyl)bis[μ-5-sulfoisophthalato-(3−)]dicadmate(II) hexahydrate (Tao *et al.*, 2003).

Adjacent chain units are connected by strong hydrogen bonding and, to a lesser extent, by π–π interactions, forming a three-dimensional framework structure (Table 2 and Fig. 3). The π–π interactions have an average distance between the aromatic ring of phen (C4–C7/C11/C12) and the aromatic ring of sip (symmetry code: $x, y-1, z$) of 3.56 Å, with an interplanar angle of 5.1 (1)°.

Experimental

The title compound was synthesized by adding a dimethylformamide solution (10 ml) of 1,10-phenanthroline (2 mmol, 0.42 g), sodium 5-sulfoisophthalate (2 mmol, 0.54 g) and 2,2′-dithiosalicylic acid (2 mmol, 0.63 g) dropwise to a stirred aqueous solution (10 ml) of lead nitrate (2 mmol, 0.71 g) at 298 K. The reaction mixture was filtered and the filtrate allowed to stand for about six weeks until yellow prismatic crystals were obtained. Prism-shaped crystals of (I) suitable for X-ray diffraction were collected by filtration, washed with water and ethanol, and finally dried in air.

Crystal data

$[Pb(C_8H_4O_7S)(C_{12}H_8N_2)(H_2O)]\cdot H_2O$
$M_r = 667.60$
Triclinic, $P\overline{1}$
$a = 7.2209\ (6)$ Å
$b = 9.6252\ (7)$ Å
$c = 15.0478\ (12)$ Å
$\alpha = 98.251\ (2)^\circ$
$\beta = 92.279\ (1)^\circ$
$\gamma = 94.196\ (2)^\circ$
$V = 1030.92\ (14)$ Å^3
$Z = 2$
$D_x = 2.151$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3639 reflections
$\theta = 1.4$–25.1°
$\mu = 8.34$ mm^{-1}
$T = 298\ (2)$ K
Prism, yellow
0.20 × 0.15 × 0.10 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2002)
$T_{\min} = 0.24$, $T_{\max} = 0.43$
7489 measured reflections
3638 independent reflections
3454 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 25.1^\circ$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.058$
$S = 1.04$
3638 reflections
306 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.77$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pb1—O8	2.432 (3)	Pb1—O2^{ii}	2.831 (3)
Pb1—N1	2.572 (3)	O1—Pb1^{i}	2.588 (3)
Pb1—O1^{i}	2.588 (3)	O2—Pb1^{i}	2.605 (3)
Pb1—O2^{i}	2.605 (3)	O5—S1	1.431 (3)
Pb1—N2	2.653 (4)	O6—S1	1.448 (3)
Pb1—O6	2.717 (3)	O7—S1	1.442 (3)
O8—Pb1—O1^{i}	76.52 (12)	O2^{i}—Pb1—O6	132.11 (10)
N1—Pb1—O1^{i}	119.70 (12)	O8—Pb1—O2^{ii}	151.86 (11)
O8—Pb1—O2^{i}	95.36 (11)	O2^{i}—Pb1—O2^{ii}	72.43 (10)
O1^{i}—Pb1—O2^{i}	50.35 (10)	O6—Pb1—O2^{ii}	125.03 (10)
N1—Pb1—N2	63.34 (11)	C20—O1—Pb1^{i}	93.3 (2)
O1^{i}—Pb1—N2	148.40 (12)	C20—O2—Pb1^{i}	92.1 (2)
O1^{i}—Pb1—O6	83.15 (11)	S1—O6—Pb1	121.72 (19)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O9^{iii}	0.82	1.76	2.567 (5)	169
O8—H8B···O3^{iv}	0.82	2.08	2.851 (5)	156
O8—H8A···O7^{v}	0.82	2.12	2.749 (5)	134
O9—H9A···O5^{vi}	0.79 (4)	1.96 (4)	2.749 (6)	172 (6)
O9—H9B···O3^{vii}	0.75 (4)	2.21 (4)	2.862 (5)	145 (5)

Symmetry codes: (iii) $x+1, y+1, z$; (iv) $x-1, y-1, z$; (v) $x-1, y, z$; (vi) $2-x, 1-y, 1-z$; (vii) $2-x, 2-y, 1-z$.

The uncoordinated water H atoms were refined subject to the restraint O—H = 0.83 (5) Å, while the carboxyl and coordinated water H atoms were refined subject to the restraint O—H = 0.82 (1) Å. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

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: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXTL* (Bruker, 2002).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1091). Services for accessing these data are described at the back of the journal.

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