



Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary

HYPERVALENT TRIORGANOLEAD(IV) DITHIOCARBAMATES
CONTAINING A 2-(Me₂NCH₂)C₆H₄ GROUP.
CRYSTAL AND MOLECULAR STRUCTURE
OF [2-(Me₂NCH₂)C₆H₄]Ph₂PbS(S)CNR₂ (R = Me, Et)

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Two new triorganolead(IV) dithiocarbamates, [2-(Me₂NCH₂)C₆H₄]Ph₂PbS(S)CNR₂ [R = Me (**1**), Et (**2**)] were prepared by reacting [2-(Me₂NCH₂)C₆H₄]Ph₂PbI with the corresponding sodium dithio ligand. Both compounds were characterized by multinuclear NMR solution studies and their crystal and molecular structure was established by single-crystal X-ray diffraction. In both cases the nitrogen atom from the pendant Me₂NCH₂ arm is coordinated intramolecularly to the metal centre [Pb(1)-N(1) 2.788(5) Å in **1** and 2.764(11) Å in **2**, respectively] in *trans* to a sulfur atom [S(1)-Pb(1)-N(1) 168.89(10)° in **1** and 170.3(2)° in **2**, respectively]. This results in a distorted trigonal bipyramidal geometry around the lead atom of hypervalent 10-*Pb*-5 species. Compounds **1** and **2** crystallize as 1:1 mixtures of *R*_{N1}- and *S*_{N1}-isomers (planar chirality induced by the non-planar PbC₃N chelate ring). In the crystals weak intermolecular S...H and C-H...π (Ph_{centroid}) contacts result in different supramolecular architectures.

INTRODUCTION

Aromatic ligands with one pendant arm containing nitrogen as donor atom, such as 2-(Me₂NCH₂)C₆H₄ or related derivatives, have been sparingly used in organolead chemistry¹⁻⁶ in high contrast to the organotin chemistry.⁷⁻³⁰ One lead(II) compound, [2-(Me₂NCH₂)C₆H₄]₂Pb,¹ and few organolead(IV) derivatives, *i.e.* the homoleptic [2-(Me₂NCH₂)C₆H₄]₄Pb,¹ and heteroleptic [2-(R₂NCH₂)C₆H₄]₂R'₂Pb [R = Me, R' = Me, Ph; R = Et, R' = Ph],² the chloride [2-(Me₂NCH₂)C₆H₄]Ph₂PbCl,² and the iodides [2-(Me₂NCH₂)C₆H₄](4-MeC₆H₄)₂PbI,³ [2-(Me₂NCH₂)C₆H₄](4-MeC₆H₄)(4-MeOC₆H₄)PbI,^{3,4} and [2-(R₂NCH₂)C₆H₄]Ph₂PbI [R = Me, Et]² were described so far and for some compounds the molecular structure was established by single-crystal X-ray diffraction. Some related

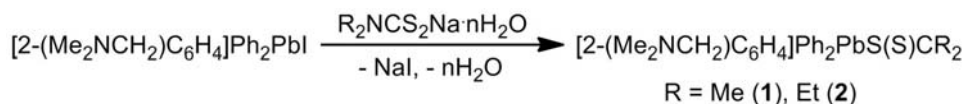
derivatives, *i.e.* [CpFe{C₅H₃(CH₂NMe₂)-2}]₂Pb,⁵ and [CpFe{C₅H₃(CH₂NMe₂)-2}]₂PbM(CO)₅ (M = Cr, Mo, W),⁶ were also recently described.

We report here on the synthesis, the solution behavior as well as the molecular structure of two new triorganolead(IV) dithiocarbamates, [2-(Me₂NCH₂)C₆H₄]Ph₂PbS(S)CNR₂ [R = Me (**1**), Et (**2**)].

RESULTS

The triorganolead(IV) dithiocarbamates, *i.e.* [2-(Me₂NCH₂)C₆H₄]Ph₂PbS(S)CNR₂ [R = Me (**1**), Et (**2**)], were prepared by metathesis reaction between the iodide [2-(Me₂NCH₂)C₆H₄]Ph₂PbI and the corresponding sodium dithiocarbamate hydrate, in chloroform (Scheme 1).

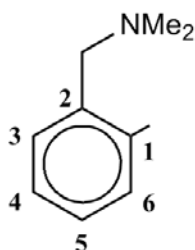
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Scheme 1

Details of the preparations are given in the Experimental section. The compounds were isolated as colourless crystals after recrystallization from a CH_2Cl_2 /hexane mixture. Both compounds exhibit a good solubility in chloroform.

The dithiocarbamates **1** and **2** were characterized by multinuclear (^1H , ^{13}C) NMR spectroscopy, including 2D experiments used to assigned the observed resonances according to the numbering scheme shown in Scheme 2. The solution NMR spectra of the isolated products, recorded in CDCl_3 , are consistent with the formation of the title compounds.



Scheme 2

The ^1H and ^{13}C NMR spectra for **1** and **2** showed the expected resonances in the alkyl as well as in the aryl regions for the organic groups attached to the lead atom and the dithiocarbamate moiety, respectively. For many aromatic resonances the satellites corresponding to lead-proton and lead-carbon couplings, respectively, were also observed.

Single crystals of **1** and **2** were grown from a CH_2Cl_2 /n-hexane mixture using the slow diffusion technique and the molecular structures were established by X-ray diffraction studies. The crystals of both compounds contain discrete monomers, with no unusual intermolecular distances shorter than the sum of the van der Waals radii between heavy atoms. Selected bond distances and angles are listed in Table 1. Figs. 1 and 2 show the ORTEP-like view of the molecular structure of **1** and **2**, respectively, with the atom numbering scheme.

Table 1

Selected interatomic distances (Å) and angles (deg) in $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Ph}_2\text{PbS(S)CNR}_2$ [R = Me (**1**), Et (**2**)]

1		2	
Pb(1)–C(1)	2.170(5)	Pb(1)–C(1)	2.193(11)
Pb(1)–C(10)	2.208(6)	Pb(1)–C(10)	2.225(11)
Pb(1)–C(16)	2.181(5)	Pb(1)–C(16)	2.193(12)
Pb(1)–S(1)	2.6334(18)	Pb(1)–S(1)	2.638(3)
Pb(1)–S(2)	3.372(2)	Pb(1)–S(2)	3.295(3)
Pb(1)–N(1)	2.788(5)	Pb(1)–N(1)	2.764(11)
C(22)–S(1)	1.742(7)	C(22)–S(1)	1.767(13)
C(22)–S(2)	1.663(6)	C(22)–S(2)	1.641(15)
C(22)–N(2)	1.328(7)	C(22)–N(2)	1.338(17)
C(23)–N(2)	1.445(8)	C(23)–N(2)	1.478(16)
C(24)–N(2)	1.441(9)	C(25)–N(2)	1.479(17)
C(1)–Pb(1)–C(10)	112.3(2)	C(1)–Pb(1)–C(10)	111.0(4)
C(1)–Pb(1)–C(16)	130.0(2)	C(1)–Pb(1)–C(16)	130.5(5)
C(10)–Pb(1)–C(16)	111.7(2)	C(10)–Pb(1)–C(16)	110.7(5)
S(1)–Pb(1)–C(1)	100.94(16)	S(1)–Pb(1)–C(1)	100.9(3)
S(1)–Pb(1)–C(10)	88.52(18)	S(1)–Pb(1)–C(10)	90.1(3)
S(1)–Pb(1)–C(16)	102.77(14)	S(1)–Pb(1)–C(16)	104.6(3)
S(1)–Pb(1)–N(1)	168.89(10)	S(1)–Pb(1)–N(1)	170.3(2)
N(1)–Pb(1)–C(1)	70.21(18)	N(1)–Pb(1)–C(1)	70.9(4)
N(1)–Pb(1)–C(10)	88.8(2)	N(1)–Pb(1)–C(10)	88.1(4)
N(1)–Pb(1)–C(16)	88.24(17)	N(1)–Pb(1)–C(16)	84.9(4)
S(2)–Pb(1)–C(1)	77.6(2)	S(2)–Pb(1)–C(1)	78.4(3)
S(2)–Pb(1)–C(10)	146.3(2)	S(2)–Pb(1)–C(10)	149.0(3)

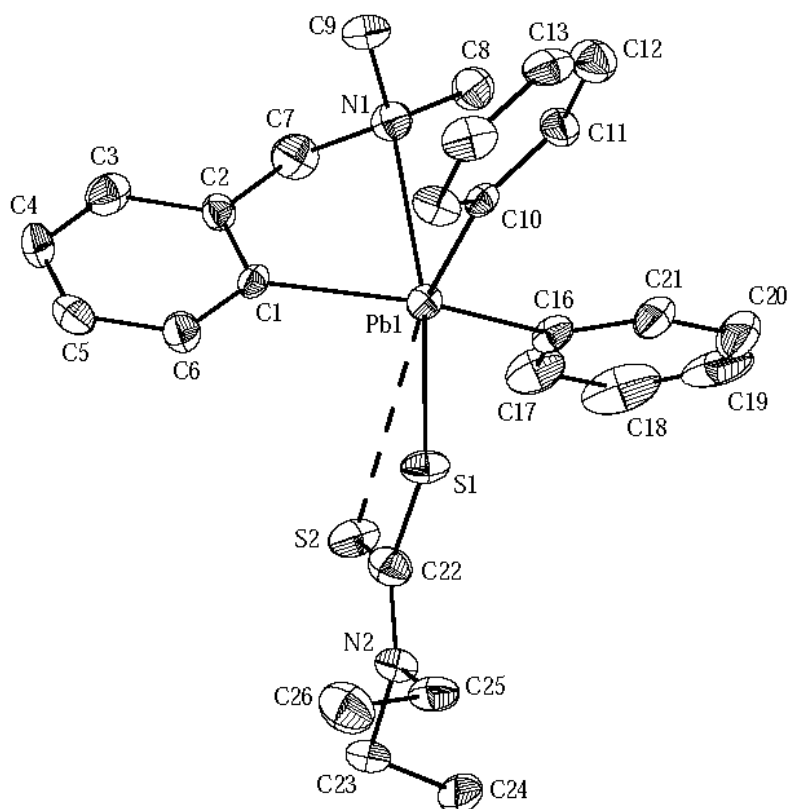


Fig. 2 – ORTEP representation at 20% probability and atom numbering scheme for R_N -2 isomer. Hydrogen atoms are omitted for clarity.

DISCUSSION

Solution behavior

The NMR (^1H , ^{13}C) spectra of compounds **1** and **2** are very similar with respect to the $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Ph}_2\text{Pb}$ moiety, showing the expected resonances in the alkyl and the aryl regions. The ^1H spectra for both compounds exhibit in the alkyl region singlet resonances for NMe_2 and CH_2 protons of the pendant arm, respectively, with the latter surrounded by lead satellites for **2**. The ^{13}C spectra contain only one set of four resonances for the phenyl groups attached to lead in **1** and **2**, respectively, thus indicating their equivalence in solution. The unambiguous assignment of the ^{13}C resonance signals for both compounds was based on the 2D correlation spectra and carbon-lead coupling constants, respectively. The magnitude of the lead-proton coupling constants for the *ortho* protons of the phenyl groups [δ 7.88 ppm, $^3J_{\text{PbH}} = 108.0$ Hz for **1**; δ 7.89 ppm, $^3J_{\text{PbH}} = 107.4$ Hz for **2**] and for the protons H_6 of the pendant arm aromatic group [δ 8.49 ppm, $^3J_{\text{PbH}} = 127.9$ Hz for **1**; δ 8.48 ppm, $^3J_{\text{PbH}} = 129.1$ Hz for **2**] are indicative for the presence of a triaryllead(IV) moiety.

The solution NMR spectra of the triorganolead(IV) dithiocarbamates **1** and **2** suggest that these compounds might have (i) a similar structure in solution as found in solid state (see subsequent discussion), *i.e.* trigonal bipyramidal (C_3N) C_2PbS core due to the intramolecular $\text{N} \rightarrow \text{Pb}$ interaction (assuming a fast conformational change in solution for the nonplanar, five-membered PbC_3N chelate ring, which gives averaged ^1H NMR signals), or, alternatively, (ii) a tetrahedral geometry around the lead atom (C_3PbS core) which will assume the lack of intramolecular coordination in solution.

Solid state structure

The molecules of both dithiocarbamates **1** (Fig. 1) and **2** (Fig. 2) contain the dithiocarbamate unit strongly attached to lead through one sulfur atom [$\text{Pb}(1)\text{--S}(1)$ 2.6334(18) Å for **1**; 2.638(3) Å for **2**], while the second sulfur atom of the dithio ligand moiety is involved only in a weak interaction to the metal centre [$\text{Pb}(1)\text{--S}(2)$ 3.372(2) Å for **1**; 3.295(3) Å for **2**; *c.f.* the sum of the corresponding van der Waals radii, $\Sigma r_{\text{vdW}}(\text{Pb}, \text{S})$ 3.85 Å].³¹ A similar coordination behavior was reported for the related triaryllead(IV) derivative $\text{Ph}_3\text{PbS}(\text{S})\text{CN}$

$(\text{CH}_2)_4 [\text{Pb}-\text{S} 2.56(1) / 3.26(1) \text{ \AA}]$.³² The asymmetry in the length of the lead-sulfur interatomic distances is reflected in the length of the carbon-sulfur bonds within a dithiocarbamato unit, *i.e.* the shorter, covalent Pb–S bond is associated with the longer, single C–S bond [C(22)–S(1) 1.742(7) for **1**; 1.767(13) Å for **2**], while the longer, weak S→Pb interaction is associated with the shorter, presumably double, C=S bond [C(22)–S(2) 1.663(6) for **1**; 1.641(15) Å for **2**].

In both cases the molecules exhibit a strong intramolecular N→Pb interaction placed *trans* to the sulfur atom of the dithiocarbamato ligand attached covalently to lead atom [S(1)–Pb(1)–N(1) 168.89(10)° for **1**; 170.3(2)° for **2**]. The lead-nitrogen interatomic distances [Pb(1)–N(1) 2.788(5) Å for **1**; 2.764(11) Å for **2**; *c.f.* $\Sigma r_{\text{vdW}}(\text{Pb}, \text{N}) 3.54 \text{ \AA}$ ³¹] are longer than those observed for [2-(Me₂NCH₂)C₆H₄]₂Ph₂PbCl [Pb–N 2.636(8) and 2.646(9) Å for the two independent, very similar, molecules which are present in the unit cell] or the related chiral iodide, [2-(Me₂NCH₂)C₆H₄](4-MeC₆H₄)(4-MeOC₆H₄)PbI [Pb–N 2.686(8) Å].⁴ Taking into account the covalent bonds at the metal centre and the strong intramolecular N→Pb interaction the overall geometry at the lead atom is distorted trigonal bipyramidal [(C,N)₂PbS core], with the axial positions occupied by the nitrogen and the sulfur atoms, while the aromatic carbon atoms are in the equatorial positions. If the weak lead-sulfur interaction which involves the second sulfur atom of the dithio ligand moiety is considered, the overall coordination geometry can be described as capped-trigonal bipyramidal, with this sulfur atom in the capping position.

The NCCCPb chelate ring is not planar, the nitrogen atom being out of the plane defined by the remaining C₃Pb unit. This results in planar chirality [with C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively]³³ and the crystals of both compounds **1** and **2** consist of a 1:1 mixture of *R_N* and *S_N* isomers separated by normal van der Waals distances between heavy atoms. However, a closer check of the crystal structures revealed weak intermolecular S⋯H interactions as well as C–H⋯π (Ph_{centroid}) distances which suggest some π interaction between a hydrogen atom and an aromatic ring (*i.e.* H⋯Ph_{centroid} contacts shorter than 3.1 Å, with an angle γ between the normal to the phenyl ring and the line defined by the H atom and Ph_{centroid} smaller than 30°). Thus, for **1** pairs of *R_N* and *S_N* isomers are held together by S⋯H_{aryl} [S(2a)⋯H(21) 2.91 Å; *c.f.* $\Sigma r_{\text{vdW}}(\text{S}, \text{H}) 3.05 \text{ \AA}$ ³¹] and C–H_{aryl}⋯π (Ph_{centroid}) [C(20)–H(20)⋯Ph_{centroid}{C(1a)–C(6a)} 2.70 Å, γ = 6.3°] interactions (Fig. 3). Such dimers are further associated through C–H_{aryl}⋯π (Ph_{centroid}) interactions [C(5)–H(5)⋯Ph_{centroid}{C(16')–C(21')} 2.85 Å, γ = 10.6°] into ribbon-like chain polymers which are developed along axis *b* (Fig. 4). Layers are built subsequently from parallel chains linked by C–H_{methyl}⋯π (Ph_{centroid}) interactions [C(23)–H(23B)⋯Ph_{centroid}{C(27)–C(32)} 2.92 Å, γ = 11.3°]. By contrast, the crystal of **2** contains only intermolecular S⋯H_{aryl} interactions which involves the sulfur atom doubly bonded in the dithiocarbamato moiety. Thus, alternating *R_N* and *S_N* isomers are connected through S(2)⋯H(12b) (2.86 Å) into polymeric chains developed along axis *a* (Fig. 5) which consequently are associated into a layer through inter-chain S(2)⋯H(18') (2.90 Å) interactions (Fig. 6).

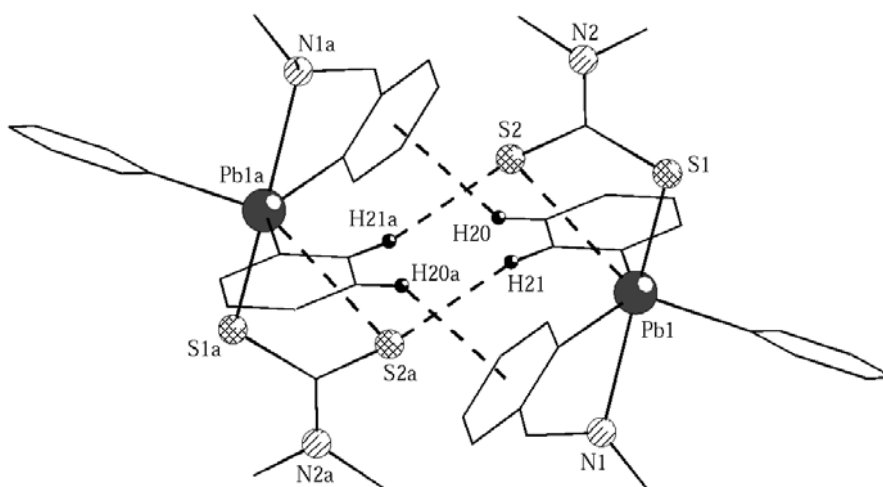


Fig. 3 – View of the dimer association of *R_N* and *S_N* isomers in the crystal of **1** based on intermolecular S⋯H and C–H⋯π (Ph_{centroid}) interactions (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms (–*x*, 1 – *y*, 1 – *z*) are given by “a”].

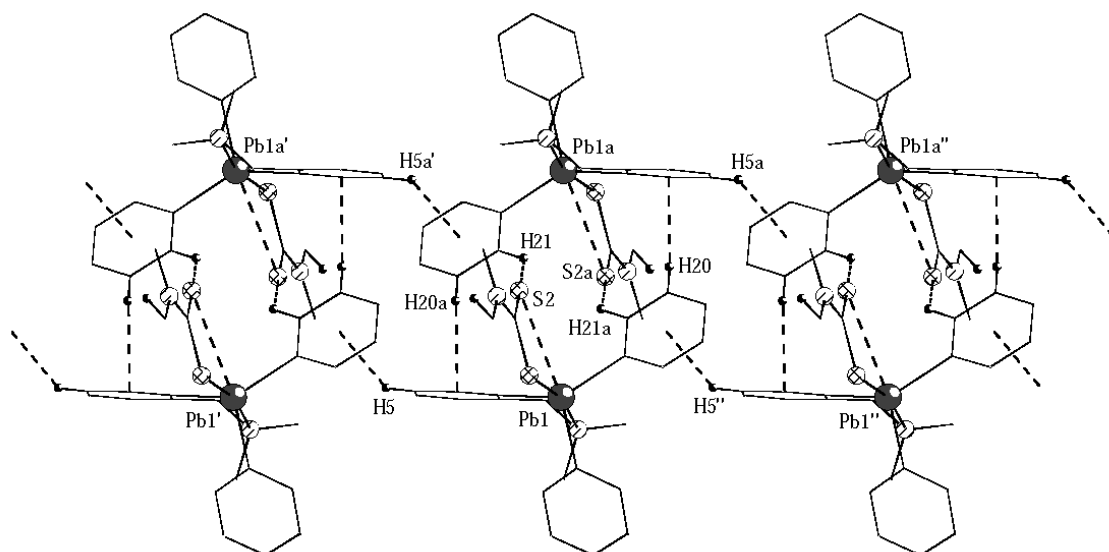


Fig. 4 – View of the polymeric ribbon-like association along axis *b* in the crystal of **1** based on intermolecular C–H \cdots π ($\text{Ph}_{\text{centroid}}$) interactions between R_N / S_N dimers (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms $(-x, 1-y, 1-z)$, $(-1+x, y, z)$, $(-1-x, 1-y, 1-z)$, $(1+x, y, z)$ and $(1-x, 1-y, 1-z)$ are given by “a”, “prime”, “prime a”, “double prime” and “double prime a”].

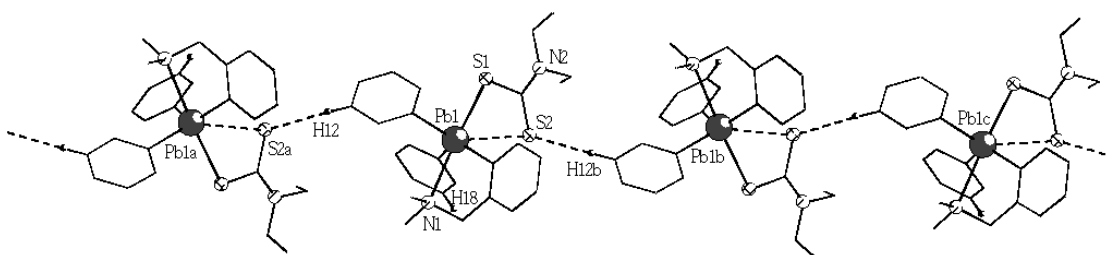


Fig. 5 – View of the chain polymeric association along axis *a* in the crystal of **2** based on intermolecular S \cdots H interactions between alternating R_N and S_N isomers (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms $(0.5+x, 0.5-y, 0.5+z)$, $(-0.5+x, 0.5-y, -0.5+z)$ and $(-1+x, y, -1+z)$ are given by “a”, “b” and “c”].

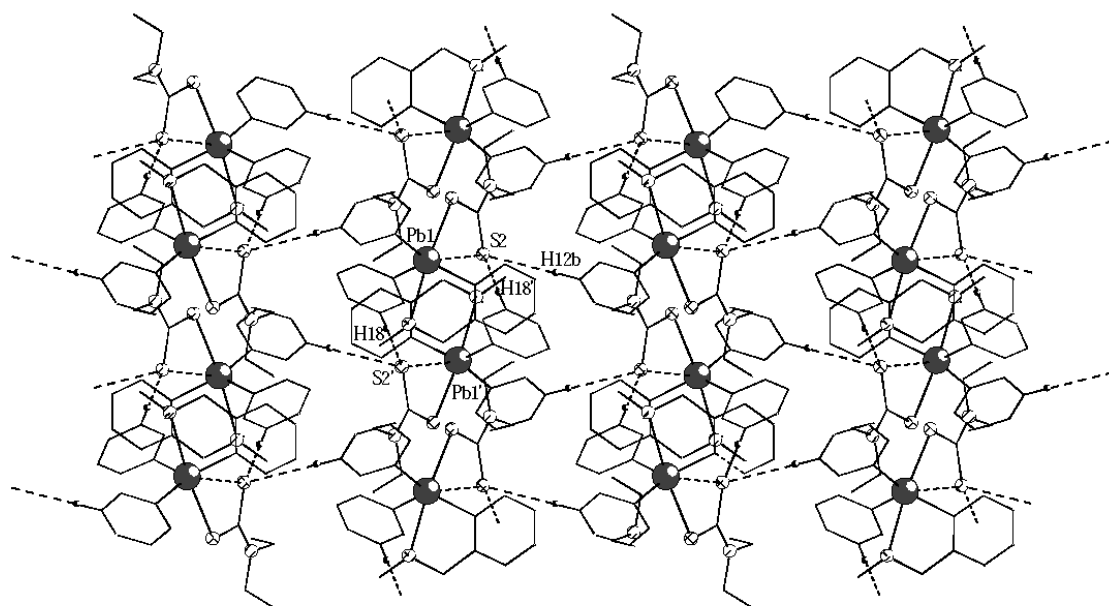


Fig. 6 – View of the layer built from chain polymers along axis *a* in the crystal of **2** based on inter-chain S \cdots H interactions (only hydrogens involved in such contacts are shown) [symmetry equivalent atoms $(-x, -y, -z)$ are given by “prime”].

EXPERIMENTAL

Solvents were dried and distilled prior to use. ^1H and ^{13}C NMR spectra, including 2D experiments, were recorded at room temperature on Bruker Avance 300 instrument using solutions in CDCl_3 . The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. CHCl_3 : ^1H 7.26, ^{13}C 77.0 ppm) for ^1H and ^{13}C NMR spectra, respectively. Microanalyses (C, H, N) are consistent with the given composition of the isolated products. The iodide [2-(Me_2NCH_2) C_6H_4] Ph_2PbI , used as starting material, was obtained using a literature method.²

Synthesis of [2-(dimethylaminomethyl)phenyl]diphenyllead(IV) dimethyldithiocarbamate, [2-(Me_2NCH_2) C_6H_4] $\text{Ph}_2\text{PbS(S)CNMe}_2$ (1)

$\text{Me}_2\text{NCS}_2\text{Na}\cdot 2\text{H}_2\text{O}$ (0.011 g, 0.8 mmol) was added to a solution of [2-(Me_2NCH_2) C_6H_4] Ph_2PbI (0.05 g, 0.8 mmol) in 25 mL anhydrous CHCl_3 , at room temperature. A white precipitate immediately formed. The reaction mixture was filtered to remove the NaCl and the clear colourless filtrate was concentrated in vacuum until a white solid deposited. The solid was filtered off and recrystallized from a CH_2Cl_2 /hexane mixture to give colourless crystals of the title compound. Yield: 0.039 g (80%). M.p. = 198 °C. ^1H NMR (300 MHz): 1.76s [6H, $\text{CH}_2\text{-N}(\text{CH}_3)_2$], 3.42s [6H, $\text{S}_2\text{CN}(\text{CH}_3)_2$], 3.44s [2H, $\text{CH}_2\text{-N}(\text{CH}_3)_2$], 7.41m (9H, $\text{H}_{3,5}$ + C_6H_5 -meta+para), 7.88dd (4H, C_6H_5 -ortho, $^3J_{\text{HH}} = 7.6$, $^4J_{\text{HH}} = 0.9$, $^3J_{\text{PbH}} = 108.0$ Hz), 8.49d (1H, H_6 , $^3J_{\text{HH}} = 7.4$, $^3J_{\text{PbH}} = 127.9$ Hz). ^{13}C NMR (75.5 MHz): 45.14s [$\text{S}_2\text{CN}(\text{CH}_3)_2$], 45.37s [$\text{CH}_2\text{-N}(\text{CH}_3)_2$], 65.26s [$\text{CH}_2\text{-N}(\text{CH}_3)_2$], $^3J_{\text{PbC}} = 32.5$ Hz], 128.52s (C_6H_5 -para), 128.72s (C_4), 129.06s ($\text{C}_{3,5}$), 129.43s (C_6H_5 -meta, $^3J_{\text{PbC}} = 106.2$ Hz), 136.45s (C_6H_5 -ortho, $^2J_{\text{PbC}} = 80.0$ Hz), 138.78s

(C_6 , $^2J_{\text{PbC}} = 60.4$ Hz), 143.56s (C_2), 157.42s (C_1), 169.23s (C_6H_5 -ipso, $^1J_{\text{PbC}} = 728.9$ Hz), 202.35s [$\text{S}_2\text{CN}(\text{CH}_3)_2$].

Synthesis of [2-(dimethylaminomethyl)phenyl]diphenyllead(IV) diethyldithiocarbamate, [2-(Me_2NCH_2) C_6H_4] $\text{Ph}_2\text{PbS(S)CNEt}_2$ (2)

Compound **2** was prepared as above from $\text{Et}_2\text{NCS}_2\text{Na}\cdot 3\text{H}_2\text{O}$ (0.014 g, 0.8 mmol) and [2-(Me_2NCH_2) C_6H_4] Ph_2PbI (**5**) (0.05 g, 0.8 mmol) in 25 mL anhydrous CHCl_3 , at room temperature. Recrystallization from CH_2Cl_2 /hexane mixture gave the title compound as colourless crystals. Yield: 0.047 g (91%). M.p. = 201 °C. ^1H NMR (300 MHz): 1.20t [6H, $\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$, $^3J_{\text{HH}} = 7.1$ Hz], 1.76s [6H, $\text{CH}_2\text{-N}(\text{CH}_3)_2$], 3.44s [2H, $\text{CH}_2\text{-N}(\text{CH}_3)_2$, $^4J_{\text{PbH}} = 15.3$ Hz], 3.89q [4H, $\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$, $^3J_{\text{HH}} = 7.1$ Hz], 7.41m (9H, $\text{H}_{3,5}$ + C_6H_5 -meta+para), 7.89d (4H, C_6H_5 -ortho, $^3J_{\text{HH}} = 7.1$, $^3J_{\text{PbH}} = 107.4$ Hz), 8.48d (1H, H_6 , $^3J_{\text{HH}} = 7.3$, $^3J_{\text{PbH}} = 129.1$ Hz). ^{13}C NMR (75.5 MHz): 12.23s [$\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$], 45.37s [$\text{CH}_2\text{-N}(\text{CH}_3)_2$], 48.93s [$\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$], 65.30s [$\text{CH}_2\text{-N}(\text{CH}_3)_2$, $^3J_{\text{PbC}} = 32.8$ Hz], 128.40s (C_6H_5 -para), 128.65s (C_4), 128.96s ($\text{C}_{3,5}$), 129.06s ($\text{C}_{3,5}$), 129.34s (C_6H_5 -meta, $^3J_{\text{PbC}} = 105.3$ Hz), 136.48s (C_6H_5 -ortho, $^2J_{\text{PbC}} = 79.9$ Hz), 138.64s (C_6 , $^2J_{\text{PbC}} = 61.7$ Hz), 143.55s (C_2 , $^2J_{\text{PbC}} = 65.6$ Hz), 157.71s (C_1), 160.59s (C_6H_5 -ipso, $^1J_{\text{PbC}} = 716.3$ Hz), 200.67s [$\text{S}_2\text{CN}(\text{CH}_3)_2$].

Crystal structure determination

Block colorless crystals of **1** and **2** were mounted with epoxy glue on cryoloops. Data collection and processing was carried on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Cell refinement gave cell constants corresponding to triclinic cell for **1** and monoclinic cell for **2** (space group $P-1$ for **1**, and $P2_1/n$ for **2**), whose dimensions are given in Table 2 along with other experimental parameters.

Table 2

Crystallographic data for [2-(Me_2NCH_2) C_6H_4] $\text{Ph}_2\text{PbS(S)CNR}_2$ [R = Me (**1**), Et (**2**)]

Compound	1	2
Molecular formula	$\text{C}_{24}\text{H}_{28}\text{N}_2\text{PbS}_2$	$\text{C}_{26}\text{H}_{32}\text{N}_2\text{PbS}_2$
M	615.79	643.85
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/n$
Temperature (K)	297(2)	297(2)
$a/\text{Å}$	9.476(4)	16.829(3)
$b/\text{Å}$	10.734(4)	8.6976(14)
$c/\text{Å}$	12.953(5)	19.273(3)
α°	94.540(7)	90
β°	107.119(6)	111.605(3)
γ°	97.579(7)	90
$V/\text{Å}^3$	1238.4(8)	2622.8(8)
Z	2	4
$D_{\text{calc}}/\text{gcm}^{-3}$	1.651	1.630
$F(000)$	600	1264
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	6.992	6.607
Crystal size (mm^3)	0.26 x 0.22 x 0.18	0.40 x 0.19 x 0.18
θ range for data collection ($^\circ$)	2.28 to 25.00	1.38 to 25.00
Reflections collected	12089	18396
Independent reflections	4351 [$R_{\text{int}} = 0.0398$]	4616 [$R_{\text{int}} = 0.0790$]
Absorption correction	Multi-Scan ⁴⁴	Multi-Scan ⁴⁴
Maximum and minimum transmissions	0.284 and 0.177	0.304 and 0.242
Data / restraints / parameters	4351 / 0 / 266	4616 / 0 / 284
Goodness-of-fit on F^2	1.097	1.236
Final R indices [$>2\sigma(I)$] ^a	$R_1 = 0.0374$ $wR_2 = 0.0695$	$R_1 = 0.0768$ $wR_2 = 0.1387$
R indices (all data) ^a	$R_1 = 0.0433$ $wR_2 = 0.0715$	$R_1 = 0.1036$ $wR_2 = 0.1473$
Largest difference peak and hole (e Å^{-3})	1.078 and -1.410	1.740 and -2.737

^a Definition of the R values: $R_1 = (\sum||F_o| - |F_c||) / \sum|F_o|$; $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.³⁵ The drawings were created with the Diamond program.³⁶

Supplementary material

Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 836479 (**1**) and 836480 (**2**)]. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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