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Crystal and Molecular Structure of Bis(diphenyldithiophosphinato)lead(II), $^{1}_{\infty}[Pb(S_2PPh_2)_2]$, a New Type of Polymer Associated through Pb···S Secondary Interactions

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Bis(diphenyldithiophosphinato)lead(II), $Pb(S_2PPh_2)_2$, was obtained either as a redistribution/decomposition product of $Ph_2Pb(S_2PPh_2)_2$ or directly as a reaction product of $Pb(OCOCH_3)_2{\cdot}3H_2O$ and $NH_4S_2PPh_2$. Its crystal and molecular structure was determined by X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$, with cell parameters $a = 9.017(2)$ Å, $b = 10.839(2)$ Å, $c = 12.808(2)$ Å, $\alpha = 99.48(2)°$, $\beta = 90.13(2)°$, $\gamma = 97.91(2)°$, and $Z = 2$. The monomeric unit contains distorted square-pyramidal PbS_4 units. Additionally, each lead atom has two weak lead–sulfur contacts of 327.0 and 344.8 pm with neighboring molecules, lying on the free side of the PbS_4 fragment. This leads to molecule pair units which are repeated in a chain polymeric structure. The coordination polyhedron around lead in the polymeric chain can be described as strongly distorted octahedron, with axial positions occupied by a sulfur atom of a neighboring molecule and a sulfur atom of the proper monomeric unit (S···Pb–S 178.0°), or, alternatively, as a ψ-caped octahedron, with the stereochemically active electron pair of lead in the capped position.

Introduction

Dithiophosphorus ligands, $R_2PS_2^-$, *i.e.* dithiophosphinates (R = alkyl or aryl) and dithiophosphates (R = alkoxy or aryloxy) exhibit a broad variety of coordination patterns; they can act as monodentate (monometallic monoconnective), iso- and anisobidentate (monometallic biconnective), or bridging (bimetallic biconnective and triconnective) ligands.[2] In main group metal compounds,[3,4] it has been frequently found that minor changes in the nature of the peripheric substituents, *i.e.* the R groups at phosphorus, not only result in different coordination modes of the dithiophosphorus ligand but also produce dramatic changes in the coordination geometry of the metal. Spectacular examples are offered by the lead derivatives, in which for every different R a new type of structure has been observed. Thus, $Pb[S_2P(OPh)_2]_2$ was described as a monocyclic dimer, and $Pb[S_2P(OBu^i)_2]_2$, as a tricyclic dimer;[5] in both cases the association was achieved through secondary metal–sulfur interactions. These are defined by interatomic distances longer than single covalent bonds and shorter than the sum of van der Waals radii.[6] In other cases, *i.e.* $Pb[S_2P(OEt)_2]_2$,[5,7] $Pb[S_2P(OPr^i)_2]_2$,[8] and $Pb(S_2PEt_2)_2$,[9] various other types of polymeric structures are formed, also through secondary bonding.

We report now a new type of polymeric association through secondary Pb···S interactions found in $Pb(S_2PPh_2)_2$. Surprisingly, this compound has been only briefly mentioned before in the literature,[10] but not fully characterized. The original paper,[10] contains only information about the infrared spectrum of $Pb(S_2PPh_2)_2$, which is compared with those of other metal diphenyldithiophosphinates. An X-ray crystal structure determination reported here, reveals a new type of structure, in which $Pb(S_2PPh_2)_2$ units are associated in pairs, which in turn, are loosely bound to form polymeric chains. The compound was obtained accidentally, in an attempt to prepare $Ph_2Pb(S_2PPh_2)_2$, but it was also synthesized by a controlled reaction from a Pb(II) salt.

Experimental Section

General Considerations. Diphenyllead dichloride and lead(II) acetate were commercial products. Diphenyldithiophosphinic acid was prepared from P_4S_{10}, C_6H_6, and anhydrous $AlCl_3$, using a literature method,[11] and the ammonium salt was obtained by bubbling dried gaseous ammonia into a benzene solution of the free acid. Microanalyses (C, H) were performed by Beller Mikroanalytisches Laboratorium (Göttingen). The infrared spectra were run in the range 4000–200 cm^{-1} on a Perkin-Elmer 283b spectrometer as KBr disks. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded using C_6D_6 solutions, on Varian Gemini spectrometers operating at 200 and 300 MHz, respectively. The ^1H and ^{31}P chemical shifts are reported in parts per million (ppm) relative to TMS and 85% H_3PO_4, respectively. The mass spectra were recorded on a Finnigan MAT 8222 apparatus, using the DCI(–) method.

Preparation of Bis(diphenyldithiophosphinato)lead(II), $Pb(S_2PPh_2)_2$. (a) A mixture of Ph_2PbCl_2 (0.72 g, 1.67 mmol) and $NH_4S_2PPh_2$ (0.89 g, 3.33 mmol) in 50 mL of anhydrous benzene was stirred under reflux for 4 h. The reaction mixture was filtered hot to remove the resulting NH_4Cl, and the clear filtrate was cooled to room temperature and evaporated slowly overnight, in open atmosphere. During this process the volume of the solution was reduced to ca. one-fourth, and yellowish crystals deposited, which were filtered off under vacuum. Yield: 0.46 g (78%—related to the expected amount of the lead(II) derivative). Mp: 194–196 °C. The compound was identified as bis(diphenyldithiophosphinato)lead(II). Anal. Calcd for $C_{22}H_{20}P_2PbS_4$: C, 40.85; H, 2.84. Found: C, 40.96; H, 2.89.

(b) Clear aqueous solutions containing $Pb(OCOCH_3)_2{\cdot}3H_2O$ (0.63 g, 1.66 mmol, in 25 mL of H_2O) and $NH_4S_2PPh_2$ (0.89 g, 3.33 mmol, in 25 mL of H_2O) were mixed, resulting in immediate precipitation of a yellowish white solid. The reaction mixture was stirred at room temperature for 15 min and was filtered off under vacuum. The precipitate was washed several times with distilled water and ethanol. After being dried under vacuum, the solid was recrystallized from hot benzene, leading to white-yellowish crystals. Yield: 1.15 g (98%). Mp: 194–196 °C.

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Table 1. Crystallographic Data for $Pb(S_2PPh_2)_2$

$C_{24}H_{20}P_2PbS_4$	$Z = 2$
triclinic	$D_{calc} = 1.917$ g·cm^{-3}
$a = 9.017(2)$ Å	fw: 705.8
$b = 10.839(2)$ Å	space group: $P\bar{1}$
$c = 12.808(2)$ Å	$T = 153$ K
$\alpha = 99.48(2)°$	μ(Mo Kα) = 7.385 mm^{-1}
$\beta = 90.13(2)°$	λ(Mo Kα radiation) = 0.710 73 Å
$\gamma = 97.91(2)°$	$R = 2.73\%$
$V = 1222.4(4)$ Å^3	$R_w = 2.84\%$

[a] $R = \sum|\Delta|/\sum|F_o|$; $R_w = [\sum(w\Delta)^2/\sum wF_o^2]^{1/2}$; $\Delta = F_o - F_c$; $S = [\sum w\Delta^2/(NO - NV)]^{1/2}$.

The compounds obtained using the above two methods showed identical spectroscopic properties. IR (cm^{-1}): 2962 w, 2856 w, 1463 m, 1459 m, 1434 m, 1377 wm, 1304 w, 1176 w, 1097 ms, 1069 w, 1025 w, 997 w, 972 w, 748 m, 742 m, 704 s, 687 s, 636 s ($\nu_{as}(PS_2)$), 608s, 557 vs ($\nu_s(PS_2)$), 489 s, 482 s, 440 w, 423 w, 346 w. ^{1}H NMR (ppm): 8.18 dm (8H, $^3J_{PH}$ = 14.3 Hz), 7.15 m (12H). $^{31}P\{^1H\}$ NMR (ppm): 60.1. MS (*m/e* (%)): 705 (14), $[M - H]^{+\bullet}$; 249 (100), $[Ph_2PS_2]^+$; 217 (12), $[Ph_2PS]^+$; 185 (3.2), $[Ph_2P]^+$.

Crystal Structure Determination. Yellowish, plate crystals of the title compound were obtained by slow evaporation of a benzene solution, and a suitable crystal of 0.5 × 0.4 × 0.4 mm^3 was used for the determination of the structure. The crystallographic data are summarized in Table 1. Data were collected on a Siemens P4 four-circle diffractometer for 6090 reflections in the 2Θ-ω mode of which were 5641 independent reflections (R_{int} = 1.00%) and 4463 ($F > 6.0\sigma(F)$) were used in the full-matrix least-squares refinement with the SHELXTL PLUS (VMS) program system.[12] The structure was solved by direct methods for the lead, and the difference Fourier synthesis revealed the positions for the other non hydrogen atoms. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated as a riding model with isotropic *U*. Absorption effects were corrected with the program DIFABS.[13] The final *R* values are $R = 2.73\%$ and $R_w = 2.84\%$ ($R = 4.14\%$ and $R_w = 3.14\%$ for all data) with weights $w^{-1} = \sigma^2(F) + 0.0002F^2$. Our goodness-of-fit (Goof) finished at 1.06. The residual electron density from a final difference Fourier synthesis was in the range of −1.78 to 1.20 e Å^{-3}. Refined values for the atomic coordinates are given in Table 2.

Results and Discussion

Bis(diphenyldithiophosphinato)lead(II), $Pb(S_2PPh_2)_2$, was isolated as yellowish crystals in an attempt to prepare $Ph_2Pb(S_2PPh_2)_2$, by reacting Ph_2PbCl_2 with the ammonium salt of the diphenyldithiophosphinic acid (1:2 molar ratio) in a benzene solution, followed by slow evaporation in open atmosphere. The process leading to this compound can be explained by the following reaction sequence:

$$2Ph_2PbCl_2 + 4NH_4S_2PPh_2 \xrightarrow[-4NH_4Cl]{} 2Ph_2Pb(S_2PPh_2)_2 \longrightarrow Ph_3PbS_2PPh_2 + [PhPb(S_2PPh_2)_3] \overset{\text{(unstable)}}{\longrightarrow} Pb(S_2PPh_2)_2 + PhS(S)PPh_2$$

This sequence is supported by ^{1}H and ^{31}P NMR studies, which will be discussed in detail in a separate publication.[14] The easy cleavage of organic groups, when organolead derivatives react with dithiophosphorus ligands, has also been previously noted by Harrison et al.,[5] who obtained lead(II) dithiophosphate, $Pb[S_2P(OPh)_2]_2$, by reacting trimethyllead(IV) acetate with diphenyldithiophosphoric acid, $(PhO)_2P(S)SH$. This is not surprising, since an acid was used. By contrast, in our case the formation of the inorganic, "naked" lead(II) derivative is due to a redistribution of the phenyl groups in the diphenyllead(IV) derivative followed by decomposition of the monophenyllead(IV) compound. A similar behavior was found for dimethyllead(IV) compounds, Me_2PbX_2, in aqueous solutions.[15] However, diorganolead(IV) dithiophosphates[16,17] and dithiophosphinates[14] can be isolated under carefully controlled conditions, but possible decomposition on storage should not be neglected.

Table 2. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (pm^2)

	x	*y*	*z*	*U*(eq)[a]
Pb(1)	24988(2)	48002(2)	48498(1)	194(1)
P(1)	47241(13)	70142(11)	37413(9)	165(3)
S(11)	37306(15)	75323(11)	50974(9)	257(4)
S(12)	47943(13)	51248(10)	34273(9)	183(3)
C(11)	66138(49)	78336(41)	37425(33)	176(13)
C(12)	69322(52)	91049(42)	41639(37)	222(14)
C(13)	83657(54)	97479(44)	41020(38)	252(15)
C(14)	94902(55)	91223(46)	36314(39)	269(16)
C(15)	91992(54)	78611(47)	32011(39)	258(16)
C(16)	77632(52)	72043(45)	32377(34)	220(14)
C(21)	37364(47)	74788(41)	26604(35)	173(13)
C(22)	34928(55)	87372(45)	27473(39)	250(15)
C(23)	27640(55)	91293(49)	19290(42)	295(17)
C(24)	22711(56)	82862(49)	10350(39)	283(16)
C(25)	25078(58)	70358(50)	9583(38)	287(16)
C(26)	32395(53)	66374(44)	17580(36)	228(15)
P(2)	7670(13)	30093(11)	26333(9)	181(3)
S(21)	1939(13)	47108(11)	32778(9)	213(4)
S(22)	19817(14)	22750(11)	36210(10)	247(4)
C(31)	−8784(49)	18997(42)	21372(34)	187(13)
C(32)	−6312(57)	7635(45)	15148(38)	260(15)
C(33)	−18435(59)	−1567(47)	11533(38)	279(16)
C(34)	−32833(57)	569(49)	14176(40)	304(16)
C(35)	−35210(56)	11828(50)	20326(42)	311(17)
C(36)	−23140(54)	21168(48)	23828(38)	260(15)
C(41)	17773(50)	32098(42)	14283(35)	200(14)
C(42)	32418(53)	29575(45)	13001(39)	254(15)
C(43)	39657(61)	31430(51)	3770(43)	347(18)
C(44)	32491(63)	35580(52)	−4230(40)	342(18)
C(45)	17675(64)	37673(50)	−3115(40)	325(17)
C(46)	10391(56)	35935(46)	6108(37)	252(15)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

To obtain further evidence about the identity of product prepared using the above reaction scheme, the title compound was also synthesized by a direct exchange reaction between lead(II) acetate and $NH_4S_2PPh_2$:

$$Pb(OCOCH_3)_2{\cdot}3H_2O + 2NH_4S_2PPh_2 \rightarrow Pb(S_2PPh_2)_2 + 2NH_4OCOCH_3 + + 3H_2O$$

The spectroscopic properties of the products obtained through the above two synthetic methods are identical. The infrared spectrum of the bis(diphenyldithiophosphinato)lead(II) shows two strong absorptions in the 650-500-cm^{-1} region, assigned to asymmetric (636 cm^{-1}) and symmetric (557 cm^{-1}) PS_2 stretching vibrations. The difference $\Delta = \nu_{as}(PS_2) - \nu_s(PS_2) = 79$ cm^{-1}, is consistent with an anisobidentate behavior of the dithioligand. The $^{31}P\{^1H\}$ NMR spectrum shows only one resonance at δ = 60.1 ppm, indicating a single type of phosphorus atoms in solution.

The crystal and molecular structure of the title compound was determined by X-ray diffraction. In the solid state the compound consists of monomeric $Pb(S_2PPh_2)_2$, associated through secondary Pb···S interactions, in a complex supramolecular structure. The monomeric unit is shown in Figure 1, and important bond distances and angles within it are listed in Table 3. In the monomeric unit the ligands form two four-membered PbS_2P chelate rings, oriented in such a way as to form a butterfly structure, in which the four sulfur atoms determine the base of a distorted tetragonal pyramid,

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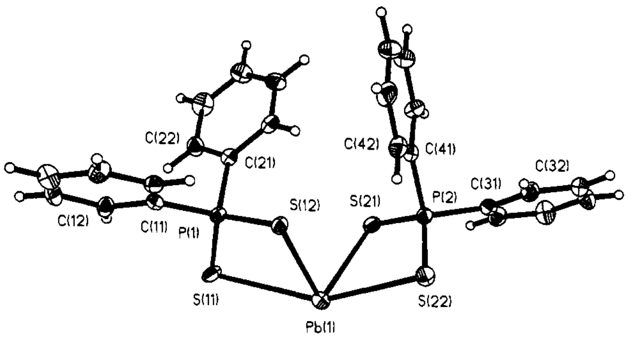

Figure 1. Molecular structure of the monomeric unit $\mathrm{Pb(S_2PPh_2)_2}$.

Table 3. Important Bond Distances (Å) and Angles (deg) within the Monomeric Unit $\mathrm{Pb(S_2PPh_2)_2}$

Pb(1)–S(11)	298.1(1)	S(11)–Pb(1)–S(12)	70.7(1)
Pb(1)–S(12)	278.5(1)	S(11)–Pb(1)–S(21)	99.3(1)
Pb(1)–S(21)	287.1(1)	S(11)–Pb(1)–S(22)	151.5(1)
Pb(1)–S(22)	290.0(1)	S(12)–Pb(1)–S(21)	93.2(1)
		S(12)–Pb(1)–S(22)	82.8(1)
P(1)–S(11)	199.0(2)	S(21)–Pb(1)–S(22)	71.3(1)
P(1)–S(12)	203.1(2)		
P(1)–C(11)	181.2(4)	S(11)–P(1)–S(12)	112.4(1)
P(1)–C(21)	182.0(5)	C(11)–P(1)–C(21)	104.8(2)
		S(21)–P(2)–S(22)	113.3(1)
P(2)–S(21)	202.8(2)	C(31)–P(2)–C(41)	102.6(2)
P(2)–S(22)	200.0(2)		
P(2)–C(31)	181.8(4)	Pb(1)–S(11)–P(1)	84.0(1)
P(2)–C(41)	182.3(5)	Pb(1)–S(12)–P(1)	88.6(1)
		Pb(1)–S(21)–P(2)	86.3(1)
		Pb(1)–S(22)–P(2)	86.0(1)

with the lead atom in the apex. The dithio ligand can be regarded as anisobidentate, with nonequivalent phosphorus–sulfur bonds (average 203.0 and 199.5 pm, respectively), whose lengths are intermediate between those observed for single P—S (207.7 ppm) and double P═S (195.4 pm) bonds in the free acid, $\mathrm{Ph_2P(S)SH}$.[18] The nonequivalence of the phosphorus–sulfur bonds within a four-membered $\mathrm{PbS_2P}$ chelate ring is correlated with that of the associated covalent lead–sulfur bonds; *i.e.*, in all cases short and long phosphorus–sulfur bonds are associated with long and short Pb–S bonds, respectively. A distortion of the tetrahedral arrangement around phosphorus atoms is observed as reflected in the magnitude of the S–P–S (average 112.8°) and C–P–C (average 103.7°) bond angles. The two four-membered $\mathrm{PbS_2P}$ chelate rings are basically planar, with the sums of the internal angles within being 355.7 and 356.9° for Pb(1)S(11)P(1)S(12) and Pb(1)S(21)P(2)S(22), respectively.

In the $\mathrm{PbS_4}$ distorted tetragonal pyramid the apical lead atom stands 130 pm above the best base plane described by the four sulfur atoms (deviations: S(11) = 59, S(12) = −74, S(21) = −51, S(22) = 66 pm). The sulfur atoms at short (Pb–S(12) = 278.5, Pb–S(21) = 287.1 pm) and long (Pb–S(11) = 298.1, Pb–S(22) = 290 pm) covalent distances, respectively, in respect with the Pb atom are in *trans* position. The angles S(12)–Pb–S(21) (93.2°) and S(11)–Pb–S(22) (151.5°), also reflect the distortion of the $\mathrm{PbS_4}$ pyramid.

A more thorough investigation of the crystal structure of this compound reveals interesting features. Thus, the monomeric $\mathrm{Pb(S_2PPh_2)_2}$ units are associated to form **symmetric dimeric pairs, $[\mathrm{Pb(S_2PPh_2)_2}]_2$,** through intermolecular Pb···S interactions of 327.0 pm (longer than a covalent Pb–S bond, but significantly shorter than the sum of van der Waals radii, ca. 380 pm[19]). Additionally, each lead atom has a further, longer intermolecular Pb···S contact of 344.8 pm with a sulfur atom belonging to a neighboring pair, thus leading to a **polymeric structure,** in which each dithiophosphinato ligand behaves as a bridging bimetallic triconnective moiety (Figure 2). The two intermolecular lead–sulfur interactions lie in *cis* position (S(12d)···Pb(1c)···S(21b) angle of 94.9°) on the "free" side of the Pb atom, opposite to the sulfur-formed base of the $\mathrm{PbS_4}$ pyramid.

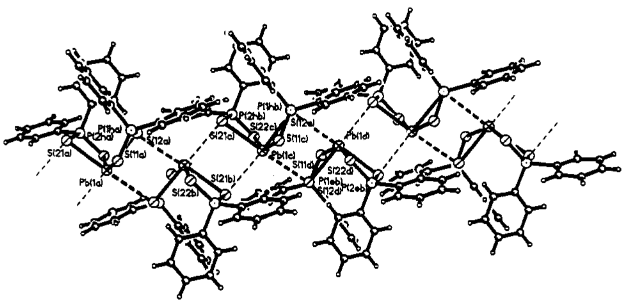

Figure 2. Supramolecular association through weak Pb···S secondary bonding in ${}^{1}_{\infty}[\mathrm{Pb(S_2PPh_2)_2}]$.

Table 4. Secondary Bond Lead–Sulfur Distances (pm) within the Dimeric Units and between them and Corresponding Bond Angles (deg) (for Atom Numbering Scheme, See Figure 2)

Pb(1c)···S(12d)	327.0	S(11c)–Pb(1c)···S(21b)	93.7
Pb(1d)···S(12c)	327.0	S(11c)–Pb(1c)···S(12d)	80.8
		S(12c)–Pb(1c)···S(21b)	164.3
Pb(1c)···S(21b)	344.8	S(12c)–Pb(1c)···S(12d)	84.9
Pb(1b)···S(21c)	344.8	S(21c)–Pb(1c)···S(21b)	87.1
		S(21c)–Pb(1c)···S(12d)	178.0
		S(22c)–Pb(1c)···S(21b)	112.1
		S(22c)–Pb(1c)···S(12d)	107.7
		S(21b)···Pb(1c)···S(12d)	94.9

In the polymeric structure the $\mathrm{PbS_4}$ pyramids of the monomeric units form an imaginary chain of lead atoms (Pb(1b)···Pb(1c) = 459.7 pm and Pb(1c)···Pb(1d) = 448.1 pm, with a Pb(1b)···Pb(1c)···Pb(1d) angle of 166.7°). The lead–lead interatomic distances are longer than the sum of van der Waals radii, therefore no interactions between the metal atoms can be considered. Within the dimeric unit the Pb···S (327.0 pm) and Pb···Pb (448.1 pm) distances are shorter than the corresponding distances observed between the dimeric units (344.8 and 459.7 pm, respectively). This supports the description of the polymeric chain as consisting of dimeric units.

Each lead atom is surrounded by six sulfur atoms: four (belonging to the mononuclear $\mathrm{Pb(S_2PPh_2)_2}$ unit) at short, covalent Pb–S distances, and two others (each belonging to neighboring $\mathrm{Pb(S_2PPh_2)_2}$ molecules) at longer, intermolecular secondary bond distances (Table 4). The coordination polyhedron around the lead atom in the polymeric structure can be described as distorted octahedron, with S(21c) and S(12d) in axial positions, with an S(21c)–Pb(1c)···S(12d) angle of 178.0°. Alternatively, if the lone electron pair of the lead atom is considered stereochemically active (a behavior which, in general, is still a subject of much speculation), the coordination polyhedron becomes a ψ-caped octahedron, with the lone pair in the caping position, most likely directed through the S(21b)S(12c)S(12d) face of the octahedron. This face appears to be significantly enlarged compared to the other ones, as reflected not only by the angles at lead, *i.e.* S(21b)···Pb(1c)–S(22c) = 112.1°, S(21b)···Pb(1c)···S(12d) = 99.3°, and S(12d)···Pb(1c)–S(22c) = 107.7°, but also by the lead–sulfur distances (Pb(1c)···S(12b) = 344.8, Pb(1c)···S(12d) = 327.0, and Pb(1c)–S(22c) = 290.0 pm) longer than those describing the other octahedron faces.

A comparison of the molecular and crystal structure of $\mathrm{Pb(S_2PPh_2)_2}$ with those already solved by X-ray diffraction for $\mathrm{Pb(S_2PEt_2)_2}$ and for the related bis(diorganodithiophosphato)lead(II), $\mathrm{Pb[S_2P(OR)_2]_2}$ (R = Et, $\mathrm{Pr^i}$, $\mathrm{Bu^i}$, Ph), is worthwhile since, as mentioned in the **Introduction**, each of these compounds displays a different type of structure. A selection of the structural data for inorganic lead(II) derivatives containing dithiophosphorus ligands, is given in Table 5. Thus, when iso-butyl and phenyl groups are attached to phosphorus in $\mathrm{Pb[S_2P(OR)_2]_2}$ (structures **a** and **b**), discrete dimers are formed through intermolecular

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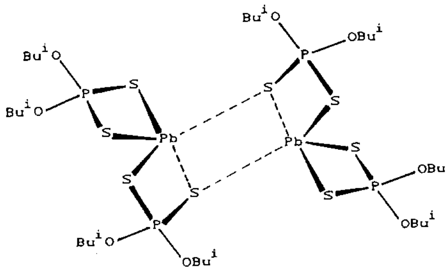
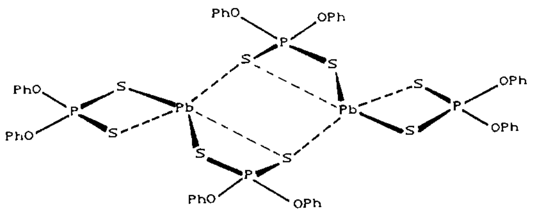
Table 5. Comparison of Selected Structural Data for $Pb(S_2PR_2)_2$ (R = Alkyl, Aryl, Alkoxy, Aryloxy)

R	P–S[a]	Pb–S[a,b]	Pb···S[a,c]	ligand[e] coordn pattern	CN[d]	deg of assocn	ref
OEt	200.8(4)	275.9(4)		BT	8[f]	polymer	4
	197.4(3)	299.8(3)	349.0(4)		(DSA)		
	199.5(4)	278.2(4)		BT			
	196.7(3)	303.5(4)	348.3(4)				
	199.5(8)	275.4(6)		BT	8		6
	196.9(7)	299.6(5)	346.9(6)				
	199.1(9)	279.0(6)		BT			
	196.8(7)	302.2(6)	347.8(6)				
OPr^i	200.0(14)	276.1(7)		BT	6[g]	polymer	7
	198.2(13)	323.2(10)	298.5(12)		(DO)		
	195.8(13)	277.2(7)		BT			
	194.4(12)	317.5(9)	302.7(11)				
OBu^i	199.4(6)	275.5(5)		BT	5[i]	dimer	4
	195.1(8)	312.7(5)	344.4(5)		(DSP)		
	198.5(7)	276.8(5)		CI			
	198.6(8)	276.2(6)					
OPh	198.4(6)	275.3(5)		BT	5[j]	dimer	4
	196.0(9)	332.3(5)	321.5(6)		(DSP)		
	199.3(6)	273.2(6)		CA			
	195.8(7)	289.6(7)					
Et	203.6(8)	274.9(5)		BT	6[k]	polymer	8
	193.1(10)	319.6(8)	310.0(8)		(DO)	(trinuclear units)	
	202.0(10)	274.9(7)		CA			
	199.4(11)	290.9(8)					
	199.1(9)	278.2(6)		BT			
	201.8(8)	293.4(6)	319.8(6)				
	201.8(10)	278.1(6)		BT			
	199.9(8)	314.4(6)	309.1(6)				
	201.6(8)	278.3(6)	343.5(6)	BT			
	198.9(9)	285.0(7)					
	201.8(8)	287.7(6)	331.6(6)	TT			
	201.4(8)	300.0(6)	326.9(6)				
Ph	203.1(2)	278.5(1)	327.0	BT	6[l]	polymer	this work
	199.0(2)	298.1(1)			(DO)	(dimeric units)	
	202.8(2)	287.1(1)	344.8	BT			
	200.0(2)	290.0(1)					

[a] In pm. [b] Distances in the PbS_2P chelate ring. [c] Bridging distances. [d] Coordination number and geometry of lead atom; abbreviations used: DSA, distorted square antiprism; DO, distorted octahedron; DSP, distorted square pyramid; DPB, distorted pentagonal bipyramid. [e] CI = chelating isobidentate; CA = chelating anisobidentate; BT = bimetallic triconnective (bridging); TT = trimetallic triconnective (see ref 2 for illustration of this terminology). [f] Two additional intermolecular Pb···O contacts at 301(1) and 303(1) pm. [g] CN = 7; ψ-DPB.[h] [h] If the stereochemically active lone pair of lead is considered. [i] CN = 6; ψ-DO.[h] [j] CN = 6; DO (one phenyl ring is assumed to occupy a coordination position). [k] CN = 7; ψ-DPB.[h] [l] CN = 7; ψ-caped octahedron.[h]



a

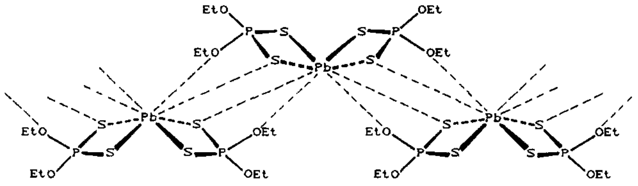


b

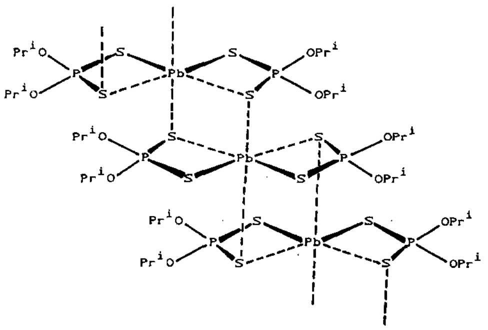
associations involving the sulfur atoms doubly bonded to phosphorus. In both cases one of the dithiophosphato ligand is chelated to the lead atom, while the other acts as a bimetallic triconnective bridge. However, the dimeric units in these two compounds were described in a different way in relation to the intermolecular lead–sulfur distances, *i.e.* for R = Bu^i, $Pb\cdots S(=P)_{bridging} > Pb\cdots S(=P)_{chelating}$ (344.4 *vs* 312.7 pm), while for R = Ph, $Pb\cdots S(=P)_{bridging} < Pb\cdots S(=P)_{chelating}$ (321.5 *vs* 332.3 pm). Moreover, even if in both dimers the coordination polyhedron around lead can be described as pseudo-pentagonal-bipyramidal, the fifth equatorial position is occupied by the stereochemically active lone pair of lead in the isobutoxy derivative but by a phenyl group in the phenoxy compound.

In other dithiophosphates, $Pb[S_2P(OR)_2]_2$, R = Et or Pr^i, and in dithiophosphinates, $Pb(S_2PR_2)_2$, R = Et or Ph, polymeric structures are always formed. However, each structure is different. Thus, in $Pb[S_2P(OEt)_2]_2$ the polymerization of the square-pyramidal PbS_4 units of the monomer arises through weak interactions between lead and both sulfur atoms (doubly bonded to phosphorus and lying in *trans* positions in the PbS_4 unit), and oxygen atoms, respectively (structure **c**). This leads to eight-coordinated lead in a distorted square antiprism geometry. In $Pb[S_2P(OPr^i)_2]_2$ the polymer is built through intermolecular lead–sulfur contacts (secondary bonds), involving the sulfur atoms (doubly bonded to phosphorus) lying in *cis* positions of the basic planar PbS_4 units (structure **d**). In the resulting staggered arrangement both sulfur atoms involved in the intermolecular interactions occupy the axial positions of the pseudo-pentagonal bipyramidal geometry around each lead atom.

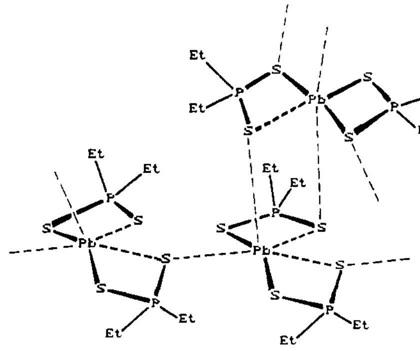
An uncommon feature of the polymeric structure of lead(II) diethyldithiophosphinate is the repeated sequence of trimeric units,



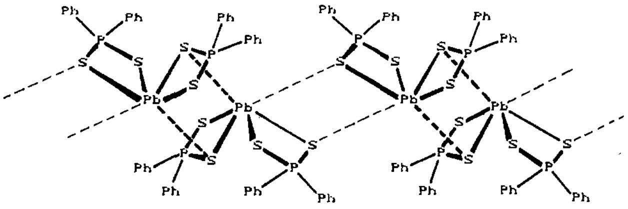
c



d



e



f

$[Pb(S_2PEt_2)_2]_3$, which contain three types of dithioligands: monometallic biconnective (chelating), bimetallic triconnective, and trimetallic tetraconnective (for terminology see ref 2) (structure e).

The polymeric structure of the title compound, $^{1}_{\infty}[Pb(S_2PPh_2)_2]$ is basically different from that observed for the related ethyl derivative, $Pb(S_2PEt_2)_2$, but has some similarities with those described for both lead(II) diethyl- and diisobutyldithiophosphates. It contains dimeric units as observed for $Pb[S_2P(OBu^i)_2]_2$, but they are linked in a polymeric chain through weak lead–sulfur intermolecular interactions like those in the ethoxy derivative. As a result, all the diphenyldithiophosphinato ligands display a bimetallic triconnective coordination pattern (structure f). The main differences in relation to the polymeric structure of $Pb[S_2P(OPr^i)_2]_2$ are the pyramidal arrangement of the PbS_4 fragment in the monomer, the *trans* position of the sulfur atoms (belonging to this fragment) involved in the intermolecular lead–sulfur contacts, and the *cis* position of the intermolecular Pb···S interactions in the polyhedron built around lead atoms.

Conclusions

The divalent lead is coordinatively unsaturated in its neutral derivatives of dithiophosphorus ligands; as a result additional secondary bonding interactions occur, leading to formation of supramolecular dimeric or polymeric structures. With different peripheric substituents at phosphorus, various structures are formed, and packing forces probably play a role in influencing the mode of association of the monomeric units. The unpredictable structural effects of a particular substituent at phosphorus suggest that structure determinations for other $Pb(S_2PR_2)_2$ derivatives with various R = alkyl, aryl, alkoxy, and aryloxy deserve further attention. In particular, the effect of very bulky (*e.g.* R = mesityl, pentafluorophenyl, etc.) or very small (*e.g.* R = methyl) substituents promises interesting results.

The case of lead(II) dithiophosphates and -phosphinates also suggests that the crystal structure determinations should not be limited at the stage of molecular unit analysis. They should be extended to the analysis of packing modes. It is likely that many supramolecular associations, like those discussed here for the lead compounds, have been ignored in the past, if the packing in the unit cell has not been studied.

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Supplementary Material Available: Tables giving crystal data, data collection, parameters, and solution and refinement data, bond lengths, bond angles, H-atom coordinates and isotropic displacement coefficents, and anisotropic displacement coefficients (7 pages). Ordering information is given on any current masthead page.