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Linear-chain bis(μ-*O*,*O*′-dimethyl dithiophosphato)lead(II)

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The title compound, $[\mathrm{Pb}(\mathrm{C_2H_6O_2PS_2})_2]$, has a twofold rotation axis passing through the Pb atom along the *b* axis. One of the two unique S atoms in a formula unit and its symmetry-equivalent S atom bridge two adjacent Pb atoms, forming a polymeric linear chain along the *c* axis. The Pb atom is coordinated by six S atoms in a distorted octahedral arrangement. The six Pb—S distances are in the range 2.860 (2)–3.145 (2) Å, with an average of 3.01 (8) Å.

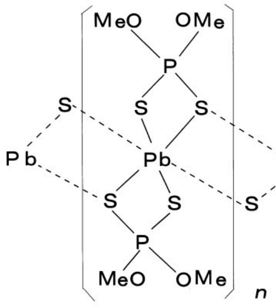
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(O–C) = 0.012 Å
R factor = 0.029
wR factor = 0.028
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

As part of a study of metal xanthates and dialkyldithiophosphates (Ito, 2003, 2004), the crystal structure of the title compound, (I), has been determined. A displacement ellipsoid plot of (I) is shown in Fig. 1. Atom S2 and its symmetry-equivalent S2$^{\mathrm{ii}}$ atom (symmetry code as in Table 1) bridge two adjacent Pb atoms, forming a linear chain. Of the six S atoms coordinated to the Pb atom, four S atoms are approximately coplanar with the Pb atom. Mean-plane calculations (Ito, 1982) show that the maximum deviations from the plane defined by seven atoms, *viz*. $\mathrm{Pb(S_2P)_2}$, are 0.164 (2) and −0.164 (2) Å for atoms S1 and S1$^{\mathrm{ii}}$, respectively. The plane normal is perpendicular to the *b* axis because of the twofold symmetry along the *b* axis.



(I)

The distorted octahedral coordination around the Pb atom and the structure of the linear chain in (I) are very similar to those in a diisopropyl analogue, bis(*O*,*O*′-diisopropyldithiophosphato)lead(II), (II) (Lawton & Kokotailo, 1972), with Pb—S distances ranging from 2.761 (7) to 3.232 (10) Å. Those authors explained the abnormally large S2—Pb—S4 angle of 152.3 (1)° in (II), which corresponds to the S2—Pb—S2$^{\mathrm{ii}}$ angle of 144.33 (7)° in (I), by the existence of a stereochemically active lone pair of electrons oriented in a direction which approximately bisects the large S2—Pb—S4 angle. According to this interpretation, the coordination around the Pb atom is a distorted pentagonal bipyramid in which the lone pair

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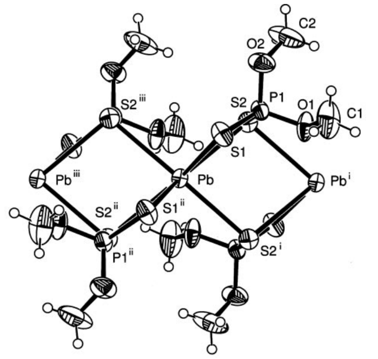

Figure 1
A view of part of the crystal structure of (I), showing 50% probability displacement ellipsoids. Atoms Pb^{i} and Pb^{iii} are related by a unit translation along the *c* axis.Symmetry codes as in Table 1.

occupies an equatorial position. On the other hand, in a diethyl analogue, bis(*O,O′*-diethyldithiophosphato)lead(II), (III) (Ito, 1972), the sulfur coordination around the Pb atom is distorted tetragonal pyramidal, with Pb—S distances ranging from 2.754 (6) to 3.022 (6) Å. Above the apex Pb atom, two S atoms of the adjacent unit approach with contact Pb···S distances of 3.469 (6) and 3.478 (6) Å. Comparison of the structures (I), (II) and (III) suggests that the differences in the sulfur coordination around the Pb atoms in these compounds probably arise from the packing characteristics of dialkyl groups in the crystalline state.

Experimental

Potassium dimethyldithiophosphate (6.0 g) and lead nitrate (5.3 g) were each dissolved in pure water (20 ml). A powder of (I) was precipitated by combining the two solutions. Recrystallization from an acetone solution at 273 K gave colourless prismatic crystals of (I).

Crystal data

$[Pb(C_2H_6O_2PS_2)_2]$
$M_r = 521.56$
Orthorhombic, *Pbcn*
$a = 17.738$ (3) Å
$b = 9.218$ (2) Å
$c = 9.216$ (1) Å
$V = 1506.9$ (4) Å^3
$Z = 4$
$D_x = 2.299$ Mg m^{-3}
$D_m = 2.292$ Mg m^{-3}
D_m measured by flotation in zinc iodide (aq)
Mo Kα radiation
Cell parameters from 25 reflections
$\theta = 15.9$–$16.5°$
$\mu = 11.97$ mm^{-1}
$T = 296$ K
Prism, colourless
0.16 × 0.12 × 0.12 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.146$, $T_{\max} = 0.238$
1834 measured reflections
1727 independent reflections
1005 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.007$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 11$
$l = -11 \rightarrow 0$
3 standard reflections every 150 reflections intensity decay: 0.2%

Refinement

Refinement on *F*
$R = 0.029$
$wR = 0.028$
$S = 1.26$
1005 reflections
75 parameters
H-atom parameters constrained
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.92$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pb—S1	2.860 (2)	P1—O1	1.585 (6)
Pb—S2	3.145 (2)	P1—O2	1.579 (7)
Pb—S2^{i}	3.033 (2)	O1—C1	1.463 (9)
S1—P1	1.976 (3)	O2—C2	1.452 (11)
S2—P1	1.987 (3)		
S1—Pb—S1^{ii}	76.0 (1)	S2—Pb—S2^{i}	80.14 (7)
S1—Pb—S2	68.04 (6)	S2—Pb—S2^{ii}	148.33 (7)
S1—Pb—S2^{i}	91.28 (6)	S2—Pb—S2^{iii}	97.75 (6)
S1—Pb—S2^{iii}	94.75 (7)	S2^{i}—Pb—S2^{iii}	172.34 (7)
S1—Pb—S2^{ii}	143.50 (6)		

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $x, -y, z-\frac{1}{2}$.

Table 2
Contact distances (Å).

Pb···O1^{i}	3.012 (6)	S2···O1^{iii}	3.336 (6)
S1···C1^{iv}	3.448 (9)		

Symmetry codes: (i) $1-x, -y, 1-z$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $x, 1-y, z-\frac{1}{2}$.

H atoms were placed in geometrically calculated positions (C—H = 0.95 Å) and allowed to ride on their parent atoms, with $U_{\rm iso} = 1.2U_{\rm eq}$(parent atom).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CrystalStructure*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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