



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu,
a devoted and talented scientist and a good friend*

SUPRAMOLECULAR SELF-ASSEMBLY IN THE LEAD(II) BIS(DI-*ISO*-BUTYLDITHIOPHOSPHATE). 1,10-PHENANTHROLINE ADDUCT, $\text{Pb}[\text{S}_2\text{P}(\text{O}i\text{Bu})_2]_2 \cdot \text{Phen}$

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Received March 18, 2010

The adduct of lead(II) bis(di-*iso*-butyldithiophosphate) and 1,10-phenanthroline is a centrosymmetric dimeric supermolecule formed through Pb \cdots S secondary interactions. In the monomeric building unit the metal center is six-coordinate (with two nitrogen atoms from 1,10-phenanthroline and four sulphur atoms from two different dithiophosphato ligands). In the dimer two additional secondary bonds from lead(II) to sulphur atoms of a second lead(II) dithiophosphato unit raises the coordination number of lead which becomes eight-coordinated. The ligand displays a dimetallic tetraconnective coordination mode. In the crystal the dimers are further interconnected into a bidimensional supramolecular structure through weak S \cdots H-C and O \cdots H-C bonds between the sulphur and oxygen atoms of a dithiophosphato ligand and 1,10-phenanthroline hydrogen atoms from different units.

INTRODUCTION

Information about the lead coordination patterns in sulfur-rich environments is important for understanding the mechanisms of lead poisoning, which is believed to be due to interactions of Pb(II) with the thiol binding sites of certain proteins.¹ This explains in part the recent interest for the structural chemistry of lead-thiolates and related compounds.²

In lead(II) sulfur compounds there is a general tendency of self-assembly leading to formation of supermolecules (*i.e.* "well defined oligomolecular species that result from the intermolecular association of a few components") or supramolecular arrays (*i.e.* "polymolecular systems that result from the spontaneous association of a non-defined

number of components").^{3,4} This most frequently occurs through Pb \cdots S secondary bonds^{5,6} or closed-shell interactions,⁷ characterized by interatomic distances intermediate between the sum of covalent radii (Pb-S 2.44 Å) and the sum of van der Waals radii (Pb \cdots S 4.15 Å).⁸ This tendency is observed in lead(II) thiolates, Pb(SR)₂, with structures strongly dependent on the nature of the R group, ranging from monomolecular to dimeric and polymeric.⁹

The lead(II) dithiophosphates, Pb[S₂P(OR)₂]₂, combine the coordination versatility of lead(II) which can display coordination numbers from two to eight,² with the remarkable diversity of coordination patterns exhibited by the dithiophosphato ligands.¹⁰ Their structural chemistry is somewhat surprising, since X-ray diffraction investigations show that by varying the remote organic group R different coordination

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geometries and/or patterns of supramolecular self-assembly are produced.¹¹ So far, compounds with R = Me (chain),¹² Et (chain),¹³ *iso*-Pr (chain),¹⁴ *n*-Pr (chain),¹⁵ *iso*-Bu (dimer),¹⁶ *cyclo*-C₆H₁₁ (chain)¹⁵ Ph (dimer).¹⁶ Surprisingly, very few nitrogen donor adducts of lead(II) dithiophosphates have been structurally characterized, *i.e.* Pb[S₂P(OEt)₂]₂.bipy and Pb[S₂P(OEt)₂]₂.en (en = ethylenediamine),¹⁷ and they are both dimeric. Lead(II) dithiophosphinates, Pb(S₂PR₂)₂, are also associated in solid state, to form supramolecular arrays, as shown by X-ray diffraction analyses of the compounds with R = Me,¹⁸ Et¹⁹ and Ph.²⁰ Lead(II) dithiocarbamates, Pb(S₂CNR₂)₂²¹ and xanthes, Pb(S₂COR)₂²² also exhibit interesting supramolecular self-assembly through Pb⋯S secondary bonds. Lead(II) dithiophosphonates, Pb[S₂P(OR)C₆H₄Me-4]₂ with R = Et and *iso*-Pr²³ underscore the structural diversity of lead(II) derivatives with dithio ligands: in the compound with R = Et addition Pb⋯π-aryl interactions are present, whereas the derivative with R = *iso*-Pr displays a polymeric structure containing eight-membered Pb₂S₄P₂ rings.

We report here the structure of a lead(II) dithiophosphate.1,10-phenantroline adduct, Pb[S₂P(OBu^t)₂]₂.Phen, which is self-assembled into dimeric supermolecules through Pb⋯S secondary interactions; the dimers are further associated into a bidimensional supramolecular array through O⋯H-C and S⋯H-C weak hydrogen bonds.

RESULTS AND DISCUSSION

The title compound was obtained from the reaction of lead(II) acetate with potassium di-*iso*-butyldithiophosphate and 1,10-phenantroline. The complex is air and light stable and is soluble in methanol and CDCl₃. The FT-IR spectra of potassium di-*iso*-butyldithiophosphate and Pb[S₂P(OBu^t)₂]₂.phen, recorded in potassium bromide pellets in 4000-400 cm⁻¹ were compared and bands associated with PS₂, (P)-O-C and P-O-(C) stretching vibrations have been identified. The title compound shows the symmetric and antisymmetric stretching modes for the PS₂ group (ν_{as}(PS₂) 673m, ν_s(PS₂) 592s, 559s). The ¹H, ¹³C and ³¹P NMR data confirm the identity of the products; they show no unusual features (see Experimental).

The X-ray analysis of Pb[S₂P(OBu^t)₂]₂.Phen reveals a centrosymmetric dimeric supermolecule,

formed by association through Pb⋯S secondary bonds. Because of the dimerization the two dithiophosphato ligands coordinated to lead are non-equivalent: the P1 ligand is terminal, bidentate chelating (monometallic monoconnective),¹¹ while the P2 ligand is bridging (bimetallic tetraconnective). Selected bond lengths and angles are listed in Table 1.

In the monomeric building unit the lead atom is six-coordinated by four sulphur atoms from two chelating dithiophosphates ligands and two nitrogen atoms from 1,10-phenantroline (Fig. 1a). In the terminal P1-based ligand the bond lengths are: Pb1-S1 3.0026(11) Å, Pb-S2 2.8946(11) Å, indicating that the dithiophosphato ligand is slightly anisobidentate, though this is not evident in the associated P-S bonds [P1-S1, 1.9783(16) Å, P1-S2 1.9770(16) Å]. In the second, bridging dithiophosphato ligand, based on P2, the lead-sulfur distances in the four-membered chelate ring are slightly longer: Pb1-S3 3.1676(12) Å, Pb1-S4 3.1364(12) Å, probably due to the participation of sulfur atoms S3 and S4 in additional interactions with Pb1'. In the bridging ligand the P-S bonds are less symmetrical and are slightly shorter than in the terminal chelating ligand: P2-S3 1.9472(16) Å, P2-S4 1.9606(15) Å.

The dimerization occurs through two Pb⋯S secondary bonds between S3 and S4 and the Pb1' center (Fig. 1b). The interatomic distances to Pb1' are: Pb1'-S3 3.6402(18) Å, Pb1'-S4 3.6684(13) Å. Both are shorter than the sum of van der Waals radii of lead and sulfur, 4.15 Å. It is noted that the Pb⋯S secondary bonds connecting the monomeric units are longer (and thus weaker) than the Pb-S bonds (Pb1-S3 and Pb1-S4) within the monomeric building unit (Fig. 2). The P-S bonds in general are somewhat less than the 2.0 Å generally observed for P-S single bonds,¹¹ suggesting some degree of delocalization of π-bonding across the S-P-S unit.

The coordination number of lead in the dimer is eight, if the secondary bonds leading to dimerization are considered. The eight-coordinate geometry is difficult to characterize because of the irregular values of the bond angles but approximates to a distorted dodecahedron (Fig 1c). Each monomer can be described as pentagonal pyramidal in geometry, with any stereochemically-active lone pair located trans to the apical N2 atom; N1, S1 – S4 make up the equatorial belt. On dimerization, two additional donors are added below the pentagonal plane (S3', S4'), causing atoms in that plane to move upwards; as a result,

angles between apical N2 and the pentagonal plane lie in the range to *ca.* 76.25(8) – 90.74(8)°, though the \angle N1-Pb1-N2 is smaller [65.50(10)°] as a result of the restricted bite angle of the 1,10-phenanthroline ligand. The coordination pattern of

the bridging ligand can be described as unsymmetrical bimetallic tetraconnective,¹¹ as shown schematically in Fig. 2. This is a rare if not unique coordination pattern in metal dialkyl(aryl)dithiophosphato complexes.¹⁰

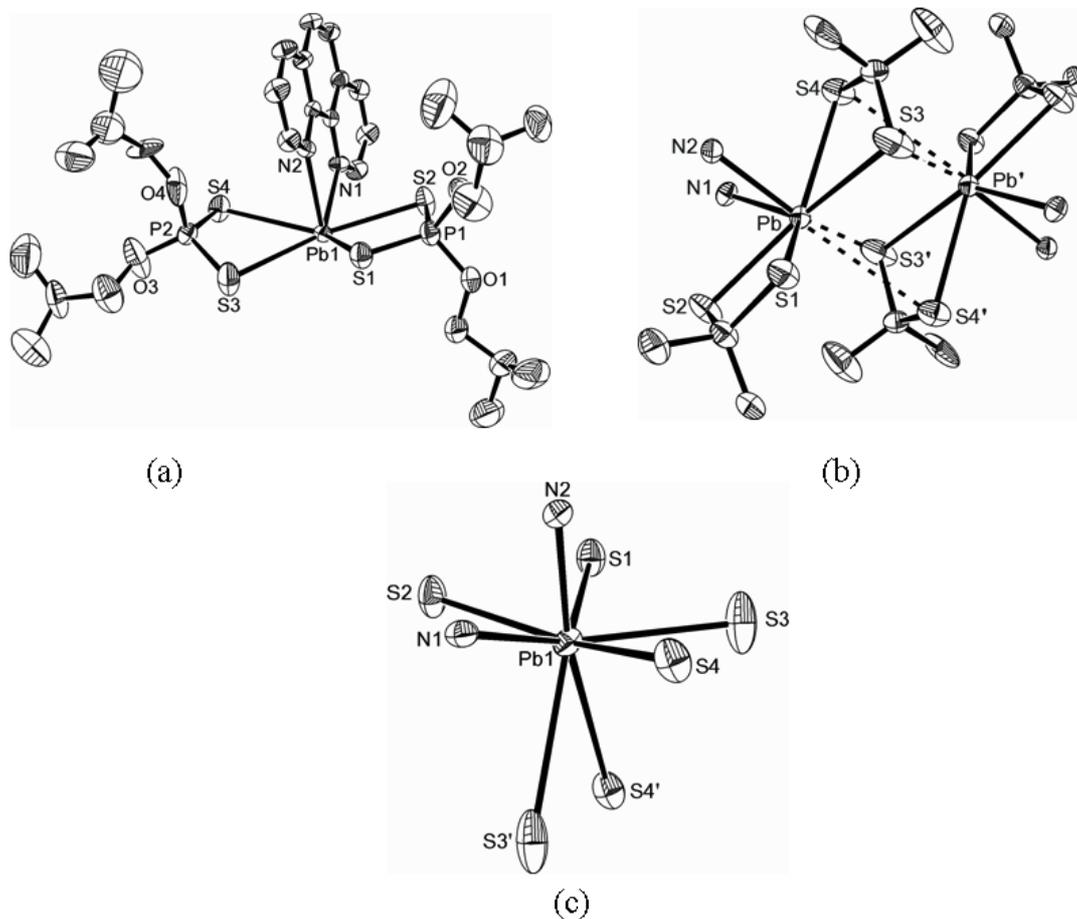


Fig. 1 – The molecular structure of $\text{Pb}[\text{S}_2\text{P}(\text{O}^i\text{Bu})_2]_2\text{.phen}$, showing (a) the monomeric building unit (only the major component of the disordered ^iBu group bonded to O4 is shown for clarity); (b) the association of the monomeric units into a dimeric supermolecule (key ligating atoms only) and (c) the coordination sphere about lead (symmetry operation: 2-x, -y, -z).

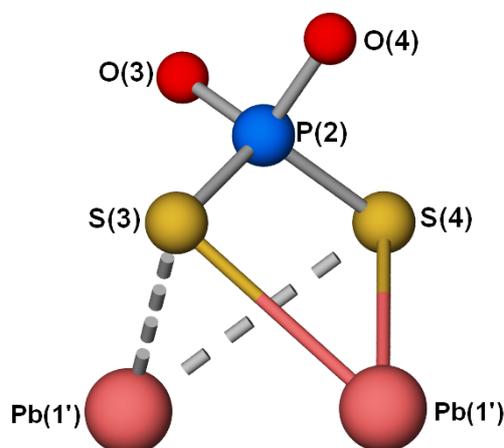


Fig. 2 – The coordination pattern of the bridging P2 ligand; geometric data: Pb1-S3 3.1676(12), Pb1-S4 3.1364(12), Pb1'-S3 3.6404(18), Pb1'-S4 3.6684(13) Å.

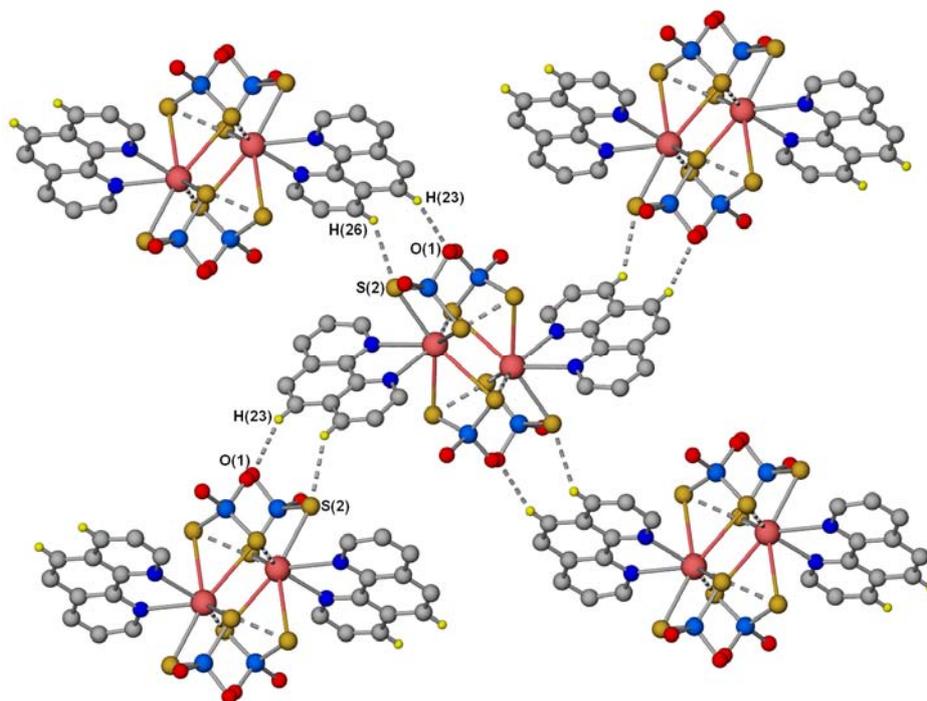
Fig. 3 – Supramolecular structure of $\text{Pb}[\text{S}_2\text{P}(\text{OBu}^i)_2]_2\cdot\text{Phen}$.

Table 1

Selected bond lengths (Å) and angles (deg) for $\text{Pb}[\text{S}_2\text{P}(\text{OBu}^i)_2]_2\cdot\text{Phen}$

Pb(1)-S(1)	3.0026(11)	Pb(1)-N(1)	2.612(3)
Pb(1)-S(2)	2.8946(11)	Pb(1)-N(2)	2.483(3)
Pb(1)-S(3)	3.1676(12)	S(1)-P(1)	1.9783(16)
Pb(1)-S(4)	3.1364(12)	S(2)-P(1)	1.9770(16)
Pb(1)(1)-S(3')	3.6404(18)	S(3)-P(2)	1.9472(16)
Pb(1)(1)-S(4')	3.6684(13)	S(4)-P(2)	1.9606(15)
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S(1)-Pb(1)-S(2)	68.50(3)	S(2)-Pb(1)-N(2)	81.78(8)
S(1)-Pb(1)-S(3)	72.92(3)	S(3)-Pb(1)-S(4)	63.46(3)
S(1)-Pb(1)-S(4)	130.93(3)	S(3)-Pb(1)-N(1)	137.90(7)
S(1)-Pb(1)-N(1)	132.45(7)	S(3)-Pb(1)-N(2)	90.74(8)
S(1)-Pb(1)-N(2)	83.20(8)	S(4)-Pb(1)-N(1)	76.88(8)
S(2)-Pb(1)-S(3)	141.28(3)	S(4)-Pb(1)-N(2)	76.25(8)
S(2)-Pb(1)-S(4)	147.40(3)	N(1)-Pb(1)-N(2)	65.50(10)
S(2)-Pb(1)-N(1)	72.17(8)	S(3')Pb(1)-S(4')	53.95(3)

Symmetry operation: $-x+2, -y, -z$

The bonds lengths between 1,10-phenanthroline nitrogen atoms and lead atom are different (Pb1-N2 2.483(3) Å and Pb1-N1 2.612(3) Å) in the same chelate ring. These values agree¹¹ with the Pb-N interatomic distances observed in $\text{Pb}[\text{S}_2\text{P}(\text{OEt})_2]_2\cdot\text{bipy}$ (which is also dimeric).¹⁷ Other lead-nitrogen distances reported in lead(II) dithiolate adducts with related nitrogen bases are longer than those observed in our compound: Pb-N 2.695(3) and 2.689(3) Å in monomeric $\text{Pb}(\text{SC}_6\text{H}_3\text{Me}_2-2,6)_2\cdot 2\text{Py}$; Pb-N 2.652(7)-2.814(7) Å in supramolecular chain-like $\text{Pb}(\text{SC}_6\text{H}_3\text{Me}_2-$

2,6)₂·1,4-Bipy; Pb-N 2.614(9) Å in supramolecular chain-like $\text{Pb}(\text{SC}_6\text{H}_3\text{Me}_2-2,6)_2\cdot\text{Pyrazine}$ (also containing $\text{Pb}\cdots\text{S}$ 3.743(3) Å secondary bonds); Pb-N 2.842(5) Å in supramolecular $2\text{Pb}(\text{SPh})_2\cdot\text{Py}$ (also containing $\text{Pb}\cdots\text{S}$ 3.422(1) and 3.212(2) Å secondary bonds).⁹

The dimeric supermolecules of $\text{Pb}[\text{S}_2\text{P}(\text{OBu}^i)_2]_2\cdot\text{Phen}$ are further self-assembled in a bidimensional supramolecular structure, by weak hydrogen bonds ($\text{O}(1)\cdots\text{H}(23)-\text{C}(23)$ 2.535 Å, $\angle\text{O}(1)\cdots\text{H}(23)-\text{C}(23)$ 158.57°; $\text{S}(2)\cdots\text{H}(26)-\text{C}(26)$ 2.851 Å, $\angle\text{S}(2)\cdots\text{H}(26)-\text{C}(26)$ 142.88°) between

1,10-phenantroline hydrogens with oxygen and sulphur atoms from the dithiophosphato ligand of different dimeric units, resulting in the formation of a bidimensional supramolecular structure (Fig. 3).

In Table 2 are listed the details of X-ray crystallographic analysis of $\text{Pb}[\text{S}_2\text{P}(\text{O}i\text{Bu})_2]_2\cdot\text{Phen}$.

Table 2

Crystal data for $\text{Pb}[\text{S}_2\text{P}(\text{O}i\text{Bu})_2]_2\cdot\text{Phen}$

Empirical formula	$\text{C}_{28}\text{H}_{44}\text{N}_2\text{O}_4\text{P}_2\text{PbS}_4$
Formula weight	870.02
Crystal system	Monoclinic
Space group	$\text{P}2_1/\text{n}$
a (Å)	10.5110(1)
b (Å)	16.0860(2)
c (Å)	21.3810(3)
β (°)	92.572(1)
V (Å ³)	3611.46(8) Agst@3
Z	4
Calculated density (mgm ³)	1.600
$\mu(\text{Mo-K}\alpha)$ (mm ⁻¹)	5.025
$F(000)$	1736
Crystal size (mm)	0.40 x 0.30 x 0.30
Theta range for data collection (°)	3.82 to 27.49.
Reflections collected	46412
Independent reflections	8267 [R(int) = 0.0738]
Reflections observed (>2 σ)	6476
Max. and min. transmission	0.3140 and 0.2384
Goodness-of-fit on F^2	1.025
Final R_1 w R_2 indices [$I > 2\sigma(I)$]	0.0338, 0.0748
R_1 w R_2 indices (all data)	0.0533, 0.0809
Largest diff. peak and hole (eÅ ³)	1.510, -1.375

EXPERIMENTAL

Lead(II) acetate, potassium di-*iso*-butyldithiophosphate, 1,10-phenantroline were commercial products. IR spectra were recorded on a FT-IR JASCO 615 apparatus in potassium bromide pellets. The NMR spectra were recorded on a Bruker instrument in saturated CDCl_3 solutions at room temperature. All chemicals were used without further purification. Experimental details relating to the single-crystal X-ray crystallographic studies are summarized in Table 2. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were refined using full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions. A semi-empirical absorption correction was applied to the data. One of the *iso*-butyl groups showed disorder in the ratio 1:1 and two others had to be restrained during refinement.

Synthesis of $\text{Pb}[\text{S}_2\text{P}(\text{O}i\text{Bu})_2]_2\cdot\text{Phen}$

Lead(II) acetate (0.2g, 0.62mmol) was dissolved in 10ml methanol and stirred for ½ hours with potassium di-*iso*-butyldithiophosphate (0.12g, 0.43mmol); after another 2 hours of continuous stirring at room temperature, a solution of 1,10-phenantroline (0.05g, 0.28mmol) in 10ml methanol was added. The white precipitate was filtered off and the colorless solution was concentrated to give white crystals, yield 60%. M.p. = 90°C.

FT-IR (cm⁻¹): $\nu_{\text{as}}(\text{PS}_2)$ 673m, $\nu_{\text{s}}(\text{PS}_2)$ 592s, 559s, $\nu(\text{P-OC})$ 908s, 950m, $\nu(\text{PO-C})$ 1002w.

NMR data: ¹H: 0.85 (12H, d CH₃), 1.90 (2H, m CH), 3.70 (4H, dd, CH₂), aromatic hydrogens of 1,10-phenanthroline (7.84, dd; 7.92, s; 8.45, dd; 9.71, dd); ¹³C: 19.0 (CH₃), 28.7 (CH), 72.3 (CH₂), 124.5, 127.3, 130.1, 138.0, 145.3, 151.0 (aromatic carbons of 1,10-phenanthroline); ³¹P: 100.7 (m, PS₂), $J_{\text{P-H}} = 8.52$ Hz).

Supporting Information

Crystallographic data for the structural analysis (in CIF format) have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 765448. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgment: The authors are grateful to Cheminova Agro A/S Denmark for providing a research sample of potassium dithiophosphate. We also thank to Prof. Julio Zukerman-Schpector from Departamento de Quimica, Universidade Federal de São Carlos, Brazil, for helpful discussions.

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