Crystal Structure of Diphenylbis(diphenyldithiophosphinato)lead(IV), PbPh₂(S₂PPh₂)₂

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The title compound, diphenylbis(diphenyldithiophosphinato)lead(IV), PbPh$_2$(S$_2$PPh$_2$)$_2$ (1), crystallizes in the space group $C2/c$ with $a=26.690(4)$, $b=6.482(2)$, $c=23.001(3)$ Å, $\beta=122.15(1)°$ (at 122 K) and $Z=4$. Using 9656 independent reflections the structure was refined to $R_w(F^2$, all)=0.078. In the crystalline state 1 has the site symmetry C_2. In the molecule the six donor atoms form a distorted octahedron, the dithiophosphinate ligand coordinating in an anisobidentate way, with the Pb–S distances being 2.6556(7) and 3.0171(6) Å, respectively.

Recently the syntheses and some spectroscopic properties of the first di- and triphenyllead(IV) diorganophosphino-dithioates were reported,[1] including them diphenylbis(diphenyldithiophosphinato)lead(IV), PbPh₂(S₂PPh₂)₂ (1). That compound was reported to decompose when stored for more than 10 days or during repeated recrystallization, and crystals suitable for X-ray structure determination were not obtained.

Complex 1 has now been synthesized as a colourless crystalline material which showed no evidence of any decomposition after 2–3 years. It was synthesized in much the same way as described in Ref. 1, except that acetone at 0 °C was used as solvent instead of benzene at room temperature. The compound is a link in NMR, IR and Raman investigations of various lead(IV) complexes in progress at the University of Iceland. The results of these studies will be given elsewhere,[2] while we report here the crystal structure of 1.

Experimental

Synthesis of 1. A crude product of 1 was obtained in 78% yield by reaction of 0.47 g (0.93 mmol) of PbPh₂Cl₂ and 0.50 g (1.67 mmol) of NH₄S₂PPh₂ in 25 ml acetone by stirring for 4 h at 0 °C, washing the filtered product with acetone (to remove NH₄Cl), then with a 1:1 mixture of acetone/diethyl ether and drying in vacuum.

Pure, colourless, needle-shaped crystals were obtained by recrystallization from methylene chloride/diethyl ether. A saturated solution of the compound in methylene chloride, in which it is sparingly soluble, was prepared

at room temperature and centrifuged when necessary. The same volume of diethyl ether was placed on top of the solution without mixing, and the stoppered glass vessel was left overnight in a refrigerator for crystallization. The resulting millimetre-size single crystals were collected, washed with diethyl ether, vacuum dried, and used for the X-ray investigations.

Analyses: Found: C50.28; H3.51. Calc. for 1: C50.28; H3.52. M.p. 200.5–201.0 °C.

Crystal structure determination. Powder diffraction diagrams were taken at room temperature with a Guinier–Hägg camera using Cu $K\alpha$ radiation and silicon as an internal standard.

Data collection was performed on a selected single crystal with an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo $K\alpha$ radiation. The crystal was cooled to 122 K by a Nonius gas-flow low-temperature device. The variation of the temperature measured with a thermocouple in the exhaust pipe were within 1 K.

The intensities of three standard reflections were recorded every 10^4 s, and the orientation of the crystal was checked after the measurements of every 300 reflections.

Data reduction was performed with the DREADD[3] programs. Those reflections (1935) that were only measured in the prescan, i.e. with the highest possible scan speed, and having intensities less than ten times the e.s.d. were omitted, as they have been shown to suffer from systematic errors.[4] The intensities of the standard reflections showed a systematic decrease during the data collection, up to 10%. The data were corrected for this

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Table 1. Crystal data and a summary of data collection and refinement results for **1**.

Formula	$C_{36}H_{30}P_2PbS_4$	
FW/g mol[1]	859.97	
Space group	$C2/c$	

Cell parameters, single crystal (122 K) and powder (295 K), respectively:

Radiation	Mo $K\alpha$	Cu $K\alpha$
a/Å	26.690(4)	26.899(18)
b/Å	6.482(2)	6.559(4)
c/Å	23.001(3)	23.181(10)
β/°	122.15(1)	122.27(4)
V/Å³	3369.0(11)	3458(3)
Calculated density (122 K)/g cm³	1.695	
Molecules per cell, Z	4	

Data collection and refinement:

Crystal size/mm³	0.12 × 0.44 × 0.10
Faces	{100} {010} {001} {10$\bar{2}$}
Radiation (Mo $K\alpha$)/Å	0.71073
Absorption coefficient μ/mm⁻¹	5.376
θ limits/°	1.80–40.96
Min., max. *hkl*	−49,41; 0,11; 0,42
Reflections collected	10 237
Independent reflections	9656 [R(int) = 0.0600]
No. of observed reflections with $I \geqslant 2\sigma(I)$	4618
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9646/0/256
Weights, w⁻¹	$\sigma^2(|F_o|^2) + (0.0302P)^2 + 4.69P$ where $P = (|F_o|^2 + 2|F_c|^2)/3$
$R(F_{obs})^a$	0.032
$R_w(F^2, all)^b$	0.078
Goodness-of-fit on F^2	1.105
Extinction coefficient	0.00124(9)
$\Delta\rho_{max}/e$ Å⁻³	5.148
$\Delta\rho_{min}/e$ Å⁻³	−5.459

[a] $R = \sum ||F_o| - |F_c||/\sum |F_o|$ calculated for reflections with $I \geqslant 2\sigma(I)$. [b] $R_w = (\sum w||F_o|^2 - |F_c|^2|/\sum |F_o|^2)^{1/2}$.

systematic decrease and for Lorentz, polarization, background and absorption effects. The Gaussian numerical integration procedure was used for the latter corrections, the transmission factors being in the range 0.460–0.633.

The systematically absent reflections, *hkl*: for $h+k = 2n+1$ and *h0l*: for $l = 2n+1$, indicated $C2/c$ or Cc as the possible space groups. The structure was first solved and refined in the latter space group, but an inspection of the structure revealed that it should be described in $C2/c$, with the lead atom on the crystallographic two-fold axis. The position of the lead atom was determined from the Patterson function, SHELXS-86,[5] and all remaining atoms were found by difference Fourier technique. Refinement of the structure was performed by SHELXL-93.[6] After anisotropic displacement parameters had been introduced for all non-hydrogen atoms the difference Fourier map still showed large peaks and holes close to the lead atom. Moreover it contained significant peaks in the expected positions for the hydrogen atoms. The high resolution of the diffraction data, giving an observation/parameter ratio of 38, allowed the inclusion of positional and thermal parameters of the hydrogen

atoms in the refinement which led to physically realistic parameters.

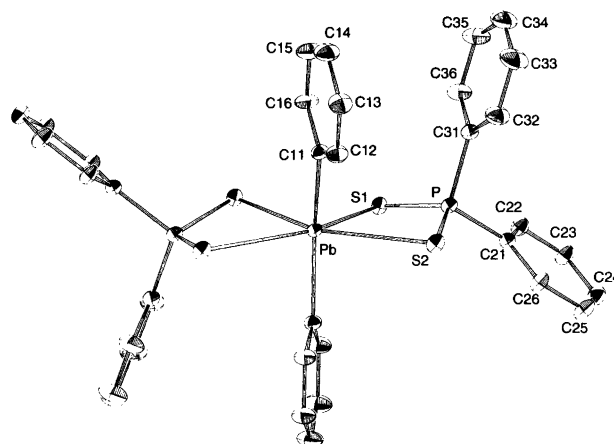Crystal data and further details from the data collec-

Fig. 1. ORTEP drawing of **1** including the labelling of the atoms. The thermal ellipsoids enclose 50% probability. The twofold axis through the lead atom is approximately perpendicular to the paper.

Table 2. Atomic coordinates ($\times$ 10^4) and equivalent isotropic displacement parameters (in $\text{Å}^2 \times 10^3$) for **1**.

Atom	x	y	z	$U_{eq}{}^a$
Pb	5000	6166(1)	2500	13(1)
S1	4659(1)	9271(1)	2964(1)	16(1)
S2	4351(1)	4360(1)	3126(1)	18(1)
P	4140(1)	7301(1)	3118(1)	14(1)
C11	4182(1)	5392(3)	1539(1)	17(1)
C12	3962(1)	3391(4)	1423(1)	22(1)
C13	3437(1)	2947(4)	809(1)	28(1)
C14	3139(1)	4499(5)	322(1)	32(1)
C15	3362(1)	6484(5)	447(2)	33(1)
C16	3889(1)	6949(4)	1062(1)	25(1)
C21	4209(1)	7975(3)	3923(1)	15(1)
C22	4164(1)	10031(3)	4078(1)	19(1)
C23	4224(1)	10509(4)	4702(1)	22(1)
C24	4329(1)	8964(4)	5172(1)	23(1)
C25	4373(1)	6921(4)	5022(1)	24(1)
C26	4313(1)	6428(3)	4397(1)	20(1)
C31	3377(1)	7828(3)	2448(1)	18(1)
C32	2960(1)	6245(5)	2221(2)	30(1)
C33	2371(1)	6636(6)	1712(2)	39(1)
C34	2199(1)	8596(6)	1435(2)	36(1)
C35	2614(1)	10179(5)	1661(2)	34(1)
C36	3203(1)	9804(4)	2166(1)	26(1)

^{a} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond distances (in Å) and angles (in°) in **1**.

Pb–C11	2.184(2)	P–S1	2.0488(7)
Pb–S1	2.6556(7)	P–S2	1.9849(9)
Pb–S2	3.0171(6)	P–C21	1.814(2)
		P–C31	1.817(2)
C–C	1.383(5)–1.401(3)		
C–H	0.89(5)–1.07(6)		
C11–Pb–C11'	153.47(11)	Pb–S1–P	90.31(3)
C11–Pb–S1	102.03(6)	Pb–S2–P	81.67(2)
C11–Pb–S1'	98.02(5)	S1–P–S2	112.68(3)
C11–Pb–S2	82.84(5)	S1–P–C21	108.46(7)
C11–Pb–S2'	86.94(5)	S1–P–C31	106.90(7)
S1–Pb–S1'	81.43(3)	S2–P–C21	110.34(7)
S1–Pb–S2	72.27(2)	S2–P–C31	111.88(8)
S2–Pb–S2'	134.36(2)	C21–P–C31	106.29(9)
C–C–A	118.2(2)–121.7(2) (A is Pb, P or C)		
C–C–H	115(3)-125(3)		

Symmetry code: '($-x+1$, y, $-z+\frac{1}{2}$).

and 2, respectively. Lists of observed and calculated squares of structure amplitudes, positional parameters and isotropic displacement parameters for the hydrogen atoms and anisotropic displacement parameters for the other atoms are available from the authors.

Results and discussion

tion and refinements are given in Table 1, atomic coordinates and U_{eq} of non-hydrogen atoms in Table 2 and selected bond lengths and angles in Table 3. Drawings of the molecule and the packing are displayed in Figs. 1

The structure of $PbPh_2(S_2PPh_2)_2$ in the solid state is presented in Figs. 1 and 2 and Table 3. In the molecule lead(IV) is six-coordinated in a distorted octahedron
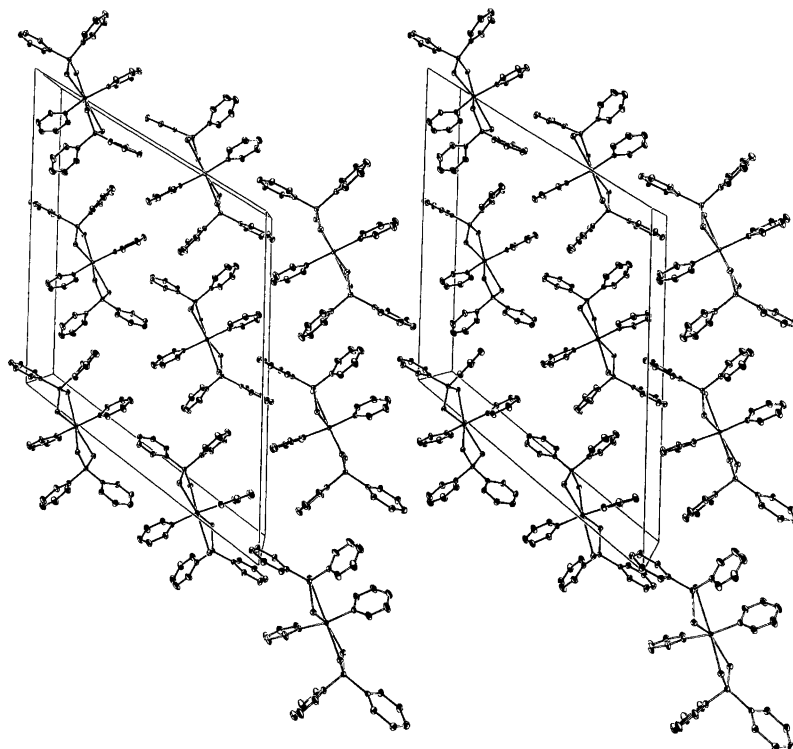

Fig. 2. ORTEP stereo view showing the packing in the unit cell of **1**. The *a*-axis is parallel up and the *b*-axis perpendicular up relative to the paper.

with C_2 site symmetry with the twofold axis through the lead atom and the centre between S1 and S1'. The lead atom is surrounded by four sulfur atoms in a nearly planar trapezoidal way with a significant difference between the Pb–S distances, Pb–S1 being 2.6556(7) and Pb–S2 3.0171(6)Å. The two Pb–C bonds are tilted towards the bigger S–Pb–S gap (S being S2 and S2') with a C–Pb–C angle equal to 153.5(1)°. The tetrahedral $Ph_2PS_2^-$ ligand coordinates in an anisobidentate fashion to the lead atom, and accordingly the P–S1 bond is longer than the P–S2 bond, 2.0488(7) vs. 1.9849(9)Å, respectively. There are no other contacts to the sulfur atoms except weak intermolecular S···H–C interactions, as can be noticed in Fig. 3, which demonstrates the mononuclear character of the compound.

Bond distances and angles in the $Ph_2PS_2^-$ ligand are consistent with those found in other compounds,[7] where longer P–S distances, and shorter metal–sulfur bonds, are also observed. In $Pb(S_2PPh_2)_2$ the Pb–S distances vary between 2.785(1) and 2.981(1)Å.[7] In $PbPh_2\{S_2P(OCH_2Ph_2)_2\}_2$[8] the six donor atoms are arranged around the lead centre nearly as in 1. For comparison the Pb–S distances (with P–S distances in parentheses) are 2.723 (1.98), 2.940 (1.93), 2.679 (2.01) and 2.957 (1.93) Å, and the Pb–C bonds are 2.176 and 2.215 Å with a C–Pb–C angle of 165.0°. The angle S–Pb–S with the two long Pb–S bonds is 132.0°.[8] Consequently there is hardly any doubt that S2 in the present lead(IV) complex 1 is rather loosely bound to the metal centre.

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