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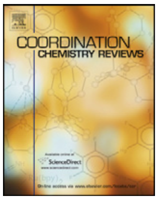

Review

Stereochemistry of lead(II) complexes containing sulfur and selenium donor atom ligands

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Contents

Abbreviations: LP, *E*, lone pair of electrons; VSEPR, valence shell electron-pair repulsion; CSD, Cambridge Structural Database; CIF, Crystallographic Information File; CCDC, Cambridge Crystallographic Data Centre; DFT, density functional theory; CN, coordination number; **I**, ψ-T, ψ-tetrahedrontetrahedron with a vacant vertex; **II**, ψ-TBP, ψ-trigonal bipyramid, trigonal bipyramid with a vacant vertex in the equatorial plane; **III**, ψ-OC, ψ-octahedron, octahedron with a vacant axial vertex; **IV**, ψ-PBP_{ax}, ψ-pentagonal bipyramid(ax), pentagonal bipyramid with a vacant axial vertex; **V**, ψ-PBP_{eq}, ψ-pentagonal bipyramid(eq), pentagonal bipyramid with a vacant equatorial vertex; CHO_2^- ($form^-$), formate ion; $SC(NH_2)_2$ (tu), thiourea; CVD, chemical vapor deposition; Me (CH_3), methyl; Et (CH_2Me), ethyl; ^{n}Pr {$(CH_2)_2Me$}, normal propyl; ^{i}Pr ($CHMe_2$), isopropyl; ^{n}Bu {$(CH_2)_3Me$}, normal butyl; ^{i}Bu (CH_2CHMe_2), isobutyl; Pent (C_5H_{11}), pentyl; Cy (C_6H_{11}), cyclohexyl; Ph (C_6H_5), phenyl; tol (C_6H_5Me), toluene; py (C_5H_5N), pyridine; H_2edta^{2-}, dihydrogenethylenediaminetetraacetate ion; dmf (Me_2NCHO), *N*,N-dimethylformamide; thf (C_4H_8O), tetrahydrofuran; bpy ($C_{10}H_8N_2$), bipyridine; 4,4′-bpy (4,4′-$C_{10}H_8N_2$), 4,4′-bipyridine; pyr ($C_3H_4N_2$), pyrazole; phen ($C_{12}H_8N_2$), 1,10-phenantroline; en ($C_2H_8N_2$), ethylenediamine; ALAD, 5-aminolevulinate dehydratase.

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ABSTRACT

The stereochemistry of lead(II) complexes with S- and Se-donor atom ligands, including mixed ligand complexes is reviewed with respect to the geometry of the first coordination sphere of the Pb(II) atom in these compounds and rationalized in terms of the valence shell electron-pair repulsion (VSEPR) model. The most comprehensively structurally characterized classes of lead(II) thio and seleno complexes are discussed, including monothio-, dithio(seleno)-, trithio- and tetrathio-complexes, as well as Pb(II) dialkyldithio(seleno)carbamates, alkylxanthates and dialkyl(aryl) phosphorodithio(seleno)lates. Data about the polyhedral shape of the primary coordination sphere, coordination number (CN), bond lengths (primary and secondary) and bond angles of the Pb(II) atom in the compounds under investigation are systematized in comprehensive tables. The particularities of the stereochemistry of Pb(II) complexes with S(Se)-donor atom ligands are comparatively discussed with the stereochemistry of lead(II) complexes with oxygen donor ligands.

1. Introduction

Lead(II) complexes with sulfur and selenium donor atom ligands have been studied actively during the last few decades. The reasons for sustained interest in these compounds lies in their significant structural diversity and multiple applications [1]. Lead is classified as a borderline soft metal in the soft acid–base concept of Pearson [2]. Lead(II) forms stable complexes with both soft and hard donor atom ligands. Under similar coordination environments, the affinity of Pb(II) towards sulfur-based ligands tends to be higher compared to harder oxygen- and nitrogen-donor ligands. Despite great advances the coordination chemistry of Pb(II) with S- and Se-donor atom ligands, rational design and tuning of the structure of the ligands to satisfy the coordination preferences and requirements of the Pb(II) atom is still a rather challenging task.

In recent years there has been a surge of research activity in the area of the coordination chemistry of divalent lead with bio-relevant ligands, which is motivated by the toxicity of lead compounds [1]. Lead is a highly undesirable environmental pollutant and its toxicity represents a problem of global magnitude. Lead poisoning was shown to induce a broad range of physiological and biochemical dysfunctions [3] and is particularly dangerous for organisms at the growing stage [4]. Some studies suggested that lead developmental toxicity is associated with interactions of Pb(II) with proteins containing thiol-rich structural zinc-binding sites [5]. Zinc substitution by lead in such proteins has severe implications on their activity because it disrupts the tetrahedral coordination at the metal site resulting in an incorrect protein folding and disruption of the transcription developmental processes [6].

A number of lead complexes with S- and Se-donor atoms have been proposed as single source precursors for bulk or nanostructured PbS and PbSe [7–9]. The binary PbS and PbSe compounds are important semiconductor materials with applications in light-emitting diodes, infrared detectors, lasers, photovoltaic devices, solar cells, bio-markers, etc. The precursors for these technologically important materials are designed to contain the required elements in a correct ratio. Under favorable conditions, the use of a molecular precursor also allows nanocrystal growth under mild conditions with greater synthetic control over size-dispersity and crystallinity.

Although a number of papers have appeared in the literature on Pb(II) complexes with S- and Se-donors, there are no general works on the structural chemistry and stereochemistry of this class of compounds. The structure of Pb(II) complexes with S- and Se-containing ligands is mainly examined in reviews together with Pb complexes having different donor atom ligands [10–12] as well as in general papers devoted to different classes of S- and Se-containing compounds, namely metal thiocarbamates [13], xanthates [14], thiophosphates and thiophosphinates [15,16], and selenophosphates [17]. The structures of a small number of S- and Se-containing Pb(II) compounds have also been considered [18]. In the above publications, only in a few cases is the stereochemistry of Pb(II) complexes with S- and Se-donors discussed.

In the present review, which is a continuation of the previously published manuscript on stereochemistry of lead(II) complexes with oxygen donors [19], an attempt is made to consider the stereochemistry of Pb(II) complexes with S(Se)-donor ligands on the common basis of the VSEPR model [20] using the same methodology described in [19]. The review covers the stereochemistry of lead(II) complexes with S- and Se-donor ligands, including mixed ligand complexes. The selection of crystal structures for analysis was made on the basis of the CSD (version 5.29, Aug 2008) and scientific journals published prior to December 1, 2009. There were 101(7) compounds giving 126(7) types of Pb atoms. The numbers in parentheses indicate the number of compounds with the corresponding Se complexes. In this work we do not consider Pb(II) complexes with NCS^- ligands, which also contain Pb–C bonds, as well as Pb(II) heterometallic complexes, Pb(II) thiolate clusters and Pb(II) complexes, whose ligands contain, along with the S(Se)-donor atoms, other donor atoms (O, N) participating in complex formation with the central atom.

For each compound we used original data, which were examined and supplemented from the calculations made using *PLATON* [21] or *Mercury* [22]. If the structural data were absent or only partially presented in a paper, we used the calculations data from CIF files of the respective structure taken from the CSD.

Some structural data for crystals of the Pb(II) complexes with S(Se)-donor ligands under study are presented in tables. As in the previous review [19], for each compound we provide its composition, overall CN of the Pb atom, bond lengths, bond angles and shape of the polyhedron of the first coordination sphere, secondary bonds, literature citations and the CCDC REFCODEs. The overall CN was taken to be the sum of the Pb(II) CN in the first coordination sphere with a LP and the number of secondary bonds.

The sum of the van der Waals radii of Pb and S(Se) atoms is equal to 3.82 (3.92) Å [23]. In this work we accept 3.60 Å as the upper limit of the Pb–S(Se) distance. At values above this, the Pb–S(Se) bond interactions are weak, and these distances can be neglected. The primary coordination sphere of the Pb(II) atom was limited to Pb–S distances of approximately 3.10 Å, which is slightly greater than the sum of ionic radii of Pb^{2+} (CN 6, 1.19 Å) and S^{2-} (1.84 Å) [24]. Only at CN 5–6 is this distance slightly higher (∼3.15 Å).

The present review discusses the stereochemistry of Pb(II) complexes, whose organic ligands contain only S(Se)-donor atoms, and their mixed-ligand complexes. The compounds are arranged based on the number of S(Se)-donor atoms in the ligand into monothio-, dithio(seleno)-, trithio- and tetrathio-complexes. Dialkyldithio(seleno)carbamates, alkylxanthates and dialkyl(aryl)-phosphorodithio(seleno)lates, which belong to the group of Pb(II) dithio(seleno) complexes are considered separately after polythio-complexes.

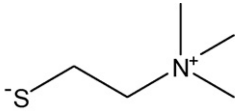
Each compound is described in terms of the structural motif, coordination environment of the Pb(II) atom, Pb–S(Se) bond lengths and proposed coordination polyhedron in the original paper. The geometry of the first coordination sphere is presented based on Pb–S(Se) bond distances and S(Se)–Pb–S(Se) bond angles of the inner coordination sphere of the Pb(II) atoms in accordance with the VSEPR model. The structural diagrams presented were redrawn from the published CIF-files using SHELXTL [25] (in selected Figures H-atoms were omitted for clarity).

2. Lead(II) monothio(seleno)complexes

2.1. Lead(II) aliphatic monothiocomplexes

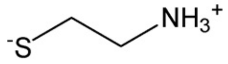
2.1.1. Aliphatic and acyclic monothiocomplexes

Relatively few crystal structures of lead(II) aliphatic and acyclic monothiolates are available. The structure of $[Pb_2(tch)_5](PF_6)_4$ (tch = $^-SCH_2CH_2NMe_3^+$, 2-(trimethylammonio)ethanethiolate, thiocholinate zwitterion, **1**) contains one-dimensional linear chains formed from Pb atoms bonded by double and triple bridging S atoms [26]. Each of six crystallographically independent Pb atoms in the structure is bonded to 5 thiolate S atoms with Pb–S distances ranging from 2.56(3) up to 3.45(3) Å. The coordination geometry of the Pb atom in the structure of $[Pb_2(tch)_5](PF_6)_4$ is described as pseudo-octahedral with a stereochemically active LP. According to the VSEPR model, the coordination polyhedra of the Pb(1A), Pb(1B) and Pb(1C) atoms can be represented as a ψ-trigonal bipyramid (**II**), while the geometries of the Pb(2A), Pb(2B) and Pb(2C) atoms as ψ-tetrahedra (**I**) (Table 1).



1

In the structure of $PbCl(aet)(NO_3)$ (aet = $^-SCH_2CH_2NH_3^+$, 2-ammonioethanethiolate, **2**) two crystallographically independent Pb(II) atoms are tetracoordinated by means of bridging S and Cl atoms [27]. The bridging S atoms generate four-membered Pb_2S_2 cycles. The Pb–S bonds in the ring are slightly asymmetric. The Pb–Cl bridging bonds are also asymmetric and connect the Pb_2S_2 cycles into polymers. Taking into account the weak interaction between the Pb(II) atoms and N and O atoms of the nitrate ions, the authors assign a pentagonal bipyramidal configuration to the coordination polyhedron with the Cl^- ions in axial positions. The coordination number of the Pb(II) ion is 7 ($PbS_2Cl_2O_2N$). According to the VSEPR model, the coordination polyhedra of the first coordination spheres of Pb(1) and Pb(2) ions can be described as type **II** with two Cl^- ions in axial positions and two S atoms in the equatorial plane (Table 1). The vacant vertex in the equatorial plane is populated by a stereochemically active LP.



2

The crystal structure of $Pb(atsqu)_2(dmf)$ ($atsqu^-$ = $Me_2NC_4O_2S^-$, 2(dimethylamino)-1-thiosquarate anion, **3**) contains Pb atoms coordinated by four S atoms and three O atoms in the shape of a pentagonal bipyramid [28]. The polymeric centrosymmetric structure of the compound comprises edge-sharing PbS_4-groups. The Pb–S bond lengths fall into the range 2.872(2)–3.065(2) Å, while the Pb–O distances to oxygen atoms of thiosquarate ligands are equal to 2.773(4) and 2.860(5) Å. The seventh coordination position is occupied by the oxygen atom O(5) from the solvated molecule of dmf (Pb–O(5) 2.806(5) Å). According to the VSEPR model, the coordination polyhedron of the Pb atom can be described as a ψ-trigonal bipyramid (**II**) with the atoms S(1A) and S(2A) in axial positions (<S(1A)–Pb–S(2A) 165.0(1)°) and the S(1) and S(2) atoms (<S(1)–Pb–S(2) 70.6(1)°) and LP—in the equatorial plane (Fig. 1).

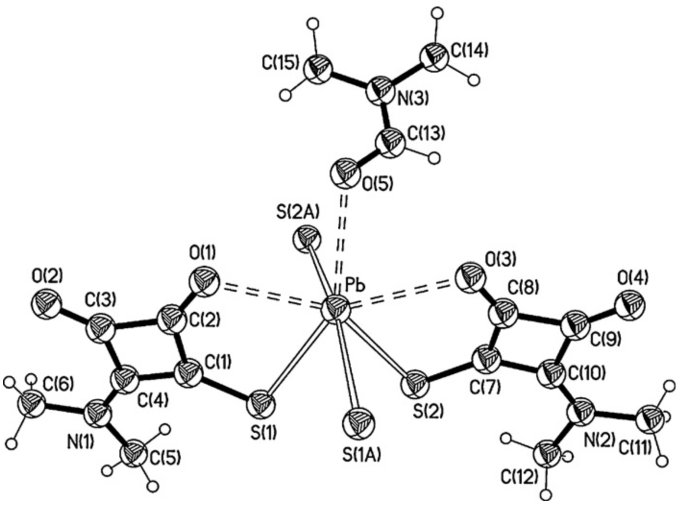
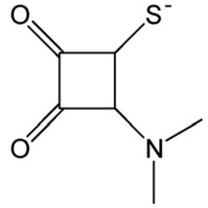


Fig. 1. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(Me_2NC_4O_2S)_2(dmf)$.



3

2.1.2. Mixed ligand thiourea complexes

The neutral monodentate thiourea (tu) ligand forms stable complexes with Pb(II) containing one, two, four and six tu ligands. Substantial contributions to the studies of the above class of compounds were made by Herbstein and coworkers [29–33] and Nardelli and coworkers [34,35].

In the crystal structure of $Pb(tu)_2(form)_2{\cdot}H_2O$ ($form^-$ = HCO_2^-, formate ion) the Pb atom is surrounded by eight donor atoms: three S atoms from tu molecules, four O atoms of formate ions and the oxygen atom from the H_2O molecule, thus forming a distorted dodecahedral polyhedron [29]. The structure is built from dimeric groups formed from symmetrically related Pb atoms bonded through the O(1) atoms from symmetrically related bridging bidentate C(3)O(1)O(3) formate ions (Fig. 2). The dimers of the structure are built into parallel polymer chains. One of the tu molecules displays a bridging function, binding together the dimers (Pb–S(1A) = 3.30(2) Å) into parallel chains, while the second tu molecule is monodentate. According to the VSEPR model [20], the coordination polyhedron of the Pb atom corresponds to a ψ-tetrahedron (**I**) formed by S(1) and S(2) atoms from tu molecules (Pb–S(1) = 2.93(2) and Pb–S(2) = 2.83(2) Å) and non-bridging O(3) atom from the bidentate-coordinated C(3)O(1)O(3) formate ligand (Pb-O(3) 2.59(4) Å). The lead(II) LP area is surrounded by four O

Table 1
Stereochemistry of lead(II) monothio(seleno)complexes.

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	2	3	4	5	6	7	8	9
Pb(II) aliphatic and acyclic monothiocomplexes								
[Pb$_2$(tch)$_5$](PF$_6$)$_4$								
Pb(1A)	5	ψ-TBP	2.91(3) S(3)	2.63(3) S(1)	162.5(7)	86.7(8)	3.27(3) S(5)^A	[26], DIXKUQ
	(4+*E*)+1	**II**	3.01(3) S(4)^A	2.81(3) S(2)				
Pb(2A)	5	ψ-T	2.58(3) S(4)		97.4(9)		3.23(3) S(2)	
	(3+*E*)+2	**I**	2.62(3) S(5)		86.7(8)		3.45(3) S(1)^A	
			2.76(3) S(3)^A		84.9(9)			
Pb(1B)	5	ψ-TBP	2.85(3) S(3)	2.59(3) S(1)	161.3(8)	87.9(8)	3.30(3) S(5)^B	
	(4+*E*)+1	**II**	3.07(3) S(4)^B	2.74(3) S(2)				
Pb(2B)	5	ψ-T	2.64(3) S(4)		89.2(8)		3.18(3) S(2)	
	(3+*E*)+2	**I**	2.73(3) S(5)		96.4(9)		3.35(3) S(1)^B	
			2.82(3) S(3)^B		87.5(9)			
Pb(1C)	5	ψ-TBP	2.78(3) S(3)	2.63(3) S(1)	167.9(8)	96.4 (8)	3.26(3) S(5)^C	
	(4+*E*)+1	**II**	3.09(3) S(4)^C	2.79(3) S(2)				
Pb(2C)	5	ψ-T	2.56(3) S(3)		89.7(9)		3.20(3) S(2)	
	(3+*E*)+2	**I**	2.84(3) S(4)		84.9(9)		3.29(3) S(1)^C	
			2.92(3) S(5)^C		94.0(9)			
PbCl(aet))(NO$_3$) Pb(1)	7	ψ-TBP	2.8031(1) Cl(1)	2.7383(1) S(1)	170.48(3)	83.92(3)	3.005(3) O(3)	[27], KEJCOS
	(4+*E*)+3	**II**	2.9879(1) Cl(2^{ii})	2.8399(1) S(2^{ii})			3.014(3) O(2)	
							3.318(1) Cl(1^i)	
Pb(2)	7	ψ-TBP	2.7693(1) Cl(2)	2.7275(1) S(2)	172.96(3)	84.01(5)	2.867(3) O(5)	
	(4+*E*)+3	**II**	3.0789(1) Cl(1)	2.8457(1) S(1^{ii})			3.2795(2) Cl(2)	
							3.187(3) O(6^i)	
Pb(atsqu)$_2$(dmf)	7	ψ-TBP	3.017(2) S(2A)	2.872(2) S(2)	165.0(1)	70.6(1)	2.773(4) O(1)	[28], XINWOG
	(4+*E*)+3	**II**	3.065(2) S(1A)	2.898(2) S(1)			2.806(5) O(5)	
							2.860(5) O(3)	
Pb(II) mixed ligand thiourea complexes								
Pb(tu)$_2$(form)$_2$·H$_2$O	8	ψ-T	2.59(4) O(3)		74(3)		2.72(4) O(2)	[29], PBFORT10
	(3+*E*)+5	**I**	2.83(2) S(2)		70(3)		2.75(4) O(1)	
			2.93(2) S(1)		89(3)		2.84(4) O(5)	
							2.91(4) O(1A)	
							3.30(2) S(1A)	

$Pb(Me_4tu)I_2$	6	ψ-T	2.75(1) S(1)		97.3(3)		3.310(4) I(2)	[36] FEXLID
Pb(1)	(3+*E*)+3	**I**	3.103(4) I(4)		97.4(3)		3.335(4) I(3)	
			3.181(4) I(1)		90.15(10)		3.57 (1) S(2^i)	
Pb(2)	6	ψ-T	2.83(1) S(2)		96.5(3)		3.301(4) I(1^i)	
	(3+*E*)+3	**I**	3.142(4) I(2)		99.0(3)		3.342(4) I(4^i)	
			3.138(4) I(3)*		93.70(10)		3.50(1) S(1)	
$Pb(tu)(ac)_2$	8	ψ-TBP	2.44(2) O_{II}	2.37(2) O^i_{IV}	125.29	75.72	3.01(3) O^i_{III}	[34], PBTUAC
	(4+*E*)+4	**II**	2.63(3) O_{III}	2.62(2) O_I			3.09(1) S	
							3.10(1) S^i	
							3.34(1) S^{ii}	
$Pb(tu)_2(NO_3)_2$	9	ψ-TBP **II**	2.68 O(21)	2.846 S(1)	140.56	79.88	2.80 O(13)	[30], BARFUV
	(4+*E*)+5		3.046 S(1b)	2.961 S(2)			2.95 O(23)	
							3.01 O(12)	
							3.10 O(22)	
							3.184 S(2a)	
$Pb(tu)(H_2edta)$	7	ψ-TBP **II**	2.390(2) O(3)	2.485(2) N(1)	116.79(6)	98.59(5)	2.728(2) N(2)	[37], IBEPIP
	(4+*E*)+3		2.534(2) O(1)	3.0493(7) S			2.733(2) O(8)	
							2.903(2) O(6)	
$[Pb(H_2edta)]\cdot 2tu\cdot H_2O$	8	ψ-TBP **II**	2.474(4) O(3)	2.585(4) N(1)	118.2(1)	93.3(1)	2.716(4) N(2)	[37], IBEPOV
	(4+*E*)+4		2.556(4) O(1)	3.069(1) S(1)			2.757(4) O(8)	
							2.907(4) O(6)	
							3.536(2) S(2)	
$Pb(tu)_2Cl_2$	7	ψ-O	2.75(4) Cl(1)	2.92(3) S(2)	83.6	84.1	3.17(3) Cl(2)	[35], CTURPB
	(5+*E*)+2	**III**		3.02(3) S(1)	75.6	84.7	3.28(3) Cl(2A)	
				3.04(3) S(1A)	80.2	91.3		
				3.10 (3) S(S2A)	88.3	95.2		
						Σ=355.3		
$Pb(tu)Br_2$ (I)	7	ψ-O	2.814(3) Br(2)	2.974(8) S(1)^c	83.1(3)	88.7(2)	3.515(3) Br(2)^b	[32], PBBRTU11
	(5+*E*)+2	**III**		2.995(6) Br(1)^c	89.72(18)	88.83(16)	3.562(3) Br(2)^a	
				3.082(8) S(1)	84.5(2)	89.4(2)		
				3.090(6) Br(1)	90.89(18)	92.5(2)		
						Σ=359.43		
$Pb(tu)_2Br_2$ (II)	7	ψ-TBP	2.926(5) S(2)	2.901(2) Br(2)	164.12(15)	79.56(11)	3.164(5) S(2)^b	[32], DARBAZ02
	(4+*E*)+3	**II**	3.100(5) S(1)^b	2.989(5) S(1)			3.282(2) Br(1)	
							3.301(2) Br(1)^b	
$Pb(tu)_2Br_2$ (I)								[33], DARBAZ
Pb(1)	6	ψ-TBP	2.995(4) Br(1)	2.857(9) S(1)	178.07(13)	84.1(3)	3.104(6) Br(2)	
	(4+*E*)+2	**II**	3.022(4) Br(1a)	2.940(11) S(3)			3.138(10) S(2)	

Table 1 (*Continued*)

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	2	3	4	5	6	7	8	9
Pb(2)	7	ψ-TBP	3.024(11) S(2)	2.946(4) Br(3)	156.8(2)	91.1(2)	3.138(8) S(4)	
	(4+*E*)+3	**II**	3.087(6) Br(4)	3.088(9) S(3)			3.161(10) S(5) 3.169(4) Br(3a)	
Pb(3)	7	ψ-TBP	3.052(8) S(5)	2.969(4) Br(5)	155.1(3)	84.17(13)	3.122(10) S(4)	
	(4+*E*)+3	**II**	3.171(9) S(6)	2.991(5) Br(6)			3.157(11) S(7) 3.170(4) Br(5b)	
Pb(4)	6	ψ-TBP	2.882(10) S(8)	2.926(4) Br(7)	174.2(3)	82.5(2)	3.065(6) Br(8)	
	(4+*E*)+2	**II**	3.063(9) S(7)	2.944(11) S(6)			3.096(4) Br(7a)	
Pb(II) aliphatic heterocyclic monothiocomplexes								
Pb(mint)$_3$(NO$_3$)$_2$	7	ψ-TBP	2.826(2) S(3)	2.524(5) O(21)	165.83(6)	79.02(14)	2.748(6) O(22)	[38], FUVJIP
	(4+*E*)+3	**II**	3.053(2) S(1)	2.850(2) S(2)			2.811(5) O(12) 3.195(2) S(1^{i})	
Pb(Hmim^{tBu})$_4$Cl$_2$	6	ψ-TBP	2.930(2) S(21)	2.870(2) S(31)	153.93(5)	92.26(6)	3.037(2) Cl(1)	[39], WADMIY
	(4+*E*)+2	**II**	3.079(2) S(11)	2.906(2) S(41)			3.079(2) Cl(2)	
Pb(II) bis{benzenethio(seleno)lates}								
Pb(SPh)$_2$	5	ψ-T	2.671(5) S(1^{i})		80.5(2)		3.373(6) S(2^{i})	[40], RAVZET
	(3+*E*)+2	**I**	2.723(5) S(2)		89.4(1)		3.519(5) S(2^{ii})	
			2.837(5) S(1)		86.0(2)			
Pb(SPh-*p*-Me)$_2$	5	ψ-T	2.650(3) S(1)		77.5(1)		3.292(4) S(2b)	[41], LERFUJ
	(3+*E*)+2	**I**	2.663(3) S(2)		86.0(1)		3.689(4) S(2c)	
			2.874(3) S(1a)		86.8(1)			
[Pb(SAr^{i})$_2$]$_3$								[42], CAWZIJ
Pb(1)	4 (4+*E*)	ψ-TBP **II**	2.896(3) S(2) 2.896(3) S(2A)	2.680(3) S(1) 2.680(3) S(1A)	147.1(1)	89.3(2)		
Pb(2)	3 (3+*E*)	ψ-T **I**	2.554(4) S(3) 2.673(3) S(2) 2.780(3) S(1)		92.6(1) 92.8(1) 73.5(1)			
[Pb(SeR$_f$)$_2$]$_2$·3tol	7	ψ-T	2.7127(11) Se(2)		87.53(4)		3.057(5) F(17)	[43], PIKSEH
	(3+*E*)+4	**I**	2.876(2) Se(1a)		81.68(4)		3.089(5) F(9a)	
			2.9704(13) Se(1)		81.87(3)		3.139(5) F(3) 3.142(5) F(2)	

Pb(SR$_f$)$_2$(thf)	7	ψ-T	2.495(10) O(1)		91.9(1)		3.211(4) F(1a)	[44], KOYFEY
	(3+*E*)+4	**I**	2.639(1) S(1)		91.9(1)		3.211(4) F(1)	
			2.639(1) S(1a)		84.4(1)		3.352(4) F(2c)	
							3.352(4) F(2b)	
Pb(SC$_6$F$_5$)$_2$	8	ψ-T	2.704(2) S(2)		75.61(7)		2.968(6) F(5)	[45], WEJMEE
Pb(2)	(3+*E*)+5	**I**	2.721(2) S(3)		86.56(8)		3.130(7) F(6b)	
			2.737(3) S(1^i)		86.77(8)		3.245(6) F(11b)	
							3.472(7) F(7d)	
							3.514(6) F(6d)	
[Pb(tab)$_3$](ClO$_4$)$_2$	5	ψ-T	2.683(3) S(3)		94.15(10)		3.424(3) S(2A)	[46], RIPROY
	(3+*E*)+2	**I**	2.701(3) S(1)		95.53(9)		3.503(3) S(1A)	
			2.763(3) S(2)		82.77(9)			
[AsPh$_4$][Pb(SPh)$_3$]	3	ψ-T	2.619(1) S(1)		91.08(5)			[47], CUKRUV
	(3+*E*)	**I**	2.623(1) S(3)		90.32(4)			
			2.647(1) S(2)		96.14(5)			
[AsPh$_4$][Pb(SePh)$_3$]	3	ψ-T	2.727(1) Se(1)		90.11(4)			[47], CUKZAC
	(3+*E*)	**I**	2.733(1) Se(3)		88.82(4)			
			2.762(1) Se(2)		96.57(4)			
[N^{n}Pr$_4$][Pb(SPh)$_3$]	3	ψ-T	2.633(3) S(4)		89.7(1)			[48], DELFOP
	(3+*E*)	**I**	2.665(3) S(3)		93.7(1)			
			2.696(3) S(2)		102.7(1)			
Pb{S(O)CPh}$_2$	8	ψ-T	2.764(4) S(1)		84.86(11)		2.77(1) O(2)	[49], SOJHOP
	(5+*E*)+3	**I**	2.831(4) S(2)		84.30(11)		2.85(1) O(1*)	
			3.022(4) S(1*)		87.49(11)		3.173(4) S(2*)	
							3.22(1) O(1)	
							3.665(4) S(2**)	
[AsPh$_4$][Pb{S(O)CPh}$_3$]·CH$_2$Cl$_2$	7	ψ-T	2.706(3) S(2)		85.02(9)		2.879(6) O(1)	[50], POGPUW
	(3+*E*)+4	**I**	2.740(3) S(3)		90.75(8)		2.905(7) O(3)	
			2.764(3) S(1)		88.85(9)		3.113(6) O(2)	
							3.298(7) O(2)^a	
Pb(II) mixed ligand bis(benzenethiolates)								
Pb{(2,6-MeSPh)$_2$(py)$_2$}	4	ψ-TBP	2.689(3) N(2)	2.6078(9) S(1)	178.58(9)	89.31(3)		[51], GAGXES
	(4+*E*)	**II**	2.695(3) N(1)	2.6079(9) S(2)				
Pb{(2,6-MeSPh)$_2$(4,4-bpy)}·0.5CH$_2$Cl$_2$	4	ψ-T	2.595(3) S(1)		84.33(8)		2.814(7) N(1^i)	[51], GAGXIW
Pb(1)	(3+*E*)+1	**I**	2.598(3) S(2)		88.0(2)			
			2.652(7) N(2)		90.8(2)			

Table 1 (*Continued*)

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	2	3	4	5	6	7	8	9
Pb(2)								
	4	ψ-TBP	2.652(8) N(21)	2.598(3) S(21)	172.8(3)	87.67(8)		
	(4+*E*)	**II**	2.668(7) N(22^{i})	2.602(3) S(22)				
Pb{(2,6-MeSPh)$_2$	4	ψ-T	2.599(3) S(1)		87.8(1)		2.848(9) N(1^{i})	[51], GAGXOC
(pyr)}	(3+*E*)+1	**I**	2.595(3) S(2)		86.3(2)		3.743(3) S(1^{iii})	
			2.614(9) N(2)		85.9(2)			
Pb$_2$(SPh)$_4$(py)								[51], GAGXUI
Pb(1)	5	ψ-TBP	2.993(2) S(3)	2.696(2) S(1^{i})	159.75(4)	97.85(5)	3.268(1) S(4)	
	(4+*E*)+1	**II**	3.000(2) S(1)	2.699(2) S(2)				
Pb(2)	6	ψ-T	2.720(2) S(3)		89.50(5)		3.212(2) S(2^{iii})	
	(3+*E*)+3	**I**	2.825(2) S(4)		86.30(5)		3.422(1) S(1^{iii})	
			2.836(2) S(4^{ii})		77.63(5)		2.842(5) N(1)	
Pb{(2,6-MeSPh)$_2$(pyC(H)O)}	5	ψ-T	2.571(5) N(1)		87.86(12)		3.1742(16) S(1A)	[52], XIRBUW
	(3+*E*)+2	**I**	2.6256(17) S(2)		87.37(11)		3.339(4) O(1A)	
			2.6636(16) S(1)		101.32(5)			
Pb{(2,6-MeSPh)$_2$(pyOMe)}	5	ψ-T	2.497(2) N(1)		88.89(5)		3.2671(6) S(1*)	[52], XIRCAD
	(3+*E*)+2	**I**	2.6179(7) S(2)		89.00(5)		3.500(2) O(1)[b]	
			2.6481(6) S(1)		99.66(2)			
Pb{(2,6-MeSPh)$_2$(pyNMe$_2$)}	3	ψ-T	2.432(2) N(1)		90.87(9)			[52], XIRCEH
	(3+*E*)	**I**	2.6070(11) S(2)		86.69(9)			
			2.6211(12) S(1)		87.55(4)			

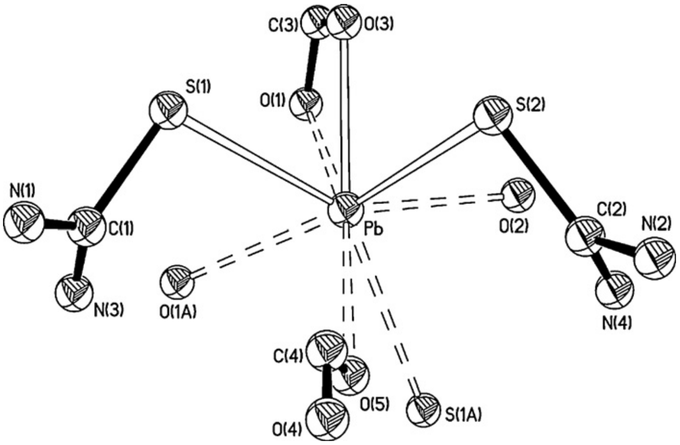
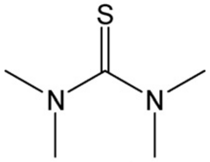


Fig. 2. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(tu)_2(CHO_2)_2{\cdot}H_2O$.

atoms from the formate groups (Pb…O 2.72(4)–2.91(4) Å) and the S(1A) atom of the tu molecule (Pb…S(1A) 3.30(2) Å), with which the central atom forms secondary bonds (Table 1).

The Pb(1) and Pb(2) atoms in $Pb(Me_4tu)I_2$ (Me_4tu, = $SC(NMe_2)_2$, 1,1,3,3-tetramethylthiourea, **4**) have the same ψ-tetrahedral geometry as the Pb atom in $Pb(tu)_2(form)_2{\cdot}H_2O$ [36]. The structure contains linear chains of alternating crystallographically independent Pb atoms, each of which is bonded along the chain by Pb–I and Pb–S bonds. One S atom and two I^- ions located at shorter distances from Pb(II) form the primary coordination sphere (Table 1).



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In the crystal structure of monothiourea lead(II) acetate, $Pb(tu)(ac)_2$ (ac^- = $MeCO_2{}^-$, acetate anion) the Pb atom forms relatively strong bonds with oxygen atoms of the carboxylate groups of both acetate ligands (Pb–O 2.37(2)–2.63(3) Å, Table 1) and moderate-strength bonds with the S atoms of three tu molecules [34]. The coordination polyhedra of the Pb atoms, which the authors consider to be distorted pentagonal bipyramids, are bound into zigzag-like chains through S atoms with the Pb–S distances of 3.09(1) and 3.10(1) Å. Adjacent polymer chains are related to each other by an inversion center and are bonded to each other by weaker Pb…S interactions (3.34(1) Å). According to the VSEPR model, the Pb atom polyhedron in $Pb(tu)(ac)_2$ can be described as a ψ-trigonal bipyramid (type **II**) with a stereochemically active LP in the equatorial plane (Table 1).

Consistent with the VSEPR model, the polyhedra of the primary coordination sphere of the Pb atoms in $Pb(tu)_2(NO_3)_2$ [30], $Pb(tu)(H_2edta)$ and $Pb(H_2edta){\cdot}2tu{\cdot}H_2O$ [37] adopt type **II** structures similar to $Pb(tu)(ac)_2$ (see Table 1).

The structure of $Pb(tu)(H_2edta)$ is built from molecular $[Pb(tu)(H_2edta)]$ units linked into twofold polymer chains by means of strong hydrogen bonds. In addition to these molecular units, the structure of $Pb(H_2edta){\cdot}2tu{\cdot}H_2O$ also contains non-bound lattice molecules of tu and H_2O. In both structures, the lead(II) atoms bind to six donor atoms of the H_2edta^{2-} ligand (4O+2N) and the S atom of a tu molecule (Pb–S = 3.0493(7) in $Pb(tu)(H_2edta)$ and 3.069(1) Å in $Pb(H_2edta){\cdot}2tu{\cdot}H_2O$). The S(2) atom of the second tu molecule in $Pb(H_2edta){\cdot}2tu{\cdot}H_2O$ is situated at a distance of 3.536(2) Å from the central atom.

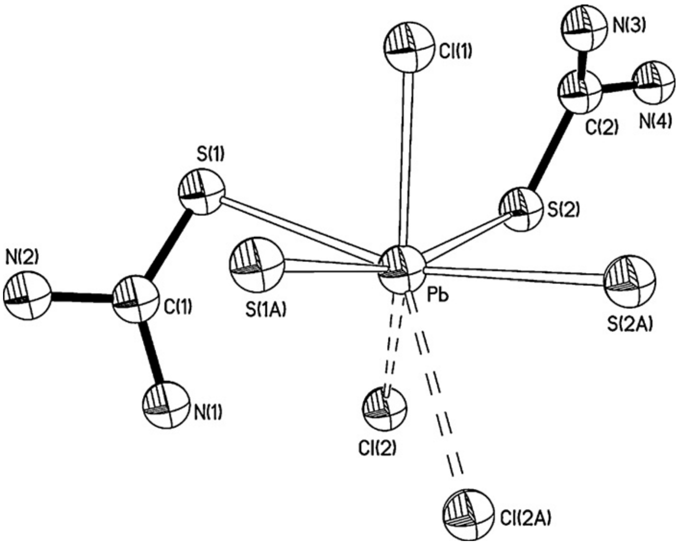


Fig. 3. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(tu)_2Cl_2$.

The coordination geometry of the Pb atoms in the structures of $Pb(tu)_2Cl_2$ [35] and $Pb(tu)Br_2$ (form I) [32] are fundamentally different from that in the structure of $Pb(tu)(ac)_2$. In the structure of $Pb(tu)_2Cl_2$ the Pb atoms (CN 7) are each bonded to four S atoms of four tu molecules and three Cl atoms, thus adopting distorted trigonal prismatic polyhedra with centered side faces [35]. According to the VSEPR model, the geometry of the Pb polyhedron can be described as a distorted ψ-octahedron (**III**) with the Cl(1) atom in the apical position and four S atoms in the equatorial plane (Table 1). The second apical position of the **III** is occupied by a stereochemically active LP (Fig. 3). The Pb atom is displaced from the polyhedron's basal plane towards the LP by 0.43 Å. The polyhedra share the S…S edges of the basal plane to generate polymeric columns.

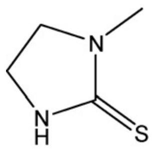
The primary coordination sphere of the Pb atom in the structure of $Pb(tu)Br_2$ (form I) is built by three Br^- ions and two S atoms, which form the coordination polyhedron as a ψ-octahedron (**III**). The Br atom with the shortest bond to Pb (2.814(3) Å) lies in the axial vertex and the stereochemically active LP in the opposing axial position [32]. The Pb atom is displaced from the equatorial plane in the LP direction by 0.15 Å. The Br^- ions of adjacent polyhedra form secondary bonds with the Pb atoms and are located in the same direction at distances of 3.515(3) and 3.562(3) Å. The values of the Br(2)–Pb–Br(1) bond angles (89.72(18)° and 90.89(18)°), which are expected to be below 90° due to repulsion between the LP and atoms forming the basal plane, are not consistent with the VSEPR-model **III**, although the sum of the angles around the Pb atom is close to 360°.

The asymmetric unit of $Pb(tu)_2Br_2$ (form 1) [33] contains tetrameric groups made up of four Pb^{2+} ions bridged by S atoms of the tu ligands. The terminal Pb atoms are six-coordinate, while the internal Pb atoms are seven-coordinate. These tertamers are further bonded into polymeric chains by bridging Br^- ions. The coordination polyhedra of the Pb(1)–Pb(4) atoms in the structure have the configuration **II** (Table 1) in agreement with the VSEPR model.

The compound $Pb(tu)_2Br_2$ (form II) is isostructural to $Pb(tu)_2Cl_2$. The coordination polyhedron of the Pb atom is described as a square pyramid with a Br^- ion in the axial vertex and S atom in the base [32]. One of the angles (Br(2)–Pb–S(2)) slightly exceeds 90° (92.67(13)°), which is in disagreement with the VSEPR model for a ψ-octahedron (**III**). Within the scope of the VSEPR model, the Pb(II) polyhedron in the structure of $Pb(tu)_2Br_2$ (form II) can be represented as a ψ-trigonal bipyramid (**II**). The axial and equatorial angles in the polyhedron are equal to 164.12(15)° and 79.56(11)°, respectively (Table 1).

2.1.3. Aliphatic heterocyclic monothiocomplexes

The crystal structures of two Pb(II) monothiocomplexes containing neutral heterocyclic thione ligands have been investigated. The crystal structure of $Pb(mint)_3(NO_3)_2$ (mint = $C_4H_6N_2S$, 1-methylimidazoline-2(3H)–thione, **5**) contains discrete dimeric $[Pb_2(mint)_6(NO_3)_4]$ units [38]. The Pb atoms in the dimer are related by a crystallographical center of symmetry and are bound by two S atoms from two mint ligands with Pb–S distances of 3.053(2) and 3.195(2) Å. The terminal mint ligands coordinated are located in the *trans*-position with respect to the bridging ligands; the Pb–S distances to the former are 2.826(2) and 2.850(2) Å. The coordination sphere of each Pb atom in the dimer is supplemented by oxygen atoms from two nitrate ions: one of them is asymmetrically bidentate, another one is monodentate. The total CN of Pb atoms are 7 and the polyhedron has been described as a distorted octahedron with a bidentate NO_3^- group occupying a single position. Taking into account the lengths of primary Pb–O and Pb–S bonds, the coordination polyhedron of the Pb atom can be represented as type **II** (Table 1) in accord with the VSEPR model.



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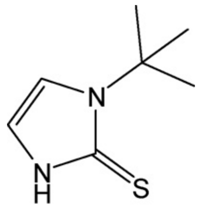
Unlike the structure of $Pb(mint)_3(NO_3)_2$ which contains dimeric units, $Pb(Hmim^{tBu})_4Cl_2$ ($Hmim^{tBu}$ = $C_7H_{12}N_2S$, 2-mercapto-1-*tert*-butylimidazole, **6**) is monomeric [39]. The Pb atom is coordinated by four mercaptoimidazole groups (Pb–S = 2.870(2)–3.079(2) Å) and two adjacent Cl^- ligands (Pb–Cl = 3.037(2) and 3.079(2) Å), forming a distorted octahedron. Taking into account the primary bonds, the coordination polyhedron of the Pb atom in the structure of $Pb(Hmim^{tBu})_4Cl_2$, as in $Pb(mint)_3(NO_3)_2$, has a ψ-trigonal-bipyramidal geometry. The difference is that the Pb atom in $Pb(Hmim^{tBu})_4Cl_2$ is coordinated by four S atoms, while the Pb ion in $Pb(mint)_3(NO_3)_2$ binds an oxygen and three S atoms. There are also differences in polyhedral angles and compositions of the second coordination spheres in both structures (Table 1).



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2.2. Lead(II) aromatic monothio(seleno)complexes

2.2.1. Bis{benzenethio(seleno)lates}

The complexes of Pb(II) with benzenethio and benzeneseleno ligands are of interest in view of their application as precursors to produce PbS and PbSe using chemical vapor deposition (CVD) techniques and a series of Pb(II) benzenethio- and benzeneseleno-complexes was synthesized and structurally investigated for this reason.

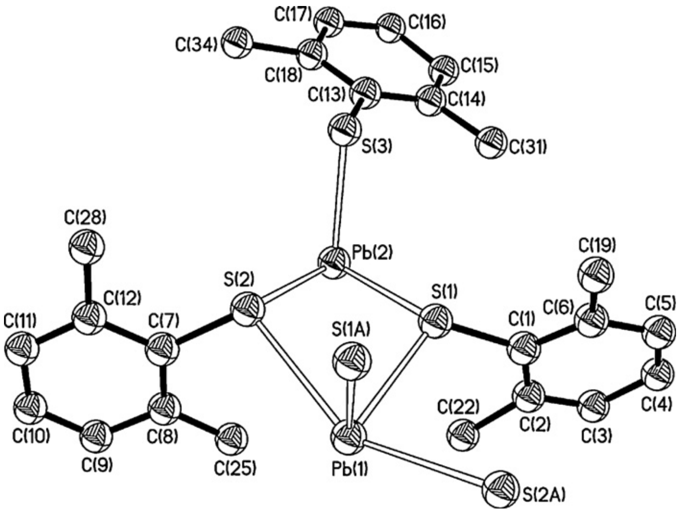
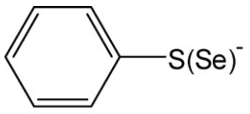


Fig. 4. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(SC_6H_3{}^iPr_2\text{-}2,6)_2$ (Only one C atom of the isopropyl group of the ligand is represented).

In the crystal structure of polymeric $Pb(SPh)_2$ (SPh^-, **7**) the Pb atom forms three strong primary bonds with three sulfur atoms (Pb–S = 2.671(5)–2.837(5) Å) and two weak bonds with two other sulfur atoms (Pb–S = 3.373(6) and 3.519(5) Å; see Table 1) [40]. The coordination polyhedron of the central atom includes three primary S atoms and can be described as a ψ-tetrahedron (**I**) (type AX_3E) with a stereochemically active LP. The bond angles (S–Pb–S 80.5(2)–89.4(1)°) in the polyhedron, which are smaller than the ideal tetrahedral angle of 109.5°, corroborate the ψ-tetrahedral geometry of the Pb atom nearest surrounding in the structure.



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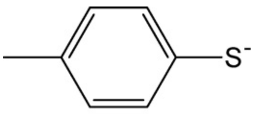
A general structural feature of a series of bis{benzenemonothio(seleno)lates}, in which one or several H atoms of the benzene group are substituted by Me [41], ^{i}Pr [42], CF_3 [43,44], F [45] and NMe_3 [46], is the ψ-tetrahedral coordination geometry around the Pb(II) atoms. The crystal structure of $Pb(SPh\text{-}p\text{-}Me)_2$ ($SPh\text{-}p\text{-}Me^-$ = 4-methylbenzenethiolate anion, **8**) is similar to that of $Pb(SPh)_2$ and is based on polymeric chains formed from vertex-bonded Pb_2S_2 of tetrameric cycles with asymmetric bridging Pb–S bonds [41]. As in the structure of $Pb(SPh)_2$, the nearest neighbors of the Pb atom include three S atoms (Pb–S = 2.650(3)–2.874(3) Å), which form a ψ-tetrahedral (**I**) polyhedron. The geometric parameters of the Pb atoms in both structures are similar, including the lengths of Pb–S secondary bonds (Table 1).



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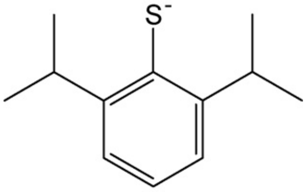
Unlike the polymeric structures of $Pb(SPh)_2$ and $Pb(SPh\text{-}p\text{-}Me)_2$, those of $[Pb(SAr^i)_2]_3$ (SAr^{i-} = $SC_6H_3({}^iPr_2\text{-}2,6)^-$, diisopropylbenzenethiolate anion, **9**) is built from trimers with two end Pb(2) atoms and the central atom Pb(1) (Fig. 4) [42]. The terminal Pb(2) atoms, just like the Pb atoms in the structures of $Pb(SPh)_2$ and $Pb(SPh\text{-}p\text{-}Me)_2$, have a ψ-tetrahedral geometry, while the central atom Pb(1) is located on a two-fold crystallographic axis and has a distorted ψ-trigonal-bipyramidal geometry with a stereochemically active LP in the equatorial plane (Table 1).



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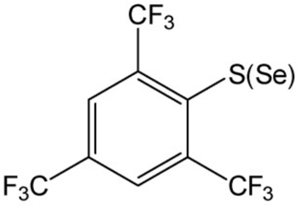
The lengths of the bonds of the Pb(2) atoms to the terminal S(3) atom of the ligand SAr^{i-} (Pb(2)–S(3) 2.554(4) Å) are slightly shorter than those involving the S atoms of bridging ligands (Pb(2)–S(2) 2.673(3) and Pb(2)–S(1) 2.780(3) Å). In the Pb(1) atom polyhedron (type **II**), the axial Pb–S bond distance is substantially longer (2.896(3) Å) than the equatorially bonded one (2.680(3) Å), while the axial and equatorial angles S–Pb(1)–S (147.1(1) and 89.3(2)°) are significantly smaller than the expected values of 180° and 120°. Secondary Pb. . .S bonds are absent (Table 1).

The Pb(II)-selenophenolate complex $[Pb(SeR_f)_2]_2$·3tol (SeR_f^- = $SeC_6H_2(CF_3)_3^-$, 2,4,6-tris(trifluoromethyl)selenophenolate anion, **10**) features a dimeric structure built from $[Pb(SeR_f)_2]_2$ units and solvate toluene molecules [43]. The central part of the dimeric complex exhibits a virtually flat Pb_2Se_2 ring formed by alternating bridging Pb and Se atoms. The distances from the Pb atom to the terminal Se atom are substantially shorter than the bridging bonds (Table 1). Four F atoms from CF_3-groups of three SeR_f^--ligands appear to interact with the Pb atom in the vicinity of the LP (Pb–F 3.057(5)–3.142(5) Å).



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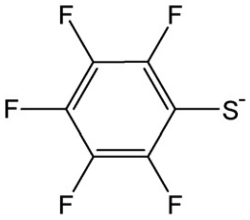
Unlike the dimeric selenium complex which crystallizes with three solvate toluene molecules, the thiophenolate analog was obtained as a monomeric complex $[Pb(SR_f)_2(thf)]$ (SR_f^-, **10**) containing a coordinated thf molecule [44]. The Pb atom forms strong bonds with the S atoms from two thiophenolate ligands (Pb–S 2.639(1) Å) as well as a strong coordination bond with the oxygen atom from thf (Pb–O 2.495(10) Å). Similarly to the Se compound, four F atoms from the CF_3-groups appear to interact with the Pb ion (3.211(4) and 3.352(4) Å). These secondary Pb. . .F bonds are significantly longer than similar bonds in the selenophenolate analog (Table 1).

Two crystallographically independent Pb atoms are present in the layered structure of $Pb(SC_6F_5)_2$ ($SC_6F_5^-$, **11**) [45]. The Pb(1) atoms are located at a crystallographic inversion center and are each surrounded by six S atoms with the Pb–S distances in the range 2.971(2)–3.036(2) Å forming a distorted octahedron. The LP of the Pb(1) atom is stereochemically inactive. The Pb(2) atoms are each coordinated by three S atoms. The Pb(2)–S bond lengths vary from 2.704(2) to 2.737(3) Å and are substantially shorter than the Pb(1)–S bond lengths. Aside from the primary bonds with S atoms, the Pb(2) atoms form secondary Pb. . .F bonds with three F atoms (Pb–F 2.968(6)–3.245(6) Å) and with two more remote F atoms at distances 3.472(7) and 3.514(6) Å. The $Pb(1)S_6$ and $Pb(2)S_3$ polyhedra form a layered structure through μ-S bridges.



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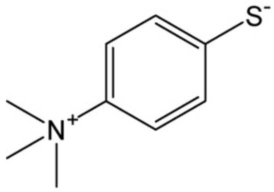
Most charged Pb(II) benzenethio(seleno) complexes are anionic complexes but a cationic thiolate complex $[Pb(tab)_3](ClO_4)_2$ (tab = $^-SC_6H_4NMe_3^+$, 4-(trimethylammonio)-benzenethiolate zwitterion; **12**) has also been prepared [46]. The structure is built from discrete complex $[Pb(tab)_3]^{2+}$ cations and ClO_4^- anions. In the cation the metal atom is coordinated by three S atoms (Pb–S 2.683(3)–2.763(3) Å) from the three tab ligands with formation of the coordination polyhedron of type **I**. Aside from the primary bonds with S atoms, the Pb atom has secondary interactions with the S atoms from two tab ligands of the adjacent cation (Pb–S 3.424(3)–3.503(3) Å). The latter are responsible for formation of cationic chains with ClO_4^- anions located between them.



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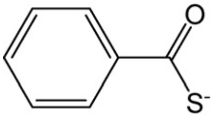
Discrete anionic trigonal-pyramidal Pb(II) thio(seleno)late complexes have been described [47,48]. The isostructural compounds $[AsPh_4][Pb(EPh)_3]$ (EPh^-, E = S, Se, **7**) contain discrete cations $[AsPh_4]^+$ and complex anions $[Pb(EPh)_3]^-$ [47]. The $[Pb(EPh)_3]^-$ anions have Pb(II) atoms coordinated by three S or Se atoms with formation of trigonal-pyramidal (ψ-tetrahedral) coordination polyhedra that correspond to the VSEPR model for AX_3E (**I**). As seen from Table 1, two distances Pb–S(Se) are close to each other and slightly smaller than the third distance. One of the E–Pb–E angles in the polyhedron is substantially larger than two others, which was attributed to steric repulsion between the ligands.

The coordination geometry of the Pb atom in the structure of $[N^nPr_4][Pb(SPh)_3]$, as in the structures of $[AsPh_4][Pb(EPh)_3]$, is trigonal-pyramidal (ψ-tetrahedral) [48]. The bond lengths Pb–S (Pb–S 2.633(3)–2.696(3) Å) and the S–Pb–S bond angles (89.7(1)–102.7(1)°) in the structure of $(N^nPr_4)Pb(SPh)_3$ have slightly larger values than the corresponding values in $[AsPh_4][Pb(SPh)_3]$ (Table 1).

Lead(II) thiobenzoate, like Pb(II) benzenethiolate, is of interest as a precursor for producing PbS nanoparticles. The crystal structures of neutral lead(II) bis(thiobenzoate) [49] and an anionic thiobenzoate complex [50] were determined. The structure of $Pb\{S(O)CPh\}_2$($S(O)CPh^-$, **13**) contains two independent thiobenzoate ligands coordinated to Pb(II) through the S atoms (Pb–S 2.764(4)–2.831(4) Å) [49]. The Pb atom also forms weak interactions with oxygen atoms from the thiobenzoate ligands (Pb–O 2.77(1) and 2.85(1) Å), which indicates a weak chelate effect. Each Pb atom is simultaneously bridged to an adjacent Pb atom via S atoms (Pb–S 3.022(4) and 3.173(4) Å) forming a dimeric unit. Both μ-S atoms bind different Pb atoms so that dimeric chains result. The Pb(II) ion is coordinated by five S atoms and is considered to be a distorted trigonal bipyramid. However, according to the VSEPR model, the coordination polyhedron of the Pb atom should be of type **I** and include only the shorter Pb–S bonds (S(1), S(2) and the bridging $S(1^*)$ atom). Three O atoms and two S atoms surround the LP void and form secondary bonds with the central atom (Table 1).



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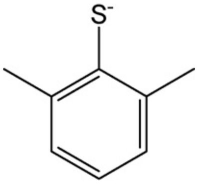
The crystal structure of the anionic thiobenzoate complex $[AsPh_4][Pb\{S(O)CPh\}_3]\cdot(CH_2Cl_2)$ is built from discrete $[AsPh_4]^+$ cations and complex $[Pb\{S(O)CPh\}_3]^-$ anions with CH_2Cl_2 present as a lattice solvent [50]. The Pb atom is bonded to three thiobenzoate ligands with strong Pb–S bonds in the range of 2.706(3)–2.764(3) Å, which give rise to a type **I** coordination polyhedron. The Pb–O distances vary from 2.879(6) up to 3.113(6) Å. Although the Pb–O distances are significantly shorter than the sum of van der Waals radii of Pb and O atoms (3.50 Å) [23], they are far longer than the primary Pb–O bonds found in the structures of Pb(II) carboxylates [19] and, therefore, were assigned as secondary bonds.

2.2.2. *Mixed ligand bis(benzenethiolates)*

Unlike $Pb(SPh)_2$, $Pb(2,6\text{-}Me_2SPh)_2$ ($2,6\text{-}Me_2SPh^- = 2,6\text{-}Me_2C_6H_3S^-$, **14**) is very soluble in a number of organic solvents, including thf, $CHCl_3$, CH_2Cl_2, tol and py. This property was used for synthesis and study of the crystal structures of the $Pb(2,6\text{-}Me_2SPh)_2$ adducts with py, 4,4′-bpy and pyr giving $Pb\{(2,6\text{-}Me_2SPh)_2(py)_2\}$, $Pb\{(2,6\text{-}Me_2SPh)_2(4,4'\text{-}bpy)\}\cdot0.5CH_2Cl_2$ and $Pb\{(2,6\text{-}Me_2SPh)_2(pyr)\}$ [51].

In the monomeric structure of $Pb\{(2,6\text{-}Me_2SPh)_2(py)_2\}$, the Pb atom is bonded to two S atoms from two *cis*-thiolate groups (Pb–S 2.6078(9) and 2.6079(9) Å) and two N atoms of *trans*-py ligands (Pb–N 2.689(3) and 2.695(3) Å). The coordination polyhedron is described as type **II** with S(1), S(2) and LP in the equatorial positions (<S(1)–Pb–S(2) 89.31(3)°) and the N(1) and N(2) atoms in the axial positions (<N(1)–Pb–N(2) 178.58(9)°) in agreement with VSEPR predictions (Table 1).



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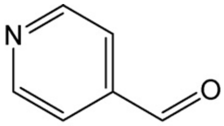
In $Pb\{(2,6\text{-}Me_2SPh)_2(4,4'\text{-}bpy)\}\cdot0.5CH_2Cl_2$, which contains two crystallographically independent Pb atoms, the Pb(1)–S, Pb(2)–S and Pb(2)–N(2) distances have values close to corresponding values in $Pb\{(2,6\text{-}Me_2SPh)_2(py)_2\}$. In contrast, the Pb(1)–N(2) and Pb(1)–N(1^i) bond lengths differ substantially as from each other (2.652(7) Å vs. 2.814(7) Å, respectively) as well as from those in $Pb\{(2,6\text{-}Me_2SPh)_2(py)_2\}$. The bond Pb(1)–N(1^i) distance should be considered as a secondary bond.

The Pb(1) and Pb(2) atoms in $Pb\{(2,6\text{-}Me_2SPh)_2(4,4'\text{-}bpy)\}\cdot0.5CH_2Cl_2$ have different coordination geometries in their first coordination spheres. The Pb(2) atom, with geometric parameters very close to those in $Pb\{(2,6\text{-}Me_2SPh)_2(py)_2\}$, has the same ψ-trigonal-bipyramidal configuration, while Pb(1) can be described as type **I** (Table 1). The 4,4′-bpy ligand acts as a bridging ligand between adjacent Pb atoms resulting in formation of two independent polymer chains built by alternately 4,4′-bpy and lead thiolate units.

The compound $Pb\{(2,6\text{-}Me_2SPh)_2(pyr)\}$ also has a chain structure [51]. The inner coordination sphere of the Pb atom, like Pb(1) in $Pb\{(2,6\text{-}Me_2SPh)_2(4,4'\text{-}bpy)\}\cdot0.5CH_2Cl_2$, is formed by two S atoms and the N(2) atom, and the geometrical parameters are similar. The Pb atom forms a strong bond with N(2) (2.614(9) Å), while the bond to N(1^i) (2.848(9) Å) is rather weak. This is comparable to the Pb(1)–N(1^i) bond (2.814(7) Å) in $Pb\{(2,6\text{-}Me_2SPh)_2(4,4'\text{-}bpy)\}\cdot0.5CH_2Cl_2$. Similarly, the coordination polyhedron can also be described as type **I** (Table 1).

The non-substituted lead(II) phenylthiolate pyridine adduct $[Pb(SPh)_2]_2(py)$ of the composition 2:1 displays a structure substantially different from that of $Pb\{(2,6\text{-}Me_2SPh)_2(py)_2\}$ [51]. The polymeric chain contains two independent Pb centers, each coordinated by five S atoms. Two *cis*-S atoms form shorter Pb(1)–S bonds (2.696(2) and 2.699(2) Å) than the other three S atoms (2.993(2), 3.000(2) and 3.268(1) Å). According to [51], the coordination polyhedron of the Pb(1) atom is a distorted square pyramid with a vacant position occupied by a stereochemically active LP. The Pb(2) atom forms three short Pb–S bonds (Pb(2)–S 2.720(2)–2.836(2) Å) and two longer interactions (Pb(2)···S 3.212(2) and 3.422(1) Å). The sixth coordination position around the Pb(2) atom is occupied by the weakly bonded N(1) atom from py (Pb(2)–N(1) 2.842(5) Å). The authors mention that the absence of an ‘open’ coordination position around the distorted Pb(2) environment indicates to the stereochemical inactivity of the LP. According to the VSEPR model, the coordination polyhedron of the Pb(1) atom should have a ψ-trigonal-bipyramidal geometry, while the Pb(2) atom polyhedron should be described as type **I** (Table 1).

In [52] the compound $Pb(2,6\text{-}Me_2SPh)_2$ was used as a structural unit for synthesis of adducts with 4-substituted pyridine: $Pb\{(2,6\text{-}Me_2SPh)_2(pyC(H)O)\}$ (pyC(H)O = 4-pyridinecarboxaldehyde, **15**), $Pb\{(2,6\text{-}Me_2SPh)_2(pyOMe)\}$ (pyOMe = 4-methoxypyridine, **16**) and $Pb\{(2,6\text{-}Me_2SPh)_2(pyNMe_2)\}$ ($pyNMe_2$ = 4-dimethylaminopyridine, **17**), which were investigated by X-ray crystallography.



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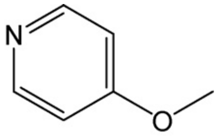

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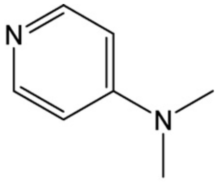

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In $Pb\{(2,6\text{-}Me_2SPh)_2(pyC(H)O)\}$ (Fig. 5) the Pb atom is bonded to two thiolate S atoms (2.6636(16) and 2.6256(17) Å) and the N(1) atom from pyC(H)O (2.571(5) Å) [52]. The Pb atom is also bonded to the thiolate ion of the adjacent adduct giving rise to a dimer. The bridging Pb–S(1A) bond at a distance of 3.1742(16) Å can be considered as secondary, while the coordination polyhedron can be represented as being of type **I**.

The same dimeric structure **I** observed for $Pb\{(2,6\text{-}Me_2SPh)_2(pyC(H)O)\}$ is found for $Pb\{(2,6\text{-}Me_2SPh)_2(pyOMe)\}$. The main differences are that the distance Pb–N(1) 2.497(2) Å is slightly smaller, while the length of the bridging Pb–S bond in the dimer is increased compared to the corresponding bond in

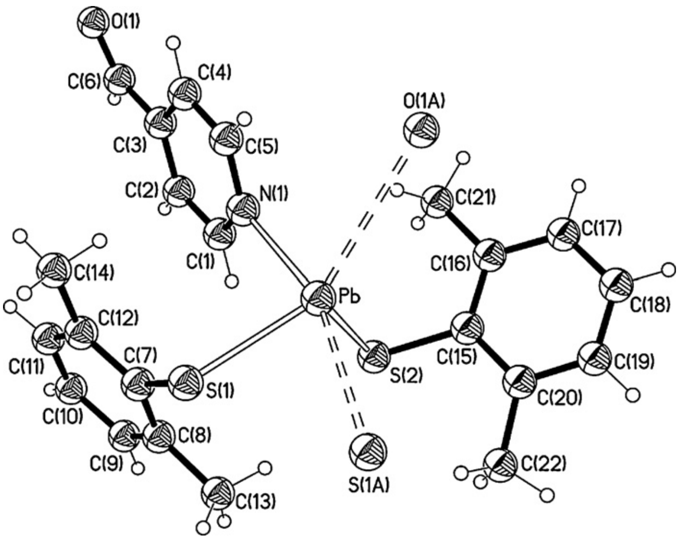


Fig. 5. ORTEP drawing of the coordination environment of the Pb(II) atom in Pb{(2,6-$Me_2C_6H_3S)_2$(pyC(H)O)}.

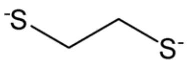
Pb{(2,6-$Me_2SPh)_2$(pyC(H)O)} (3.2671(6) Å vs. 3.1742(16) Å). The Pb atom is also considered to be type **I**.

Unlike the dimeric structures of the pyC(H)O and pyOMe adducts, Pb{(2,6-$Me_2SPh)_2(pyNMe_2)$} is monomeric. The Pb atoms are each bonded to the pyridine N atom (Pb–N(1) 2.432(2) Å) and two thiolate ions (Pb–S = 2.6070(11), 2.6211(12) Å) with formation of center of type **I**. The values of bond angles N–Pb–S and S–Pb–S (86.69(9)–90.87(9)°) are smaller than those of an ideal tetrahedron (109.5°), corroborating the assignments as a ψ-tetrahedron. Secondary Pb. . .S bonds are absent.

3. Lead(II) polythio(seleno)complexes

3.1. Lead(II) dithio(seleno)lates

The ethane-1,2-dithiolate anion, $S_2C_2H_4{}^{2-}$ (edt^{2-}, **18**) is the simplest dithiolate ligand. In the polymeric structure of Pb(edt) each Pb atom is chelated by an edt^{2-} ligand, forming Pb(edt) units in which the Pb–S bonds (2.655(3) and 2.660(3) Å) are rather strong [53]. In addition, the Pb atom interacts with four dithiolate S atoms from the adjacent Pb(edt) units with the Pb–S distances falling in the range of 3.032(3)–3.584(3) Å. The coordination geometry of the Pb atom can be formally thought of as a strongly distorted octahedron; however, the presence of long Pb. . .S interactions (3.376(3) and 3.584(3) Å) and a large angle between them (128.17(8)°) prompted the authors to describe the Pb atom polyhedron as a ψ-pentagonal bipyramid with a stereochemically active LP in the equatorial plane (type AX_6E, **V**, ψ-PBP_{eq}). The coordination polyhedron defined by the ligands of the inner coordination sphere of the Pb(II) ion can be represented as type **II** in compliance with the VSEPR theory. This places the strongly bonded S(1) and S(2) atoms (<S(1)–Pb–S(2) 95.49(6)°) and LP in equatorial positions and the $S(1)^b$ and $S(2)^a$ atoms (3.032(3) and 3.056(3) Å; <$S(1)^b$–Pb–$S(2)^a$ 136.61(6)°) in axial positions. The most remote $S(2)^d$ and $S(1)^c$ atoms located near the LP form secondary bonds with the central atom (Table 2).



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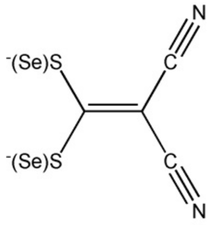
Hummel and coworkers have synthesized and structurally investigated a large group of Pb(II) complexes with dicyanoethylenedithiolate ligands [54–58]. The crystal structures of two polymorphs (α- and β-) of neutral Pb(dedt) ($dedt^{2-} = S_2C{=}C(CN)_2{}^{2-}$, **19**; has also been abbreviated as *i*-mnt^{2-}) have been described [54]. The structure of the α-form is built from centrosymmetrical dimers $[Pb_2(dedt)_2]$ with substantially different Pb–S bond lengths. The Pb–S(2) bond length of 2.66(1) Å corresponds to a strong covalent bond, while the Pb(II) bonds with bridging atoms S(1e) and S(1) are substantially weaker (2.90(1) and 2.95(1) Å). Aside from the bonds to the nearest S atoms, the Pb atom also forms contacts with two more remote S atoms (3.31(1) and 3.51(1) Å) and two N atoms at distances of 2.68(4) Å and 2.74(4) Å (Table 2). In terms of the VSEPR model the coordination polyhedron in α-Pb(dedt) can be described as type **II** (Table 2).



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β-Pb(dedt) contains two crystallographically independent Pb atoms and two non-equivalent $dedt^{2-}$ ligands [54]. The Pb(1) atoms located on the two-fold axis are symmetrically chelated by the S atoms from a $dedt^{2-}$ ligand (Pb(1)–S 2.819(3) Å). The Pb(1) atom also interacts with the S atoms from two adjacent $dedt^{2-}$ ligands (Pb(1)–S 2.993(3) Å) and four N atoms (Pb(1)–N(1) 2.869(9) and Pb(1)–N(2) 3.23(1) Å). Excluding the N atoms forming secondary bonds, the coordination polyhedron is type **II**. The axial and equatorial S–Pb–S angles are 156.9(1) and 64.2(1)°, respectively (Table 2). The Pb(2) atom occupying a general position in the structure is also chelated by the S atoms of a $dedt^{2-}$ ligand (Pb(2)–S 2.769(6)–3.069(12) Å) and forms a bond with the S(1) atom (3.093(5) Å) of the adjacent unit with formation of a centrosymmetrical dimer. Similar to Pb(1), the coordination polyhedron of the Pb(2) is type **II** (Table 2).

The structures of a number of anionic Pb(II) complexes with dicyanoethylenedithio(seleno)late ligands were investigated. In $[AsPh_4]_2[Pb(dedt)_2]$ the Pb atom is chelated by the S atoms from both $dedt^{2-}$ ligands [55]. The Pb atom forms substantially asymmetric Pb–S bonds with one of these ligands (Pb–S 2.689(4) and 2.978(4) Å), while the other ligand is far less asymmetrical (2.735(5) and 2.845(4) Å). The $Pb(dedt)_2{}^{2-}$ units are linked via the bridging S atom (Pb–S = 3.355(5) Å) into centrosymmetric dimers with the Pb. . .Pb distance being 3.7230(7) Å. The coordination polyhedron is described as a square pyramid with a stereochemically active LP in the vertex. According to the VSEPR model, the coordination polyhedron of the Pb atom in $[AsPh_4]_2[Pb(dedt)_2]$ should correspond to type **II** with the LP in one of the equatorial positions (Table 2).

The crystal structure of $[AsPh_4]_2[Pb(dedt)_2]$ has been redetermined with higher accuracy ($R = 0.028$) [59]. According to that report, the Pb atoms in the dimeric complex anion $[Pb(dedt)_2]_2{}^{4-}$ are six-coordinate with three short Pb–S and three long distances (Table 2). The Pb. . .Pb distance is 3.697 Å, slightly smaller than the corresponding distance 3.7230(7) Å found in [55]. The geometric parameters of the Pb atom enable one to represent its geometry in compliance with the VSEPR model as type **II**.

The compound $[AsPh_4]_2[Pb(deds)_2]$ ($deds^{2-} = Se_2C{=}C(CN)_2{}^{2-}$, **19**) is isostructural to its dithiolate analog $[AsPh_4)_2[Pb(dedt)_2]$ and the polyhedron of the Pb atom in the structure have the same coor-

Table 2
Stereochemistry of lead(II) polythio(seleno)lates.

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	2	3	4	5	6	7	8	9
Pb(II) dithio(seleno)lates								
Pb(edt)	6 (4+*E*)+2	ψ-TBP **II**	3.032(3) S(1)^{b} 3.056(3) S(2)^{a}	2.655(3) S(2) 2.660(3) S(1)	136.61(6)	95.49(6)	3.376(3) S(2)^{d} 3.584(3) S(1)^{c}	[53], DISWIL
α-Pb(dedt)	7 (4+*E*)+3	ψ-TBP **II**	2.68(4) N(2g) 2.90(1) S(1e)	2.66(1) S(2) 2.95(1) S(1)	138.7(8)	81.6(3)	2.74(4) N(1c) 3.31(1) S(2b) 3.510(1) S(1b)	[54], GIGBIH
β-Pb(dedt)								[54], GIGBON
Pb(1)	8 (4+*E*)+4	ψ-TBP **II**	2.993(3) S(21) 2.993(3) S(21^{i})	2.819(3) S(1) 2.819(3) S(1^{i})	156.9(1)	64.2(1)	2.869(9) N(1) 2.869(9) N(1^{i}) 3.23(1) N(21) 3.23(2) N(21^{i})	
Pb(2)	8 (4+*E*)+4	ψ-TBP **II**	2.976(8) S(22) 3.093(5) S(1)	2.769(6) S(21) 3.069(12) S(22^{i})	143.9(2)	77.66(14)	2.93(1) N(22) 3.05(1) N(21) 3.05(1) N(1^{i}) 3.404(9) S(22^{ii})	
[$AsPh_4$]$_2$[Pb(dedt)$_2$]	5 (4+*E*)+1	ψ-TBP **II**	2.845(4) S(21) 2.978(4) S(12)	2.689(4) S(11) 2.735(5) S(22)	143.83(17)	90.91(17)	3.355(5) S(12^{i})	[55], SARMUT
[$AsPh_4$]$_2$[Pb(dedt)$_2$]	6 (4+*E*)+2	ψ-TBP **II**	2.857(1) S(1) 3.003(1) S(3^{i})	2.704(1) S(3) 2.764(1) S(2)	141.91(2)	90.21(3)	3.268(1) S(4^{i}) 3.597(1) S(3^{ii})	[59], SARMUT01
[$AsPh_4$]$_2$[Pb(deds)$_2$]	5 (4+*E*)+1	ψ-TBP **II**	2.912(4) Se(21) 3.059(3) Se(11)	2.839(3) Se(12) 2.981(3) Se(22)	143.5(1)	92.11(8)	3.493(3) Se(11^{i})	[56], KUHZAH
[K(18C6)]$_2$[Pb(dedt)$_2$]	6 (4+*E*)+2	ψ-TBP **II**	2.817(2) S(4) 2.8874(19) S(2)	2.6779(19) S(3) 2.776(2) S(1)	142.08(6)	94.42(7)	3.104(6) O(2A) 3.429 (2) S(1A)	[60], SEGJIY
[K(18C6)]$_2$[Pb(dedt)$_2$]	6 (4+*E*)+2	ψ-TBP **II**	2.8611(19) S(3) 2.873(2) S(2)	2.6912(18) S(4) 2.7321(19) S(1)	136.61(6)	95.49(6)	3.368(2) S(4^{i}) 3.453(5) O(10^{i})	[60], VAZXEA
K_2[Pb(dedt)$_2$]·$2H_2O$	8 (4+*E*)+4	ψ-TBP **II**	2.88(1) S(2) 2.88(1)) S(2^{i})	2.88(1) S(1) 2.88(1) S(1^{i})	113.6(3)	113.6(3)	3.46(1) S(2^{ii}) 3.46(1) S(2^{iii}) 3.47(1) S(1^{ii})) 3.47(1) S(1^{ii1})	[57], KAJMUD
Pb(mnt)	8 (3+*E*)+5	ψ-T **I**	2.797(9) S(1) 2.807(6) S(2) 2.853(9) S(1^{i})		66.5(2) 144.6(3) 78.1(2)		2.82(2) N(1) 2.89(2) N(2) 3.00(2) N(1^{i})) 3.408(6) S(2^{i}) 3.531(6) S(2^{ii})	[58], SEHDOY
[$AsPh_4$]$_2$[Pb(mnt)$_2$]	5 (4+*E*)+1	ψ-TBP **II**	2.875(6) S(11) 2.903(6) S(22)	2.694(6) S(21) 2.706(6) S(12)	152.6(2)	94.9(2)	3.616 S(22^{i})	[58], SEHDUE
[Pb_2(Bmm^{Me})$_5$](ClO_4)$_4$·H_2O_6								
Pb(1)	6 (5+*E*)+1	ψ-O **III**	2.7573(14) S(4)	2.8162(17) S(2) 2.9239(15) S(1) 2.9588(16) S(3) 3.1418(16) S(10)	86.56(4) 78.43(4) 82.61(4) 79.29(4)	84.78(5) 86.00(5) 87.19(5) 97.52(5) $\Sigma = 355.49$	3.164(6) O(4)	[61], LIQWAK

Pb(II) mixed ligand dithiolates								
$PbCl_2$(mbit)	6 (4+*E*)+2	ψ-TBP **II**	2.864(3) Cl(1^i) 2.930(3) S(1)	2.755(4) Cl(2) 2.801(4) S(2^i)	162.16(13)	91.6(2)	3.031(3) Cl(1) 3.461(5) Cl(2^i)	[62], VUTSIM
[Pb{S(O)CPh}$_2$ {S_2CP(Cy)$_3$}]	7 (4+*E*)+3	ψ-TBP **II**	2.626(5) O(1) 2.885(2) S(3)	2.626(3) S(2) 2.755(2) S(1)	133.0(1)	90.34(7)	3.002(6) O(2) 3.350(2) S(4) 3.693(2) S(4)^a	[50], POGRAE
Pb(II) trithio- and tetrathiolates								
[(Tm^{Ph})Pb](ClO$_4$)	6 (3+*E*)+3	ψ-T **I**	2.693(2) (S1^i) 2.693(2) S(1) 2.693(2) S(1^{ii})		89.84(7) 89.84(7) 89.84(7)		2.94(3) O(1^{ii}) 2.94(2) O(1) 2.94(2) O(1^i)	[63], EBEXEO
[Pb(Tm^{Ph})$_2$] ·3.5(MeCN)	6 (3+*E*)+3	ψ-T **I**	2.848(1) S(1) 2.848(1) S(1^i) 2.848(1) S(1^{ii})		87.20(2) 87.20(2) 87.20(2)		3.171(1) S(2) 3.171(1) S(2^i) 3.171(1) S(2^{ii})	[64], WOHGUV
Pb(dmit)(dmf)	6 (4+*E*)+2	ψ-TBP **II**	2.610(7) O 3.133(2) S(5^{ii})	2.633(2) S(2) 2.648(2) S(1)	176.8(2)	82.35(7)	3.201(7) O^i 3.495(2) S(5^i)	[65], XOWFIY
Pb_2(S_4Ph)(en)	5 (4+*E*)+1	ψ-TBP **II**	2.95 S(2^i) 3.03 S(1^i)	2.58 S(1) 2.62 S(2)	163.43	74.38	2.90 N(1)	[66], HIXDAU

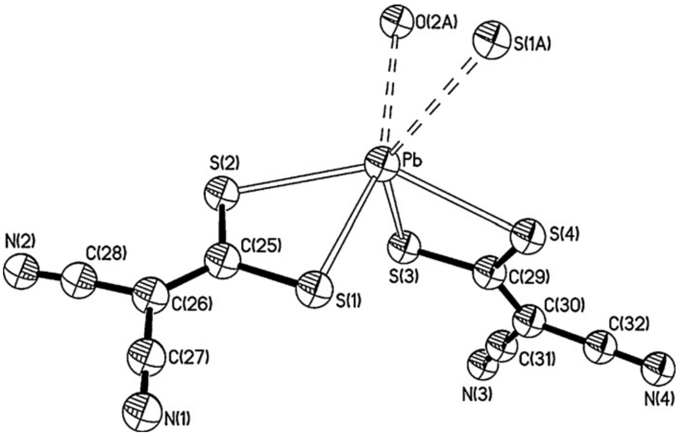


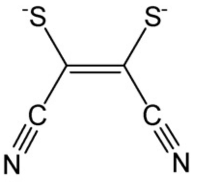
Fig. 6. ORTEP drawing of the coordination environment of the Pb(II) atom in $[K(18C6)]_2[Pb(S_2C=C(CN)_2)_2]$.

dination geometry (type **II**) [56]. The Pb–Se distances are naturally longer than the respective Pb–S distances in $[AsPh_4]_2$[Pb(dedt)$_2$]. The axial and equatorial angles are similar in both structures (Table 2).

The centrosymmetric dimers formed from complex anions [Pb(dedt)$_2$]$^{2-}$ through bridging Pb–S bonds are also observed in the two known structures of [K(18C6)]$_2$[Pb(dedt)$_2$], one of which is polymeric [60]. In the complex anion [Pb(dedt)$_2$]$^{2-}$ the Pb atom is coordinated by two dedt^{2-} ligands. The average values of four primary Pb–S bonds are identical for the two structures (2.789 Å). The bridging Pb. . .S bond lengths in the two structures are slightly different (3.368(2) vs. 3.429 (2) Å). The coordination polyhedra of the Pb atoms in both [K(18C6)]$_2$[Pb(dedt)$_2$] structures were described as distorted square pyramidal with an 'open' position occupied by the LP of the Pb atom. According to the VSEPR model, the coordination polyhedron geometry of the Pb atoms in these structures should correspond to type **II** with the LP of the Pb^{2+} ion in one of the equatorial positions. In the structure of [K(18C6)]$_2$[Pb(dedt)$_2$] (Fig. 6) the S(4) and S(2) atoms (Pb–S(4) 2.817(2) and Pb–S(2) 2.8874(19) Å; <S(4)–Pb–S(2) 142.08(6)°) are located in the axial positions of the polyhedron, while the equatorial plane is formed by the S(3) and S(1) atoms (Pb–S(3) 2.6779(19) and PbS(1) 2.776(2) Å; <S(3)–Pb–S(1) 94.42(7)°) and a stereochemically active LP. The bridging S(1A) atom and the O(2A) atom of the complex cation [K(18C6)]$^+$ form secondary bonds with the Pb atom and are located in the vicinity of the void area assigned to the LP (Table 2).

The structure of K_2[Pb(dedt)$_2$]·$2H_2O$ is slightly different the previously mentioned Pb(II) dithiolate complexes [57]. The Pb atom is located on the two-fold axis and is coordinated by two symmetrical chelate dedt^{2-} ligands with four equal Pb–S bond lengths (Pb–S 2.88(1) Å) which are by 0.1 Å larger than the average value of the bond lengths (2.789 Å) in [K(18C6)]$_2$[Pb(dedt)$_2$] [60]. The anions $[S_2C{=}C(CN)_2]^{2-}$ form a pyramidal geometry about the Pb atom with a stereochemically active LP. The shortest distances from the Pb atom to the S atoms of the adjacent complex are 3.46(1) and 3.47(1) Å.

Neutral and anionic complexes of Pb(II) with 1,2-dicyanoethylene-1,2-dithiolate ligands are described in [58]. In Pb(mnt) (mnt^{2-} = S(NC)C=C(CN)S^{2-}, **20**) the Pb atom, just as in α-Pb(dedt) [54], is chelated by the S atoms from the mnt^{2-} ligand. However, unlike α-Pb(dedt) where the Pb–S bonds are essentially asymmetric, in Pb(mnt) the arrangement is symmetrical (2.797(9) and 2.807(6) Å). The Pb atom also forms a strong bridging bond with the S(1^i) atom (Pb–S(1^i) 2.853(9) Å) of the adjacent Pb(mnt) complex.



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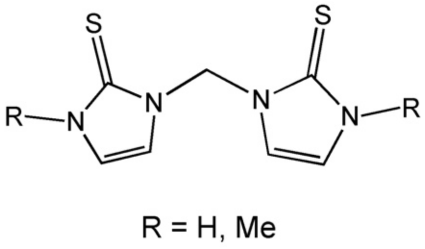
In addition to three covalent Pb–S bonds, the Pb atom forms contacts with three N atoms (2.82(2)–3.00(2) Å) and two relatively distant S atoms (3.408(6) and 3.531(6) Å) from other mnt^{2-} ligands. These contacts are predominantly ionic in character and should be considered as secondary bonds. Taking into account three covalent Pb–S bonds around the Pb atom and a stereochemically active LP, the authors describe the Pb(II) coordination polyhedron as a distorted tetrahedron (PbS_3E). However, the described polyhedron does not comply with the VSEPR model for type **I**, since the S(1)–Pb–S(1^{i}) angle is 144.6(3)°, substantially larger than the ideal tetrahedral value.

The compound $[AsPh_4]_2[Pb(mnt)_2]$ is isostructural to $[AsPh_4]_2[Pb(dedt)_2]$ [55] and adopts a centrosymmetric dimeric structure with a ψ-trigonal-bipyramidal coordination polyhedron [58]. There is a slight difference in the length of the bridging Pb. . .S bond in the dimers (3.616 Å in $[AsPh_4]_2[Pb(mnt)_2]$ vs. 3.355(5) Å in $[AsPh_4]_2[Pb(dedt)_2]$). The axial and equatorial angles in the coordination polyhedron of the Pb atom in $[AsPh_4]_2[Pb(mnt)_2]$ are slightly larger than those of $[AsPh_4]_2[Pb(dedt)_2]$ (Table 2).

The dinuclear lead(II) bis(mercaptoimidazolyl)methane complex, $[Pb_2(Bmm^{Me})_5](ClO_4)_4 \cdot H_2O$ (Bmm^{Me} = 1,1′-methylenebis(1H-imidazole-2(3H)-thione), **21** with R = H) is formed from complex cations $[Pb_2(Bmm^{Me})_5]^{4+}$ built from two $[Pb(Bmm^{Me})_2]^{2+}$ fragments connected via a fifth Bmm^{Me} ligand [61]. The two crystallographically distinct Pb atoms have different coordination environments. The Pb(1) atoms are five-coordinated by the S atoms of the ligands. The coordination geometry of the Pb(1) atom is square-pyramidal (ψ-octahedron (**III**), in accord with the VSEPR model) with the S(4) atom (Pb(1)–S(4) 2.7573(14) Å) in the axial position and four S atoms (Pb(1)–S 2.8162(17)–3.1418(16) Å) in the basal locations. The sixth vacant position of the ψ-octahedron is occupied by a stereochemically active LP. There is also a relatively short contact (3.164(6) Å) from Pb(1) to one of the O atoms of the ClO_4^- anion. The perchlorate ion is located in the vicinity of the void assigned to the LP, which lies directly across from S(4). The Pb(2) atoms are six-coordinated by S atoms (Pb(2)–S 2.7767(16)–3.0661(16) Å). The resulting polyhedron has a distorted geometry with the angles between the *cis*- and *trans*-S atoms falling into the ranges 78–104° and 159–171°, respectively. The geometric parameters of the Pb(2) atom suggest that the LP is stereochemically inactive.



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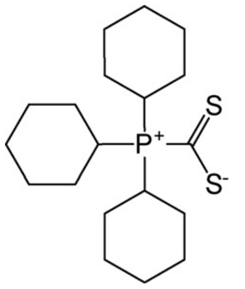
3.1.1. Mixed ligand dithiolates

Although $PbCl_2(mbit)$ (mbit = $1,1^{i}$-methylenebis(3-methylimidazole-2(3H)-thione, **21** with R = Me) contains an essentially identical anion as in $[Pb_2(Bmm^{Me})_5](ClO_4)_4 \cdot H_2O$, the crystal structures of the two compounds differ significantly both in the coordination polyhedra and the supramolecular motifs realized. The polymeric structure of $PbCl_2(mbit)$ [62] is built from distorted octahedral $PbCl_4S_2$ groups bonded through common edges by long bridging Pb–Cl bonds. The closest environment of the Pb atom in the structure is occupied by the S atoms (2.801(4) and 2.930(3) Å) and two Cl^- ions (2.755(4) and 2.864(3) Å). Both Cl ions are bridging as well with the bridge distances being significantly longer (3.031(3) and 3.461(5) Å), giving rise to twisted polymeric Pb–Cl strands. The bridging mbit ligands bind adjacent strands into a polymeric unit. The geometry of the Pb atom is described as a distorted octahedron. According to the VSEPR model, the polyhedron can be represented as type **II** with the Cl(2) and S(2^{i}) atoms and the LP in the equatorial plane (<Cl(2)–Pb–S(2^{i}) 91.6(2)°) and the Cl(1^{i}) and S(1) atoms in the bipyramid axial positions (<Cl(1^{i})–Pb–S(1) 162.16(13)°) (see Table 2).

Unlike the polymeric structure of $Pb\{S(O)CPh\}_2$ [49], the crystal structure of the mixed-ligand lead(II) complex $Pb[\{S(O)CPh\}_2\{S_2CP(Cy)_3\}]$ ($S_2CP(Cy)_3$ = *P*-tricyclohexyldithiocarbonato, **22**) is molecular [50]. Weak interactions (Pb. . .$S(4)^a$ 3.639(2) Å) give rise to a dimeric unit. The central atom is bonded by three S atoms (Pb–S 2.755(2)–2.885(2) Å) and forms a comparatively strong bond an O atom of one of the thiobenzoate ligands (2.626(5) Å), while the other is substantially weaker (3.002(6) Å). The Pb atom forms anisobidentate Pb–S bonds (2.885(2) and 3.350(2) Å) with the $S_2CP(Cy)_3$ ligand. The coordination geometry is considered to be trigonal-pyramidal formed by three primary Pb–S bonds. Taking into account the fact that the Pb–O(1) bond is relatively short (2.626(5) Å), it can be considered as primary. The coordination polyhedron can be represented in this case as type **II** (Table 2) as expected from the VSEPR model.



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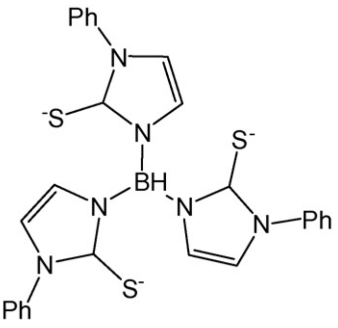
3.2. Lead(II) trithio- and tetrathiolates

Trithiolato and tetrathiolato ligands contain three or four donor S centers. The structure of $[(Tm^{Ph})Pb](ClO_4) \cdot (MeCN)$ (Tm^{Ph-} = tris(2-mercapto-1-phenylimidazolyl)hydroborate anion, **23**) was investigated in view of the problem of lead poisoning and its interaction with proteins, in particular, with 5-aminolevulinate dehydratase (ALAD) [63]. The Pb atom in $[(Tm^{Ph})Pb]^+$ is coordinated by three donor S atoms located at equal distances from the central atom (2.693(2) Å). The nearest contacts of the Pb atom with the O(1) atoms of disordered ClO_4^- anions are at 2.94(2) Å. The crystal structure of the complex cation $[(Tm^{Ph})Pb]^+$ is similar to the active center of Pb(II)-ALAD [67]. Both have the trigonal-pyramidal geometry with very similar average Pb–S bond lengths (2.7 and 2.8 Å, respectively).



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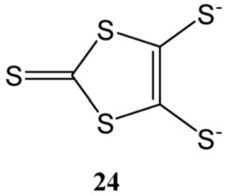
In $[Pb(Tm^{Ph})_2]\cdot3.5(MeCN)$ each Pb atom coordinates two $(Tm^{Ph})^-$ ligands [64]. One of them is normally η^3-coordinated to the Pb atom, as in the case of $[(Tm^{Ph})Pb]^+$, while the second $(Tm^{Ph})^-$ ligand is coordinated with an inverted η^4-configuration. The η^3-coordinated $(Tm^{Ph})^-$ ligand forms longer bonds (2.848(1) Å) than the corresponding distances in $[(Tm^{Ph})Pb]^+$. The latter Pb–S distances are substantially shorter than the Pb–S bond lengths with the “inverted” η^4-ligand (3.171(1) Å). The authors noted that, aside from the interaction with three S atoms of the “inverted” ligand, the central atom had also a contact along the triple axis with the H atom of this ligand (Pb. . .H–B(2) 2.39 Å). Taking into account a substantial difference in the Pb–S bond lengths for η^3- and η^4-coordinated ligands, the authors describe the structure of $[Pb(Tm^{Ph})_2]\cdot3.5(MeCN)$ as strongly-bonded ionic pairs $[(Tm^{Ph})Pb][Tm^{Ph}]$. The coordination polyhedron of the Pb atom, as in $[(Tm^{Ph})Pb][ClO_4]\cdot(MeCN)$, can be represented as type **I** with three primary and three secondary Pb–S bonds (Pb–S 2.848(1) Å; Pb. . .S 3.171(1) Å) in accordance with the VSEPR model. The bond angles S–Pb–S are similar for both structures (Table 2).

The 2-thioxo-1,3-dithiole-4,5-dithiolato ligand contains five S atoms, however, only three of them participate in coordination with Pb(II). In the structure of Pb(dmit)(dmf) ($dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate dianion, **24**) the Pb atom is coordinated by two chelating S atoms of the dithiolate fragment of the $dmit^{2-}$ ligands, two S atoms from thiocarbonyl groups of adjacent complexes and two oxygen atoms from the dmf ligands [65]. The Pb–S bond lengths to the dithiolate fragments of the $dmit^{2-}$ ligand are very similar (2.633(2) and 2.648(2) Å), while the distances to the S atoms from the thiocarbonyl groups are substantially longer (3.133(2) and 3.495(2) Å). The central atom forms a comparatively strong bond with the O atom from the dmf ligand (2.610(7) Å) and a rather weak bridging bond with the O^i atom from the dmf ligand of the adjacent complex (3.201(7) Å). The coordination geometry of the Pb atom is described as distorted octahedral. According to the VSEPR model, the coordination polyhedron can be represented as type **II** with the chelate atoms S(1) and S(2) and LP in the equatorial plane (<S(1)–Pb–S(2) 82.35(7)°) and the O and $S(5^{ii})$ atoms in the axial positions of the bipyramid (<O–Pb–$S(5^{ii})$ 176.8(2)°). The Pb(dmit)(dmf) units form a polymeric structure through the Pb. . .O and Pb. . .S(5) interactions.



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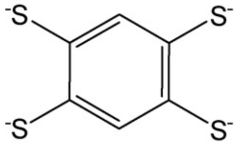
The crystal structure of the mixed ligand lead(II) complex with 1,2,4,5-benzenethiolate and ethylenediamine, $Pb_2(S_4Ph)(en)$ (S_4Ph^{4-} = 1,2,4,5-$S_4C_6H_2{}^{4-}$, **25**) was solved by synchrotron X-ray powder diffraction [66]. In this structure the Pb atoms form strong chelate bonds with the S(1) and S(2) atoms (Pb–S(1) 2.58 and Pb–S(2) 2.62 Å) from the ligand. In their turn, all the metal atoms form bridging bonds with the $S(1^i)$ and $S(2^i)$ atoms of adjacent $Pb_2(S_4Ph)(en)$ units. The lengths of Pb–S bridging bonds are equal to 2.95 and 3.03 Å, respectively. The Pb atoms are connected through the bridging en molecules with the Pb–N distance equal to 2.90 Å. The coordination environment of the Pb atom is described as square pyramidal S_4N. According to the VSEPR model, the coordination polyhedron of the Pb atom in the structure of $Pb_2(S_4Ph)(en)$ corresponds to the type **II** (Table 2).



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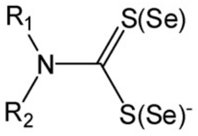
4. Lead(II) dialkyldithio(seleno)carbamates and alkylxanthates

4.1. Dialkyldithio(seleno)carbamates

Lead(II) dialkyldithio(seleno)carbamates have found extensive application in different technologies ranging from use as collecting reagents for flotation of sulfide minerals to production of nanocrystalline PbS and PbSe semiconductor materials. This class of compounds has been investigated quite extensively. Several structures of lead(II) dialkyldithiocarbamates, $Pb(S_2CNR_2)_2$, (**26**) including both homoleptic and heteroleptic examples have been reported ($R_1 = R_2$ = Me [68], Et [69], ^{i}Pr [71], ^{n}Pr [72], Pent [8], Cy [8]); (R_1 = Et; $R_2 = {}^i$Pr [73,74], Cy [75]). The crystal structure of the only lead(II) diethylselenocarbamate, $Pb(Se_2CNEt_2)_2$ was also investigated [70]. In all structural investigated dialkyldithio(seleno)carbamates, as well as in bis(pyrrolidinecarbodithiolato)lead(II), $Pb(pdtc)_2$ [77], the Pb(II) polyhedron has a ψ-trigonal-bipyramidal configuration (type **II**) (Table 3).

The crystal structure of $Pb(Me_2dtc)_2$ contains monomeric complexes [68]. The Pb atom is located on the two-fold crystallographic axis and is chelated by two crystallographically-equivalent dithiocarbamate ligands with slightly asymmetric bond lengths (2.779(5) and 2.873(6) Å). The complexes $[Pb(Me_2dtc)_2]$ are located along the *c* crystallographic axis in such a way that each Pb atom forms moderate intermolecular contacts with two S atoms of the next complex (Pb···S 3.361(6) Å), giving rise to a chain-like structure.



$R_1 = R_2$ = Me, Et, ^{n}Pr, ^{i}Pr, Pent, Cy
R_1 = Et; $R_2 = {}^i$Pr, Cy

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On the basis of the analysis of Pb and S atom coordinates on electron density two-dimensional projections, the structure of lead(II) diethyldithiocarbamate, $Pb(Et_2dtc)_2$ ($Et_2dtc^- = S_2CNEt_2{}^-$, **26**) was described as a dimer [76]. Complete determination of the structure of $Pb(Et_2dtc)_2$ was described in [69]. The crystal structure of $Pb(Et_2dtc)_2$, like that of $Pb(Me_2dtc)_2$, is built from monomeric complexes. All four S atoms from the two carbamate ligands chelate the central atom. The distances are somewhat asymmetric with two being somewhat short and the other two being more than

Table 3
Stereo chemistry of lead(II) dialkyldithio(seleno)carbamate, alkylxanthate and mixed ligand complexes.

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	2	3	4	5	6	7	8	9
Pb(II) dialkyldithio(seleno)carbamates								
Pb(Me$_2$dtc)$_2$	6 (4+*E*)+2	ψ-TBP **II**	2.873(6) S(1) 2.873(6) S(1*)	2.779(5) S(2) 2.779(5) S(2*)	126.8(2)	105.5(2)	3.361(6) S(2^{i}) 3.361(6) S(2^{*i})	[68], MTCBPB
Pb(Et$_2$dtc)$_2$	6 (4+*E*)+2	ψ-TBP **II**	2.885(11) S(2) 2.940(10) S(4)	2.744(9) S(1) 2.786(9) S(3)	133.2(4)	96.2(4)	3.445 S(1A) 3.553 S(3A)	[69], PBETCA01
Pb(Et$_2$dsc)$_2$	6 (4+*E*)+2	ψ-TBP **II**	2.952(3) Se(4) 3.013(3) Se(2)	2.827(3) Se(3) 2.849(3) Se(1)	141.90(11)	97.48(10)	3.473(3) Se(3A) 3.617(3) Se(1A)	[70], BOKMUJ
Pb(^{i}Pr$_2$dtc)$_2$	6 (4+*E*)+2	ψ-TBP **II**	2.843(5) S(2) 2.859(5) S(4)	2.673(4) S(1) 2.681(4) S(3)	138.6(2)	97.7(2)	3.513(4) S(3^{i}) 3.541(4) S(1^{i})	[71], IPTCPB
Pb(^{n}Pr$_2$dtc)$_2$ Pb(A)	6 (4+*E*)+2	ψ-TBP **II**	2.926(3) S(3A) 2.960(2) S(2A)	2.711(3) S(1A) 2.763(2) S(4A)	136.2(1)	80.3(1)	3.155(3) S(2A^{i}) 3.652(3) S(1B^{i})	[72], JADJIH
		ψ-TBP **II**			137.0(1)	95.7(1)		
Pb(B)	6 (4+*E*)+2		2.784(3) S(4B) 2.994(3) S(2B)	2.704(2) S(1B) 2.747(3) S(3B)			3.268(3) S(1A) 3.433(3) S(2A)	
Pb{S$_2$CN(Pent)$_2$}$_2$ Pb(1)	6 (4+*E*)+2	ψ-TBP **II**	2.824(3) S(1) 2.929(3) S(4)	2.735(2) S(3) 2.743(2) S(2)	140.85(8)	90.11(8)	3.310(3) S(5) 3.362(2) S(3^{i})	[8], BEQXAX
		ψ-TBP **II**			136.19(8)	90.71(8)		
Pb(2)	5 (4+*E*)+1		2.832(3) S(5) 2.885(3) S(8)	2.673(3) S(7) 2.690(3) S(6)			(3.718(8)) S(4))	
Pb(Cy$_2$dtc)$_2$	5 (4+*E*)+1	ψ-TBP **II**	2.844(9) S(3) 2.870(9) S(2)	2.647(8) S(1) 2.670(8) S(4)	137.36(2)	95.90(3)	3.654(8) S(4^{i})	[8], BEQWUQ
Pb(Et^{i}Prdtc)$_2$	6 (4+*E*)+2	ψ-TBP **II**	2.862(3) S(2) 2.880(2) S(4)	2.675(2) S(3) 2.714(2) S(1)	138.60(5)	99.11(4)	3.488(2) S(1^{i}) 3.497(2) S(1^{ii})	[73], NAYNUW
Pb(Et^{i}Prdtc)$_2$	6 (4+*E*)+2	ψ-TBP **II**	2.873(2) S(2) 2.873(2) S(2^{i})	2.695(2) S(1) 2.695(2) S(1^{i})	138.72(8)	99.09(7)	3.497(2) S(1^{ii}) 3.492(2) S(1^{iii})	[74], NAYNUW01
Pb(EtCydtc)$_2$	6 (4+*E*)+2	ψ-TBP **II**	2.841(2) S(4) 2.883(2) S(2)	2.700(2) S(3) 2.710(2) S(1)	140.9(1)	98.9(1)	3.457(2) S(4^{ii}) 3.508(2) S(2^{i})	[75], XAVYAU
Pb(pdtc)$_2$	8 (4+*E*)+4	ψ-TBP **II**	2.893(4) S(2) 2.893(4) S(2^{i})	2.895(4) S(1) 2.895(4) S(1^{i})	119.2(1)	111.2(1)	3.280(5) S(1^{ii}) 3.280(5) S(1^{iii}) 3.476(1) S(2^{ii})) 3.476(1) S(2^{ii1})	[77], NINDUJ
Pb(II) mixed ligand diethyldithiocarbamate								
[Pb(Et$_2$dtc)$_2$(phen)]$_2$ Pb(1)	7 (5+*E*)+2	ψ-O **III** ψ-O **III**	2.584(11) N(6)	2.937(6) S(3) 2.953(5) S(1) 3.007(5) S(2) 3.022(5) S(4)	85.7(3) 83.2(3) 80.1(3) 79.9(3)	60.1(2) 60.25(4) 80.1(2) 155.55(12) $\Sigma = 356.0$	2.768(10) N(5) 3.378(5) S(6) 3.630(6) S(5)	[78], RESVOA
Pb(2)	8 (5+*E*)+3		2.584(10) N(8)	2.953(5) S(8) 2.982(5) S(7) 3.002(6) S(5) 3.017(5) S(6)	71.5(2) 84.2(2) 89.9(3) 76.1(2)	59.81(13) 60.32(14) 83.4(2) 148.44(11) $\Sigma = 351.97$	2.749(10) N(7) 3.362(5) S(4)	

Pb(II) alkylxanthates								
$Pb(Etxan)_2$	7 (4+*E*)+3	ψ-TBP **II**	2.84(3) S(2) 2.95(3) S(4)	2.74(3) S(1) 2.79(3) S(3)	136.7	98.2	3.32(3) S(1A) 3.37(3) S(3A) 3.50(3) S(4A)	[80], PBEXAN
$Pb(^nBuxan)_2$	4 (4+*E*)	ψ-TBP **II**	2.77(9) S(2) 3.03(8) S(4)	2.76(6) S(3) 2.83(4) S(1)	141.2(2)	91.7(1)		[81], PBBXAN
$Pb(^iPrxan)_2\cdot py$	7 (4+*E*)+3	ψ-TBP **II**	2.896(13) S(2) 3.057(16) S(4)	2.722(19) S(3) 2.833(18) S(1)	127.7(5)	95.0(6)	2.55(4) N 3.323(18) S(2^i) 3.408(18) O(1^i)	[82], PBISXP
$(Et_4N)[Pb(Etxan)_3]$	8 (6+*E*)+2	ψ-PBP$_{ax}$ **IV**	2.754(4) S(3)	2.942(3) S(1) 2.946(3) S(5) 3.029(3) S(6) 3.086(3) S(4) 3.126(3) S(2)	89.80(9) 86.44(8) 89.44(8) 61.11(9) 84.54(10)	58.54(8) 59.53(8) 77.43(8) 80.20(8) 84.38(8) $\Sigma = 360.08$	3.545(3) S(2A) 3.555(3) S(1A)	[84], EAEXPB01
Pb(II) mixed ligand alkylxanthates								
Pb(Etxan)(quin-8-O)	5 (4+*E*)+1	ψ-TBP **II**	2.479(6) N(1) 2.548(4) O(8')	2.296(5) O(8) 2.705(3) S(1)	136.1(2)	87.5(1)	3.173(3) S(2)	[84], BUMMOL
$Pb(^iPrxan)_2(phen)$	8 (6+*E*)+2	ψ-PBP$_{ax}$ **IV**	2.562(16) N(2)	2.671(16) N(1) 2.917(6) S(3) 2.927(6) S(4) 3.040(6) S(2) 3.185(6) S(1)	64.8(5) 76.9(4) 89.8(4) 80.4(4) 77.9(4)	57.23(15) 61.14(16) 74.6(4) 78.3(4) 79.86(16) $\Sigma = 351.13$	3.115(6) S(2A) 3.297(14) O(1A)	[85], VINNAH

0.1 Å longer (see Table 3). The complex $[Pb(Et_2dtc)_2]$ forms columns extending parallel to the crystallographic *c* axis. In the Pb(II) coordination polyhedron (Fig. 7) the S(1) and S(3) atoms (<S(1)–Pb–S(3) 96.2(4)°) and the stereochemically active LP lie in the equatorial plane of the bipyramid, while S(2) and S(4) occupy the axial positions (<S(2)–Pb–S(4) 133.2(4)°).

The compound $Pb(Et_2dsc)_2$ – the selenium analog of $Pb(Et_2dtc)_2$ – was examined for possible application as a single-source precursor for PbSe nanocrystals [70]. It is isostructural to $Pb(Et_2dtc)_2$, and the Pb atom is coordinated by four Se atoms of two chelating carbamate ions. The coordination polyhedron is a distorted trigonal bipyramid with a stereochemically active LP occupying the equatorial position (type **II**) (Fig. 8) The axial and equatorial Pb–Se distances (2.952(3), 3.013(3) and 2.827(3), 2.849(3) Å, respectively) are longer than the respective Pb–S distances in the structure of $Pb(Et_2dtc)_2$ by approximately 0.1 Å. The intermolecular contacts are similar in both structures (Table 3).

The complex $Pb(^iPr_2dtc)_2$ formed by Pb atoms and chelate *N*,*N*-di(isopropyl)dithiocarbamate ligands exists as isolated molecules in the solid state [71]. The complex has approximate C_2 symmetry with similar values of the Pb–S bond lengths in both chelate rings (Table 3). $Pb(^iPr_2dtc)_2$ exhibits weak intermolecular Pb...S interactions (3.513(4) and 3.541(4) Å) that suggest a similar weakly polymeric structure similar to the previously discussed alkyldithio(seleno)carbamate complexes.

The structure of lead(II) *n*-dipropyldithiocarbamate complex $Pb(^nPr_2dtc)_2$ is substantially different from that of $Pb(^iPr_2dtc)_2$ and other lead(II) dialkyldithiocarbamates in that it has a chain-like structure [72]. It is built from neutral discrete tetrameric complexes formed by four-coordinate groups PbS_4. In each group the central atom is chelate-bonded with the S atoms of both carbamate ligands with formation of four-membered rings. The geometric parameters of the Pb–S bond lengths and the S–Pb–S bond angles within the PbS_4 groups are similar to those in the structures of dialkyldithiocarbamates (Table 3).

The structure of lead(II) dipentyldithiocarbamate, $Pb\{S_2CN(Pent)_2\}_2$ contains two crystallographically nonequivalent Pb atoms, each of them coordinated by four S atoms—two from each chelating dithiocarbamate ligand [8]. The Pb–S bond lengths in each chelate ring are asymmetric and have values characteristic for dialkyldithiocarbamates. Through weak Pb...S interactions the Pb atoms complexes build polymeric chains (Table 3).

In the crystal structure of lead(II) dicyclohexyldithiocarbamate, $Pb(Cy_2dtc)_2$ two S atoms of the cyclohexyldithiocarbamate ligands form comparatively strong coordination bonds to Pb (Pb–S(1) 2.647(8), Pb–S(4) 2.670(8) Å), while two others are considerably weaker (2.844(9) and 2.870(9) Å) [8]. The complexes form polymeric chains with the nearest contact between the Pb atom and S atom of the adjacent complex being 3.654(8) Å.

Two crystal structures of lead(II) dithiocarbamate complexes with two substituents on the N atom were investigated. The structure of $Pb(Et^iPrdtc)_2$ [73] is similar to those of $Pb(Me_2dtc)_2$ [68] and $Pb(Et_2dtc)_2$ [69]. The Pb atom is coordinated by four S atoms – two from each chelating ligand. The corresponding bond lengths have similar values and the intermolecular contacts are also very close (Table 3). As in the structures of $Pb(Me_2dtc)_2$ and $Pb(Et_2dtc)_2$, the monomeric molecules form pseudo-polymeric chains. The structure of $Pb(Et^iPrdtc)_2$ was originally reported to belong to non-centrosymmetric space group Cc [73], but in [74] the space group was proposed to be C2/c. In this setting, the Pb atom lies on a two-fold axis, as in the structure of $Pb(Me_2dtc)_2$ [68].

The structure of bis(*N*-ethyl-*N*-cyclohexyldithiocarbamato)lead (II), $Pb(EtCydtc)_2$ ($EtCydtc^- = S_2CN(Et)(Cy)^-$, **26**) contains zigzag-like polymeric chains [75]. The Pb atom is asymmetrically bonded to two S atoms from both carbamate ligands. The values of the Pb–S

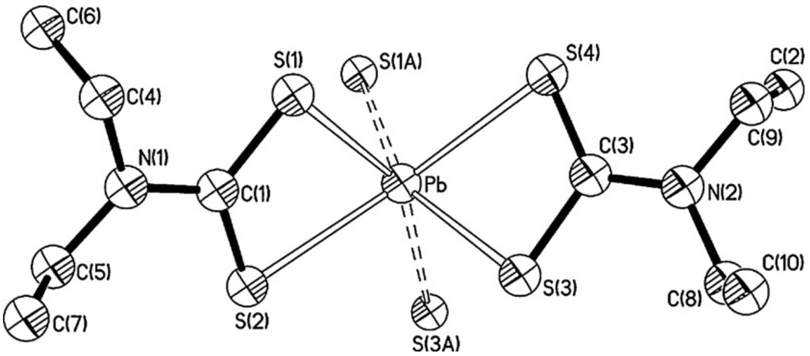


Fig. 7. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(S_2CNEt_2)_2$.

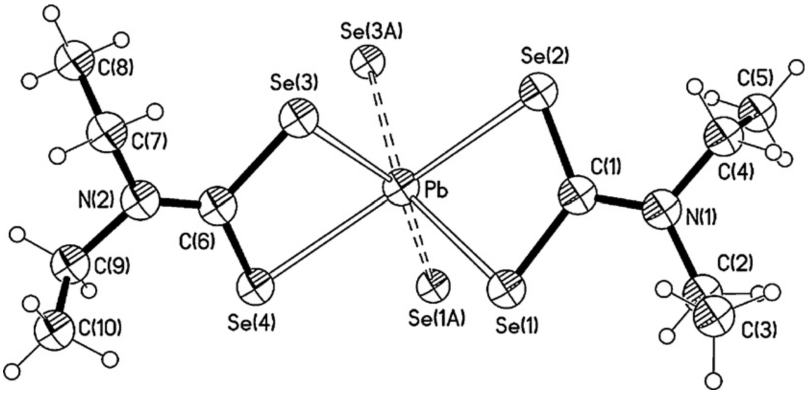
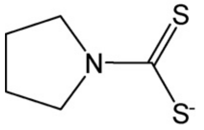


Fig. 8. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(Se_2CNEt_2)_2$.

bond lengths and S–Pb–S angles are similar to those in the structures of other dialkyldithiocarbamates (Table 3). The molecules are bonded to each other by weak Pb. . .S interactions into polymeric chains: Pb. . .S(4^{ii}) 3.457(2), Pb. . .S(2^{i}) 3.508(2) Å. These values are typical for the Pb. . .S interactions in the structures of dialkyldithiocarbamates.

In the series of structurally investigated dialkyldithiocarbamates, the crystal structure of $Pb(pdtc)_2$ ($pdtc^-$ = pyrrolidinecarbodithiolate anion, **27**) is unique [77]. The Pb atom, similarly to $Pb(Me_2dtc)_2$ [68], is located on the two-fold crystallographic axis; however, unlike $Pb(Me_2dtc)_2$ in which the Pb–S bond lengths in the chelate cycle are asymmetric and differ from each other by 0.1 Å, in $Pb(pdtc)_2$ the four primary Pb–S bonds are equal within experimental error (Pb–S 2.894(4) Å). The S–Pb–S bond angles are also similar, 119.2(1)° and 111.2(1)°. The complexes build two anti-parallel columns along the *c* axis through Pb. . .S interactions exhibiting two relatively moderate distances (3.280(5) Å) and two weaker ones (3.476(1) Å).



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4.1.1. Mixed ligand diethyldithiocarbamate

One lead(II) diethyldithiocarbamate complex with phenanthroline was investigated. The asymmetric unit of $[Pb(Et_2dtc)_2(phen)]_2$ contains two crystallographically independent Pb atoms, each of which is surrounded by four S atoms from diethyldithiocarbamate ligands and two N atoms from the coordinated phen molecule [78]. The Pb atoms also weakly interact with the S atoms of one of diethyldithiocarbamate ligands of an adjacent complex (Pb(1). . .S(6) 3.378(5) and Pb(2). . .S(4) 3.362(5) Å). This results in formation of non-centrosymmetric dimers. The primary Pb–S bond lengths in chelate rings of both complexes have similar values and fall into the range 2.937(6)–3.022(5) Å. The same can be said about the Pb-N bond lengths (2.584(11), 2.768(10) and 2.584(11), 2.749(10) Å).

The coordination geometry of the Pb atoms is described as a distorted pentagonal bipyramid, in which the base is formed by four S atoms from both diethyldithiocarbamate ions and the strongest-bonded N atom of the phen ligand. The weakly bonded S atom from the carbamate ligand of the adjacent complex and the second, less strongly bonded N atom from the phen ligand are located in the apical positions of the bipyramid. The presence of weak interactions of the Pb(1) and Pb(2) atoms with the S atoms from the ligands of the adjacent monomeric complex led the authors to conclude that the LPs of the Pb^{2+} ions are stereochemically inactive. The geometry of the primary coordination sphere of both of the unique Pb atoms can be described as ψ-octahedral (Fig. 9) with the more strongly bonded N atoms (2.584(11) Å) in one of the axial positions and the LP in the opposing axial vertex. Four S atoms from two chelating carbamate ligands occupy the equatorial sites of the ψ-octahedra (type **III**). The weakly bonded S atoms from the carbamate ligands also interact with the Pb atom of an adjacent molecule to give dimeric structures (Table 3).

4.2. Alkylxanthates

Alkylxanthate complexes (^-S_2COR, **28**) have been investigated far less completely than the dialkyldithiocarbamates. The structures of neutral complexes $Pb(S_2COR)_2$ (R = Me [79], Et [80], ^{n}Bu [81], ^{i}Pr [82]) have been examined as well as the structures of the

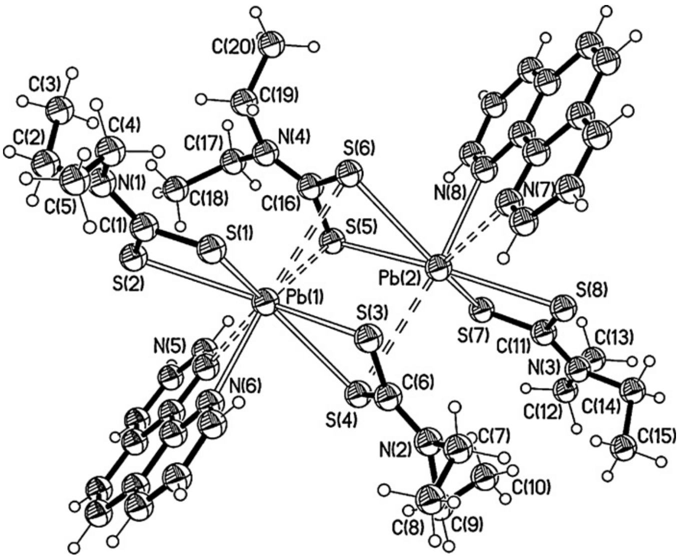
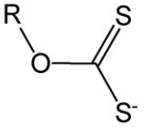


Fig. 9. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(S_2CNEt_2)_2(phen)$.

anionic complex $[Et_4N][Pb(S_2COEt)_3]$ [83] and two mixed ligand alkylxanthate complexes. The Pb atom geometry in the $Pb(S_2COR)_2$ complex considering just the primary Pb–S bonds is type **II** in accord with VSEPR theory.

In the crystal structure of the methyl xanthate complex $Pb(Mexan)_2$ ($Mexan^- = S_2COMe^-$) the coordination environment of the Pb atom is a distorted octahedron [79]. The S–Pb–S angles in the basal plane of the PbS_6 polyhedron differ insignificantly from 90° (89.9(2)–90.3(2)°), indicating that the LP is stereochemically inactive.



R = Me, Et, ^{i}Pr, ^{n}Bu

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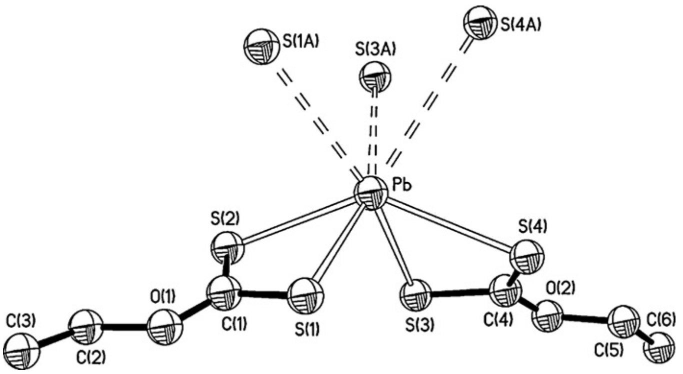


Fig. 10. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(S_2COEt)_2$.

The crystal structure of $Pb(Etxan)_2$ ($Etxan^- = S_2COEt^-$), similar to $Pb(Et_2dtc)_2$ [69], is built from molecular $[Pb(Etxan)_2]$ units, in which the Pb atoms are chelated by two xanthate ligands through asymmetric Pb–S bonds [80]. The bond lengths are very similar in both structures (Table 3). Aside from four primary Pb–S bonds, each Pb atom forms three contacts with S atoms of the adjacent complex with distances of 3.32(3), 3.37(3) and 3.50(3) Å. Weak interactions link the $[Pb(Etxan)_2]$ molecules into chains. The Pb(II) polyhedron (Fig. 10) features the S(2) and S(4) atoms (Pb–S(2) 2.84(3) and Pb–S(4) 2.95(3) Å; <S(2)–Pb–S(4) 136.7°) in axial positions, and the S(1), S(3) atoms (Pb–S(1) 2.74(3) and Pb–S(3) 2.79(3) Å; <S(1)–Pb–S(3) 98.2°) and a LP in the equatorial plane of a trigonal bipyramid (type **II**) (Table 3).

Lead(II) *n*-butylxanthate, $Pb(^nBuxan)_2$ ($^nBuxan^- = S_2CO^nBu^-$) crystallizes with two *n*-butylxanthate ligands chelating the Pb atom with asymmetric Pb–S bonds [81]. The distances of one of the ligands are nearly equal length (2.77(9) and 2.83(4) Å), while the bond lengths to the other ligand are substantially different (2.76(6) and 3.03(8) Å). The value of the distance of 3.03(8) Å is equal to the sum of ionic radii of Pb^{2+} and S^{2-} [24], indicating substantial weakening of this bond as compared to three other Pb–S bonds in the structure.

Lead(II) isopropylxanthate crystallizes from pyridine solution as the adduct $Pb(^iPrxan)_2{\cdot}py$ ($^iPrxan^- = S_2CO^iPr^-$) [82]. The solvate py molecule does not coordinate to the Pb ion. The geometric parameters of the bonds in the structure of $Pb(^iPrxan)_2{\cdot}py$ are very similar to those in the structure of $Pb(^nBuxan)_2$, except for the axial S–Pb–S angle (127.7(5)°; see Table 3). $Pb(^iPrxan)_2{\cdot}py$ forms polymeric chains through weak interactions with the S atoms (3.323(18) Å) of the adjacent complexes.

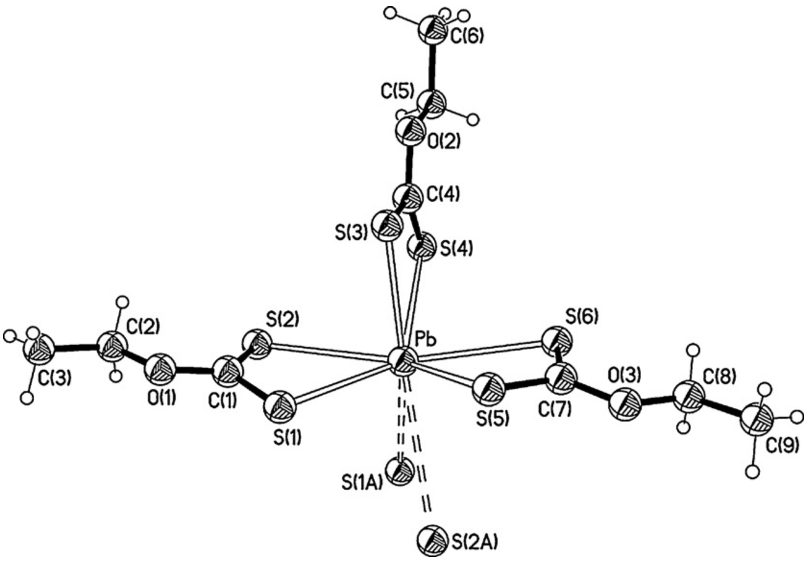


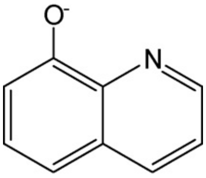
Fig. 11. ORTEP drawing of the coordination environment of the Pb(II) atom in $(Et_4N)[Pb(S_2COEt)_3]$.

The crystal structure of the anionic alkylxanthate complex $[Et_4N][Pb(Etxan)_3]$ was first described in [83] and more completely in [84]. The metal atom is asymmetrically chelated by three ethylxanthate ligands so that one of the ligands is substantially asymmetric, while other two are less asymmetric. The S atoms of all three coordinated ligands are located at one side from the central atom indicating to the presence of a stereochemically active LP. The coordination polyhedron is a ψ-pentagonal bipyramid (**IV**, ψ-PBP_{ax}) (Fig. 11), whose axial position is occupied by the S(3) atom with the shortest distance Pb–S in the polyhedron (2.754(4) Å). The second axial position of the polyhedron is occupied by the LP. The basal plane of the ψ-pentagonal bipyramid is formed by five S atoms (Pb–S 2.942(3)–3.126(3) Å; see Table 3). The sum of angles around the Pb atom in the ψ-pentagonal bipyramid equatorial plane is 360° within experimental error. Comparatively weak interactions of the Pb atom with S atoms in the adjacent molecule (Pb. . .S = 3.545(3), 3.555(3) Å) give rise to dimers.

4.2.1. Mixed ligand alkylxanthates

The crystal structures of two lead(II) mixed ligand alkylxanthate complexes were reported: Pb(Etxan)(quin-8-*O*) (quin-8-O^- = quinolin-8-olate anion, **29**) [84] and $Pb(^iPrxan)_2(phen)$ [85].

The structure of Pb(Etxan)(quin-8-*O*) is built from dimeric complexes $[Pb(Etxan)(quin\text{-}8\text{-}O)]_2$ [84]. Each Pb atom in the dimer is bonded to two S atoms from the ethylxanthate ligands, O and N atoms from the quin-8-O^- ligand and the bridging O atom from a symmetry related quin-8-O^-. In the four-membered Pb_2O_2 ring the bridging Pb–O bonds are asymmetric—2.296(5) and 2.548(4) Å. The Pb atom also forms asymmetric bonds with the S atoms from the ethylxanthate ligand (2.705(3) and 3.173(3) Å). The distances from the Pb atom to the O and N atoms from the quin-8-O^- ligand are 2.296(5) and 2.479(6) Å. The coordination polyhedron of the central atom in the structure of Pb(Etxan)(quin-8-*O*) can be represented as type **II**. The N atom of the bound ligand and O atom from the adjacent molecule sit in axial positions (<N(1)–Pb–O(8^i) 136.1(2)°), while the O atom from the bound ligand, an S atom and the LP occupy equatorial positions (<O(8)–Pb–S(1) 87.5(1)°). The Pb atom forms only a weak, secondary bond with the other S atom from the $Etxan^-$ ligand (Table 3).



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In $Pb(^iPrxan)_2(phen)$ the Pb atom is bonded to five S atoms—four from two isopropylxanthate ligands of one complex and the S atom from the isopropylxanthate ligand of the adjacent complex [85]. The Pb atom forms bonds of virtually the same lengths with the S atoms of one isopropylxanthate ligand (Pb–S(3) 2.917(6), Pb–S(4) 2.927(6) Å), while the second isopropylxanthate ligand chelates the Pb atom asymmetrically (Pb–S(2) 3.040(6), Pb–S(1) 3.185(6) Å). The S(2) atom is simultaneously a bridging atom (Pb···S(2A) 3.115(6) Å) binding the complexes into a polymeric chain. The phen ligand in the mixed ligand is bonded asymmetrically (2.562(16) vs. 2.671(16) Å).

The coordination polyhedron of the Pb atom considering only the S atoms was described as a distorted tetragonal pyramid [85]. According to the VSEPR model, the coordination polyhedron of the Pb atom (Fig. 12) should be a ψ-pentagonal bipyramid (**IV**, ψ-PBP_{ax}). In this interpretation the N(2) atom is in one of the axial positions and a stereochemically active LP in other. The equatorial plane of the polyhedron is formed by the N(1) atom and four S atoms from both isopropylxanthate ligands. The S(2A) and O(1A) atoms from the isopropylxanthate ligand of the adjacent complex form secondary bonds with the central atom (Table 3).

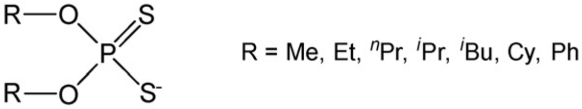
5. Lead(II) dialkyl(aryl) phosphorodithio(seleno)lates

The chalcogeno-phosphate, -phosphite and -phosphonate ligands, $X_2PE_2^-$, (E = S; X = OR (**30**), R (**31**) or E = S, Se, $X_2 = R_1(O\text{-}R_2)$ (**32**)) form stable complexes with many metals. Comprehensive reviews by Haiduc with co-authors [15,16] have been devoted to the structural chemistry of metal phosphor-1,1-dithiolate complexes throughout the periodic table, including Pb. Recent advances in coordination chemistry of diselenophosphate, diselenophosphite and diselenophosphonate metal complexes, including two lead(II) diselenophosphonate complexes, are presented in the review [17]. These reviews discuss mainly the coordination patterns, molecular structures and supramolecular associations in the structurally studied phosphor-1,1-dithiolato metal complexes. Information on the stereochemistry of the central atom of the structurally studied complexes, in particular those of Pb(II), is rather limited. In this review, the main focus of the crystal structures of Pb(II) complexes with phosphor-1,1-dithio(seleno)late ligands is placed on the central atom stereochemistry and coordination polyhedron structure.

5.1. Dialkyl(aryl)dithiophosphates

The review [15] examines four structurally studied lead(II) dithiophosphates $Pb\{S_2P(OR)_2\}_2$ with R = Et [86,87], ^{i}Bu [87], Ph [87] and ^{i}Pr [88,89]. During the 15 years that have passed since that review, three more lead(II) dithiophosphates $Pb\{S_2P(OR)_2\}_2$ have been structurally characterized: R = Me [90], Pr [91] and Cy [91]. Based on the structure of the coordination polyhedron in the structures of lead(II) dithiophosphates, the compounds can be divided into two groups: those with R = Et, ^{i}Bu and Ph having the ψ-trigonal-bipyramidal structure (type **II**) while those with R = ^{i}Pr, Me, Pr and Cy showing substantially different structures.

In [86] the structure of lead(II) diethyldithiophosphate $Pb(Et_2dtp)_2$ ($Et_2dtp^- = S_2P(OEt)_2^-$, **30**) is described as containing monomeric $Pb(Et_2dtp)_2$ units. The metal atom is anisobidentate-coordinated by the S atoms of both diethyldithiophosphate ligands with the Pb–S bond lengths falling in the range 2.754(6)–3.022(6) Å (Table 4). Besides four primary bonds, the Pb atom forms bridging Pb···S bonds with the atoms belonging to the adjacent $Pb(Et_2dtp)_2$ units (3.469(6) and 3.478(6) Å). The Pb atom has contacts with O atoms on adjacent molecules at distances of 3.00(1) and 3.04(2) Å. The coordination polyhedron of the Pb atom with its closest ligands is described as a distorted tetragonal pyramid with the Pb atom in the apical position and four S atoms in the basal plane. The Pb atom is located 1.48 Å above the basal plane. According to the VSEPR model, the coordination polyhedron of the Pb atom in the structure of $Pb(Et_2dtp)_2$ should have the type **II** configuration.



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A repeated study of the crystal structure of $Pb(Et_2dtp)_2$ [87] confirmed the main features of the of that determined previously [86] (Table 4). The authors mentioned that the Pb atom polyhedra formed polymeric chains through secondary Pb. . .S bonds.

The structure of lead(II) diisobutyldithiophosphate $Pb(^iBu_2dtp)_2$ ($^iBu_2dtp^- = S_2P(O^iBu)_2^-$, **30**) contains dimeric

Table 4
Stereochemistry of lead(II) phosphor-1,1-dithio(seleno)late complexes.

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Pb(II) dialkyl(aryl)dithiophosphates								
Pb(Et$_2$dtp)$_2$	8 (4+*E*)+4	ψ-TBP **II**	2.996(5) S(2) 3.022(6) S(4)	2.754(6) S(1) 2.790(6) S(3)	138.2 (2)	94.1(2)	3.00(1) O(3^{ii}) 3.04(2) O(1^{i}) 3.469(6) S(2^{i}) 3.478(6) S(4^{ii})	[86], PBEDTP
Pb(Et$_2$dtp)$_2$	8 (4+*E*)+4	ψ-TBP **II**	2.998(3) S(2) 3.035(4) S(4)	2.759(4) S(1) 2.782(4) S(3)	138.2 (2)	94.1(2)	3.03(1) O(3^{ii}) 3.01(1) O(1^{i}) 3.409(4) S(2^{i}) 3.483(4) S(4^{ii})	[87]
Pb(^{i}Bu$_2$dtp)$_2$	7 (4+*E*)+3	ψ-TBP **II**	2.762(6) S(4) 3.127(5) S(2)	2.755(5) S(1) 2.768(5) S(3)	156.2(2)	93.0(2)	3.444(5) S(2A) 3.479(1) O(2A) 3.605 S(2B)	[87], VEWPUI
Pb(Ph$_2$dtp)$_2$	5 (4+*E*)+1	ψ-TBP **II**	2.896(7) S(2) 3.215(6) S(4^{i})	2.732(6) S(1) 2.753(5) S(3)	155.4(3)	86.9(2)	3.323(5) S(4)	[87], VEWREU
Pb(^{i}Pr$_2$dtp)$_2$	8 (6+*E*)+2	ψ-PBP$_{eq}$ **V**	2.985(12) S(2A) 3.027(11) S(4A)	2.761(7) S(1) 2.772(7) S(3) 3.175(9) S(4) 3.232(10) S(2)	172.6(2)	75.5(1) 66.6(2) 152.3(1) 67.1(2) $\Sigma = 361.5$	3.426 O(1^{ii}) 3.558 O(3^{i})	[89], PBIPPS10
Pb(^{i}Pr$_2$dtp)$_2$	8 (4+*E*)+4	ψ-TBP **II**	2.985(12) S(2A) 3.027(11) S(4A)	2.761(7) S(1) 2.772(7) S(3)	172.6(2)	75.5(1)	3.175(9) S(4) 3.232(10) S(2) 3.426 O(1^{ii}) 3.558 O(3^{i})	[89], PBIPPS10
Pb(Me$_2$dtp)$_2$	8 (6+*E*)+2	ψ-PBP$_{eq}$ **V**	3.033(2) S(2^{ii}) 3.033(2) S(2^{iii})	2.860(2) S(1) 2.860(2) S(1^{i}) 3.145(2) S(2) 3.145(2) S(2^{i})	172.34(2)	76.0(1) 68.04(6) 148.33(7) 68.04(6) $\Sigma = 360.41$	3.012(6) O(1^{i}) 3.012(6) O(1^{ii})	[90], YAGGOD
Pb(Me$_2$dtp)$_2$	8 (4+*E*)+4	ψ-TBP **II**	3.033(2) S(2^{ii}) 3.033(2) S(2^{iii})	2.860(2) S(1) 2.860(2) S(1^{i})	172.34(2)	76.0(1)	3.012(6) O(1^{i}) 3.012(6) O(1^{ii}) 3.145(2) S(2) 3.145(2) S(2^{i})	[90], YAGGOD
Pb(Pr$_2$dtp)$_2$	8 (6+*E*)+2	ψ-PBP$_{eq}$ **V**	2.9298(9) S(2) 3.1172(9) S(4)	2.8011(8) S(3) 2.8409(8) S(1) 3.1383(8) S(4)^{a} 3.2128(8) S(2)^{b}	178.08(2)	73.97(2) 67.09(2) 152.59(2) 68.38(2) $\Sigma = 362.03$	3.050(2) O(1)^{a} 3.428(2) O(3)^{b}	[91], EBEDUL
Pb(Pr$_2$dtp)$_2$	8 (4+*E*)+4	ψ-TBP **II**	2.9298(9) S(2) 3.1172(9) S(4)	2.8011(8) S(3) 2.8409(8) S(1)	178.08(2)	73.97(2)	3.050(2) O(1)^{a} 3.1383(8) S(4)^{a} 3.2128(8) S(2)^{b} 3.428(2) O(3)^{b}	[91], EBEDUL
Pb(Cy$_2$dtp)$_2$	7 (6+*E*)+1	ψ-PBP$_{eq}$ **V**	2.9270(8) S(2)^{a} 3.2052(9) S(4)^{b}	2.8566(8) S(1) 2.7536(9) S(3) 3.0926(8) S(4) 3.3240(8) S(2)	169.67(2)	77.08(2) 69.50(2) 148.58(2)65.16(2) $\Sigma = 360.32$	3.260(2) O(4)^{b}	[91], EBEFAT

Table 4 (*Continued*)

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
$\mathrm{Pb(Cy_2dtp)_2}$	7 (4+*E*)+3	ψ-TBP **II**	2.8566(8) S(1) 3.0926(8) S(4)	2.7536(9) S(3) 2.9270(8) S(2)[a]	146.26(2)	85.42(2)	3.2052(9) S(4)[b] 3.260(2) O(4)[b] 3.3240(8) S(2)	[91], EBEFAT
Pb(II) mixed ligand diethyldithiophosphates								
$\mathrm{Pb(Et_2dtp)_2(bpy)}$	7 (6+*E*)+1	ψ-$\mathrm{PBP_{ax}}$ **IV**	2.58(2) N(1)	2.63(2) N(2) 2.929(7) S(4) 2.948(7) S(3) 3.000(6) S(2) 3.118(7) S(1)	62.8(5) 87.0(5) 90.1(5) 88.3(4) 85.3(5)	66.6(2) 68.4(2) 74.2(2) 74.6(5) 77.7(5) $\Sigma = 361.5$	3.212(6) S(1A)	[92], JAYCUH
$\mathrm{Pb(Et_2dtp)_2(en)}$	7 (6+*E*)+1	ψ-$\mathrm{PBP_{ax}}$ **IV**	2.50(1) N(1)	2.57(1) N(2) 2.967(5) S(3) 3.074(5) S(2) 3.173(5) S(1) 3.177(5) S(4)	69.8(4) 80.7(4) 86.7(4) 75.6(4) 85.5(4)	63.8(1) 65.4(1) 71.8(1) 76.3(3) 78.9(3) $\Sigma = 356.2$	3.190(5) S(1^{i})	[92], JAYCOB
$\mathrm{[\{Pb(Et_2dtp)_2\}_2(en)]}$ Pb(1)	7 (4+*E*)+3	ψ-TBP **II**	2.93(1) S(4) 3.05(2) S(1)	2.82(1) S(2) 2.96(1) S(3)	142.0(4)	93.6(5)	3.11(1) S(6) 3.21(1) S(5) 3.29(1) S(5^{i})	[92], JAYDAO
Pb(2)	7 (4+*E*)+3	ψ-TBP **II**	2.50(3) N(1) 3.15(2) S(8)	2.48(4) N(2) 2.80(1) S(7)	135.1(1)	86.7(8)	3.22(1) S(6^{i}) 3.26(1) S(4^{i}) 3.21(4) O(6)	
Pb(II) dialkyl(aryl)dithiophosphinates								
$\mathrm{Pb(S_2PMe_2)_2}$	6 (4+*E*)+2	ψ-TBP **II**	2.918(4) S(4b) 3.065(3) S(2a)	2.692(4) S(1a) 2.837(3) S(3a)	150.9(1)	86.4(1)	3.298(4) S(2b) 3.485(5) S(4a)	[93], ZAXWOK
$\mathrm{Pb(S_2PEt_2)_2}$ Pb(1)	6 (4+*E*)+2	ψ-TBP **II**	2.909(8) S(4) 3.091(6) S(8^{i})	2.749(5) S(1) 2.749(7) S(3)	146.0(2)	91.9(2)	3.196(8) S(2) 3.435(6) S(9^{i})	[94], VOMTOG
Pb(2)	6 (4+*E*)+2	ψ-TBP **II**	2.934(6) S(6) 3.100(8) S(2)	2.781(6) S(7) 2.782(6) S(5)	144.2(2)	91.31(19)	3.144(6) S(8) 3.269(6) S(11)	
Pb(3)	6 (4+*E*)+2	ψ-TBP **II**	2.850(7) S(10) 3.000(6) S(11)	2.783(6) S(9) 2.877(6) S(12)	154.5(2)	89.19(17)	3.198(6) S(6) 3.316(6) S(12^{ii})	
$\mathrm{Pb(S_2PPh_2)_2}$	6 (4+*E*)+2	ψ-TBP **II**	2.900(1) S(4) 2.981(1) S(1)	2.785(1) S(2) 2.871(1) S(3)	151.5(1)	93.2(1)	3.270 S(2A) 3.448 S(3B)	[95], HEFHAB
β-$\mathrm{Pb(S_2P^{i}Bu_2)_2}$ Pb(1)	6 (4+*E*)+2	ψ-TBP **II**	2.893(2) S(1) 2.982(2) S(4)	2.766(2) S(2) 2.767(3) S(3)	157.29(6)	94.84(8)	3.296(2) S(5a) 3.361(2) S(8)	[96]
Pb(2)	5 (4+*E*)+1	ψ-TBP **II**	2.906(2) S(8) 2.918(2) S(5)	2.698(2) S(6) 2.773(2) S(7)	149.86(6)	92.58(7)	3.337(2) S(4)	
α-$\mathrm{Pb(S_2P^{i}Bu_2)_2}$ Pb(1)	6 (4+*E*)+2	ψ-TBP **II**	2.895(2) S(1) 2.932(2) S(4)	2.723(3) S(3) 2.786(2) S(2)	149.56(7)	92.70(8)	3.312(2) S(10) 3.502(2) S(7)	[96]
		ψ-TBP **II**						

Pb(2)	6(4+*E*)+2	ψ-TBP **II**	2.887(3) S(8) 2.932(2) S(6)	2.690(2) S(5) 2.803(3) S(7)	148.52(8)	91.44(8)	3.274(3) S(16) 3.508(2) S(2)	
Pb(3)	5(4+*E*)+1	ψ-TBP **II**	2.902(2) S(12) 2.984(2) S(10)	2.759(3) S(9) 2.773(3) S(11)	156.15(7) 159.31(7)	94.1(1) 94.8(1)	3.248(2) S(6)	
Pb(4)	6(4+*E*)+2	ψ-TBP **II**	2.877(3) S(13) 3.023(3) S(16)	2.771(3) S(14) 2.773(25 S(15)			3.220(2) S(4) 3.311(3) S(8)	
Pb(II) mixed ligand dialkyldithiophosphinates								
Pb(S$_2$P^{i}Bu$_2$)$_2$(phen)	7 (6+*E*)+1	ψ-PBP$_{ax}$ **IV**	2.534(3) N(2F)	2.656(3) N(1F) 2.955(1) S(2) 2.993(1) S(4) 3.040(1) S(1) 3.206(1) S(3)	63.80(8) 85.28(7) 83.76(7) 86.20(6) 84.35(6)	65.12(3) 67.73(3) 71.24(6) 74.46(6) 79.74(3) Σ = 358.29	3.364(1) S(3A)	[97], EFOZUV
Pb(S$_2$P^{i}Bu$_2$)$_2$(bpy)								
Pb(1)	7(6+*E*)+1	ψ-PBP$_{ax}$ **IV**	2.503(4) N(1p)	2.584(4) N(2p) 2.924(2) S(2) 2.961(1) S(1) 3.065(2) S(3) 3.167(2) S(4)	64.2(1) 84.7(1) 84.5(1) 85.1(1) 85.5(1)	64.91(4) 69.35(5) 72.3(1) 75.38(10) 75.82(4) Σ = 357.76	3.415(1) S(7)	[97], EFUBAJ
Pb(2)	7(6+*E*)+1	ψ-PBP$_{ax}$ **IV**	2.515(4) N(3p)	2.571(4) N(4p) 2.948(1) S(5) 2.979(1) S(6) 3.027(1) S(7) 3.149(2) S(8)	64.0(1) 88.75(10) 84.14(10) 84.3(1) 85.92(10)	65.75(4) 68.94(4) 73.33(11) 74.39(11) 77.28(4) Σ = 359.69	3.431(1) S(3)	
Pb(S$_2$P^{i}Bu$_2$)$_2$(4,4'-bpy)	7 (6+*E*)+1	ψ-PBP$_{eq}$ **V**	2.666(5) N(2) 2.681(5) N(1)	2.812(2) S(4) 2.921(1) S(2) 2.999(1) S(3) 3.093(2) S(1)	177.0(1)	66.36(5) 70.59(4) 143.13(6) 78.62(5) Σ = 358.7	3.295(2) S(1^{i})	[98]
Pb(II) alkyl(aryl)phosphonodithio(seleno)ates								
Pb{Fc(EtO)PS$_2$}$_2$	5 (4+*E*)+1	ψ-TBP **II**	2.854(2) S(22) 3.008(2) S(2)	2.737(2) S(21) 2.740(2) S(1)	154.19(4)	92.45(5)	(3.703(1) S(22A))	[99], HALYID
Pb{Fc(^{i}PrO)PS$_2$}$_2$	4 (4+*E*)	ψ-TBP **II**	2.943(4) S(2) 2.950(3) S(22)	2.721(3) S(21) 2.736(4) S(1)	141.97(8)	93.84(12)		[100], BAZWOP
Pb{(*p*-MeO)Ph(EtO)PS$_2$}$_2$	8 (4+*E*)+4	ψ-TBP **II**	3.0706(11) S(2B) 3.0706(11) S(2C)	2.8404(11) S(1) 2.8404(11) S(1A)	154.10(3)	91.65(3)	2.930(3) O(2B) 2.930(3) O(2D) 3.133(1) S(2) 3.133(1) S(2A)	[101], HAHFEC
Pb{(*p*-MeO)Ph(^{i}PrO)PS$_2$}$_2$	5 (4+*E*)+1	ψ-TBP **II**	2.8954(12) S(2) 2.8954(12) S(2^{i})	2.7363(11) S(1) 2.7363(11) S(1^{i})	150.21(3)	95.18(3)	3.45(1) S(2^{ii})	[101], HAHFIG
Pb{Ph(EtO)PSe$_2$}$_2$	5 (4+*E*)+1	ψ-TBP **II**	2.9335(9) Se(2) 3.2235(10) Se(12)	2.8522(9) Se(11) 2.9249(12) Se(1)	156.37(3)	97.05(3)	3.390(1) Se(12^{i})	[102], PARLEA

Table 4 (*Continued*)

Compound	Overall CN	Shape of the polyhedron	Pb–S(Se) bond distances in the polyhedron (Å)		Bond angles S(Se)–Pb–S(Se) (°) in the polyhedron between the atoms		Secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
$Pb\{Ph(MeO)PSe_2\}_2$	5 (4+*E*)+1	ψ-TBP **II**	3.0652(5) Se(4) 3.1327(5) Se(2A)	2.8296(6) Se(1) 2.8757(5) Se(3)	153.16(1)	86.09(1)	3.2689(5) Se(2)	[102], PARLAW
Pb(II) imidodithio(seleno)phosphinates								
$Pb\{(SPPh_2)_2N\}_2$	4 (4+*E*)	ψ-TBP **II**	2.943(4) S(2) 2.943(4) $S(2^i)$	2.695(4) S(1) 2.695(4) $S(1^i)$	176.4(1)	86.4(1)		[103], YEYYUW
$Pb\{(SePPh_2)_2N\}_2$	4 (4+*E*)	ψ-TBP **II**	2.997(2) Se(1) 2.997(2) Se(1a)	2.874(3) Se(2) 2.874(3) Se(2a)	141.8(1)	113.0(1)		[104] RIZLER
$Pb\{(SeP^iPr_2)_2N\}_2$	5 (4+*E*)+1	ψ-TBP **II**	2.991(1) Se(1) 3.099(1) Se(3)	2.777(1) Se(2) 2.875(1) Se(4)	173.61(1)	96.68(2)	3.574(2) $Se(3^i)$	[105]
$Pb\{(TeP^iPr_2)_2N\}_2$	5 (4+*E*)+1	ψ-TBP **II**	3.196(1) Te(1) 3.308(1) Te(3)	2.946(1) Te(2) 3.084(1) Te(4)	169.54(3)	93.22(2)	3.597(1) Te(3A)	[105]
$Pb\{PhC(S)NP(S)(O^iPr)_2\}_2$	5 (4+*E*)+1	ψ-TBP **II**	2.834(2) S(2a) 3.005(2) S(2b)	2.698(1) S(1b) 2.701(2) S(1a)	166.49(5)	100.71(5)	(3.732 S(2c))	[106], WITQOF

groups $[Pb(^iBu_2dtp)_2]_2$ [87]. Unlike the structure of $Pb(Et_2dtp)_2$ in which both dithiophosphate ligands chelate the Pb atom in an anisobidentate fashion, the structure of $Pb(^iBu_2dtp)_2$ shows one dithiophosphate group chelating the Pb atom symmetrically (Pb–S 2.768(5), 2.762(6) Å), while the second group is bonded to the central atom in an essentially anisobidentate fashion (2.755(5) vs. 3.127(5) Å). The S atom having furthest from the lead ion is also bound to the Pb atom of the adjacent unit (3.444(5) Å). This creates a planar, centrosymmetric four-membered Pb_2S_2 rings.

The coordination geometry around the Pb atom is described in [87] as an extremely distorted square-based pyramid with the stereochemically active LP occupying the sixth position of the octahedron (type **III**). According to the VSEPR model, the coordination polyhedron of the Pb atom in $Pb(^iBu_2dtp)_2$ should be of type **II** similar to $Pb(Et_2dtp)_2$ [86,87]. The geometrical parameters are consistent with two S atoms lying in the axial positions (<S(4)–Pb–S(2) 156.2(2)°) and two S atoms and the LP occupying the equatorial plane (<S(1)–Pb–S(3) 93.0(2)°); see Fig. 13). Two more remote S atoms, as well as another O atom, from adjacent molecules form secondary bonds with the Pb atom (Table 4).

The compound $Pb(Ph_2dtp)_2$ ($Ph_2dtp^- = S_2P(OPh)_2{}^-$, **30**) exists as a centrosymmetric dimer [87]. As in $Pb(Et_2dtp)_2$ and $Pb(^iBu_2dtp)_2$, the Pb atom is coordinated by two dithiophosphate groups, one of which forms asymmetric bonds with the central atom (Pb–S(3) 2.753(5) and Pb–S(4) 3.323(5) Å). Simultaneously, the S(4) atom has a bridging function, linking the units into dimers. Unlike $Pb(^iBu_2dtp)_2$, in which the bridging bond in the dimer is longer than the chelating bond, here the bridge bond (3.215(6) Å) is slightly shorter than the chelating one (3.323(5) Å).

The coordination environment of the Pb atom in $Pb(Ph_2dtp)_2$, like that of $Pb(^iBu_2dtp)_2$, comprises five S atoms and is considered by the authors as square-pyramidal. However, unlike $Pb(^iBu_2dtp)_2$, in which the vacant sixth position of the octahedron is supposedly occupied by the LP of the Pb^{2+} ion, in $Pb(Ph_2dtp)_2$ this position appears to be occupied by the Ph group. As in $Pb(^iBu_2dtp)_2$, the coordination polyhedron can be assigned to a ψ-trigonal-bipyramid (type **II**) (Table 4).

The crystal structures of $Pb\{S_2P(OR)_2\}_2$ with $R = {}^iPr$ [88,89], Me [90], Pr [91] and Cy [91] are characterized by the presence of strongly asymmetric chelate Pb–S bonds. Here the bridging Pb–S bonds to the adjacent Pb atoms are, with one exception, substantially shorter that the bonds with the ligands's own Pb atoms.

The crystal structure of lead(II) diisopropyldithiophosphate, $Pb(^iPr_2dtp)_2$ ($^iPr_2dtp^- = S_2P(O^iPr)_2{}^-$, **30**) was first briefly described in [88] and later in more detail in [89]. The Pb atom is coordinated by six S atoms, four S atoms from two chelating isopropyldithiophposphate groups and two bridging S atoms belonging to adjacent $Pb(^iPr_2dtp)_2$ units. The observed bond lengths (2.761(7)–3.232(10) Å) and bond angles around the Pb atom enabled the authors [88,89] to assume the presence of 7 electron pairs. The LP is considered to be stereochemically active, and the structure is consistent with predictions from the VSEPR model [20]. The coordination polyhedron of the Pb atom (PbS_6E) is represented as a distorted pentagonal bipyramid with the LP in the equatorial position (**V**, ψ-PBP_{eq}; Fig. 14). The axial positions are occupied by the bridging S atoms (Pb–S(2A) 2.985(12), Pb–S(4A) 3.027(11) Å; <S(2A)–Pb–S(4A) 172.6(2)°) belonging to the adjacent units, while the equatorial plane is formed by the chelating S atoms of both of the isopropyldithiophposphate ligands and the LP. Two *cis*-bonds in the bipyramid equatorial plane (Pb–S(2) 3.232(10), Pb–S(4) 3.175(9) Å) adjacent to the LP are the longest in the structure. The angle between them is equal to 152.3(1)°. The stereochemically active LP is thought to be oriented towards the bisector of the <S(2)–Pb–(S4) 152.3(1)°. The lengths of two other equatorial Pb–S bonds remote from the LP are 2.761(7) and 2.772(7) Å (Table 4).

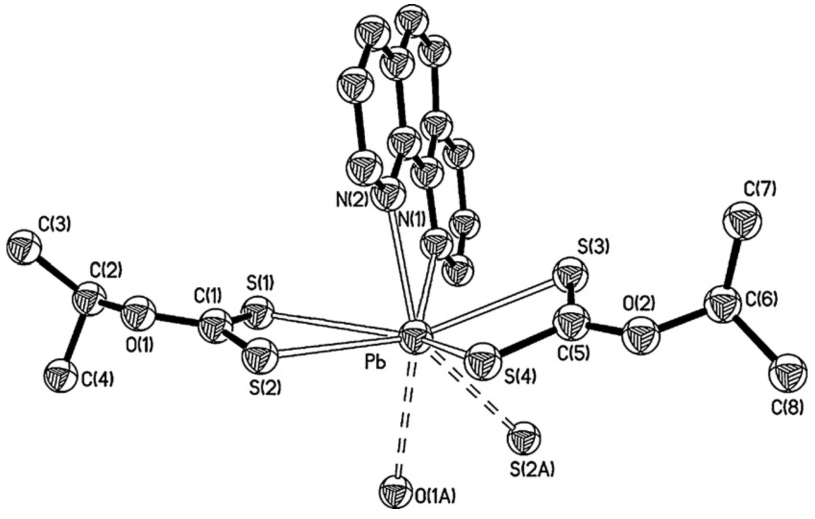


Fig. 12. ORTEP drawing of the coordination environment of the Pb(II) atom in [$Pb(S_2CO^iPr)_2(phen)$].

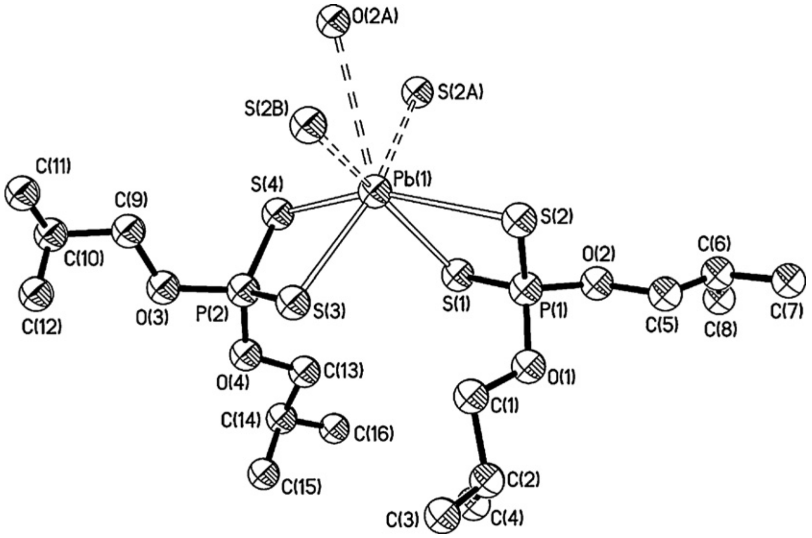


Fig. 13. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb\{S_2P(O^iBu)_2\}_2$.

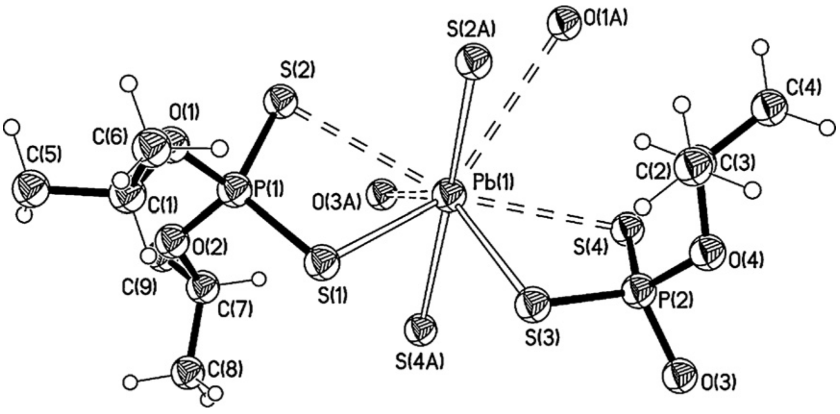


Fig. 14. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb\{S_2P(O^iPr)_2\}_2$.

Taking into account the assignment of the Pb...S(2) and Pb...S(4) bonds as secondary, the coordination polyhedron of the Pb atom in the structure of $Pb(^iPr_2dtp)_2$ can be described as a ψ-trigonal bipyramid (type **II**) similar to the polyhedral structures in Pb(II) dialkyldithiocarbamates and alkylxanthates (Table 4).

The Pb(II) coordination polyhedra in $Pb\{S_2P(OR)_2\}_2$ (R = Me [90], Pr [91] and Cy [91]), as in $Pb(^iPr_2dtp)_2$, were described as type **V**.

In $Pb(Me_2dtp)_2$ ($Me_2dtp^- = S_2P(OMe)_2^-$, **30**) the Pb atom is located on a crystallographic two-fold axis [90]. As in $Pb(^iPr_2dtp)_2$, the Pb atom is surrounded by six S atoms with the Pb–S distances falling into the range 2.860(2)–3.145(2) Å. The coordination environment of the Pb atoms and the structures of linear polymer chains are similar in both compounds. The coordination geometry of the Pb atom in Pb(Me$_2$dtp)$_2$, as for Pb(^{i}Pr$_2$dtp)$_2$, can be described as type **II** (Table 4).

The structure of lead(II) dipropyldithiophosphate Pb(Pr$_2$dtp)$_2$ (Pr$_2$dtp$^-$ = S$_2$P(OPr)$_2$$^-$, **30**) [91] is similar to that of its isopropyl-analog Pb(^{i}Pr$_2$dtp)$_2$. Both the Pb–S bond lengths and the bond angles have similar values (Table 4). In Pb(Pr$_2$dtp)$_2$, as in Pb(^{i}Pr$_2$dtp)$_2$, both dithiophposphate ligands are anisobidentate. One of the S atoms of both ligands is also coordinated to the adjacent Pb atom. The structural polyhedra are linked into zigzag polymer chains through these bridging S atoms. The coordination polyhedron of the Pb atom in the structure of Pb(Pr$_2$dtp)$_2$, in accordance with the VSEPR model, can be represented as type II (Table 4).

The structure of lead(II) dicyclohexyldithiophosphate, Pb(Cy$_2$dtp)$_2$ (Cy$_2$dtp$^-$ = S$_2$P(OCy)$_2$$^-$, **30**) is similar to that of Pb(Pr$_2$dtp)$_2$ [91]. In both structures the ligands are anisobidentate, while one of the S atoms of each ligand is bridging. Unlike the structure of Pb(Pr$_2$dtp)$_2$, in which the bridging bonds formed by the most remote chelating S atoms with adjacent Pb atoms are shorter than the respective chelating Pb–S bonds, in the structure of Pb(Cy$_2$dtp)$_2$ the situation is mixed. The bridging bond (Pb...S(4)^b 3.2052(9) Å) is longer than the chelate bond (Pb–S(4) 3.0926(8) Å) for one ligand, but reversed for the other. The bridging bond formed between S(2) and an adjacent Pb ion is substantially shorter than the chelate bond (Pb^a–S(2) 2.9270(8) Å vs. Pb...S(2) 3.3240(8) Å). As in the structure of Pb(Pr$_2$dtp)$_2$, the coordination polyhedron in Pb(Cy$_2$dtp)$_2$ can be represented as type **II** (Table 4).

According to the DFT studies of Pb(Me$_2$dtp)$_2$ complex with the type **V** structure, the stereochemical activity of the LP of the Pb^{2+} ion coordinated by the six S atoms in this compound is very low and corresponds to 99.17% s and 0.83% p character. For Pb(Et$_2$dtp)$_2$ [86] with the type **II** coordination geometry the composition of the Pb(II) LP is 96.42% s and 3.58% p indicating more stereochemical activity in this compound. The data obtained by the DFT method do not allow assignment of the coordination geometry of the Pb atoms in Pb(Me$_2$dtp)$_2$ and Pb(R$_2$dtp)$_2$ (R = ^{i}Pr, Pr, Cy) to the type **V** with a stereochemically active LP.

5.1.1. *Mixed ligand diethyldithiophosphates*

Three structures of lead(II) diethyldithiophosphate with the chelating nitrogen donors bipyridine (bpy) and ethylenediamine (en) have been reported. These include Pb(Et$_2$dtp)$_2$(bpy), Pb(Et$_2$dtp)$_2$(en) and [{Pb(Et$_2$dtp)$_2$}$_2$(en)] [92].

The crystal structure of Pb(Et$_2$dtp)$_2$(bpy) contains centrosymmetric dimeric [Pb(Et$_2$dtp)$_2$(bpy)]$_2$ groups [92]. Each Pb atom in the dimer is chelated by two dithiophosphate groups, one of which is chelated almost symmetrically (Pb–S(4) 2.929(7), Pb–S(3) 2.948(7) Å), while another one binds in an anisobidentate fashion (Pb–S(2) 3.000(6), Pb–S(1) 3.118(7) Å). The longer distance in the dithiophosphate group results from the participation of the S(1) atom in the bridging bond between Pb atoms in the dimer. Besides the dithiophosphate groups, each metal atom in the dimer is virtually symmetrically bidentate-bound by the bpy molecule (Pb–N 2.58(2), 2.63(3) Å) and forms a rather weak bond with the bridging S(1A) atom. The geometry of the Pb(II) coordination polyhedron (CN 7) is considered to be a pentagonal bipyramid with the atoms N(1) and S(1A) in the axial positions and the N(2) and four S atoms in the equatorial plane. According to [92], the Pb(II) LP in Pb(Et$_2$dtp)$_2$(bpy) is stereochemically inactive. The coordination polyhedron according to the VSEPR model should be a ψ-pentagonal bipyramid with a vacant axial position (**IV**; Fig. 15). The N(1) atom forming the shortest Pb–N bond (Pb–N(1) 2.58(2) Å) is located in the second axial vertex of the bipyramid. The basal plane is formed by the N(2) atom and four S atoms of both coordinated dithiophosphate groups. The bridging atom S(1A) located in the LP area forms a secondary bond with the Pb atom (Pb...S(1A) 3.212(6) Å) (Table 4).

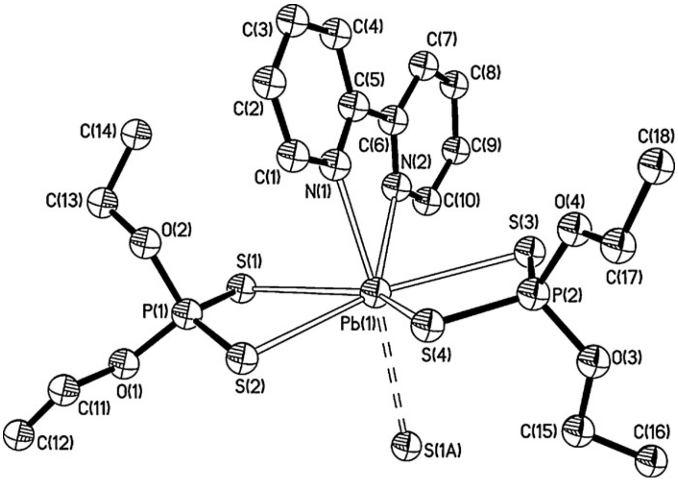


Fig. 15. ORTEP drawing of the coordination environment of the Pb(II) atom in Pb{S$_2$P(OEt)$_2$}$_2$(bpy).

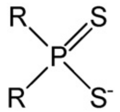
Unlike dimeric Pb(Et$_2$dtp)$_2$(bpy), Pb(Et$_2$dtp)$_2$(en) is an one-dimensional polymer [92]. The Pb(Et$_2$dtp)$_2$(en) units are linked through almost symmetric bridging bonds (Pb–S 3.173(5) Å and 3.190(5) Å). The dithiophosphate groups have different functions in the structure. One Et$_2$dtp$^-$ group chelates the Pb atom, while another is chelating/bridging, thus forming a S-bridge bond with the adjacent Pb atom. Both dithiophosphate groups and the ethylenediamine ligand are anisobidentate-bonded to the central atom.

The geometry of the coordination polyhedron is described as a distorted square antiprism with a vacant position assigned to the Pb^{2+} ion stereochemically active LP. The coordination polyhedron of the Pb atom in Pb(Et$_2$dtp)$_2$(en), like in the bipyridine analog, should be a ψ-pentagonal-bipyramid with a vacant axial position (type **IV**). The bond angles between the axial atom N(1) and the equatorial atoms are less than 90°, which is in full agreement with the VSEPR model. The sum of angles around the central Pb atom formed by equatorial atoms is ~356° (Table 4).

The structure of the 2:1 ethylenediamine complex [{Pb(Et$_2$dtp)$_2$}$_2$(en)] is much more complicated than that of Pb(Et$_2$dtp)$_2$(bpy) or Pb(Et$_2$dtp)$_2$(en). The structure contains two different types of Pb atoms linked together dimers [Pb(Et$_2$dtp)$_3$]$_2$ that are doubly bridged by [Pb(Et$_2$dtp)(en)] units to give tetrameric units. These units are further linked into polymeric chains. The Pb(1) atom is surrounded by three dithiophosphate groups and a bridging S atom and has been described as a distorted pentagonal bipyramid similar to that of Pb(Et$_2$dtp)$_2$(bpy) [92]. The coordination polyhedron in the [Pb(Et$_2$dtp)(en)] units is square pyramidal. The apical position of the square pyramid is occupied by the chelating ethylenediamine, while its distorted equatorial plane is formed by four S atoms from the anisobidentate-bonded dithiophosphate groups. The stereochemically active LP in the [Pb(Et$_2$dtp)(en)] units is located opposite to the ethylenediamine. The analysis of interatomic distances and bond angles performed with *Mercury* [22] shows that both Pb environments may be described as type **II** (Table 4) within the scope of the VSEPR model.

5.2. *Dialkyl(aryl)dithiophosphinates*

The stereochemical aspects of the metal complexes of all groups of the periodic table with the dithiophosphinate ligands, in particular coordination patterns, molecular structures and supramolecular association in the structures were examined in [16]. The above-mentioned review briefly discusses the crystal structures of three previously reported complexes of lead(II) with dithiophosphinate ligands, $^{-}S_2PR_2$ (**31**, R = Me [93], Et [94], Ph [95]). Since publication of [16], the structures of α- and β-$Pb(S_2P^iBu_2)_2$ [96], as well as those of a number of lead(II) mixed ligand dithiophosphinates with N-donors—phen and bpy, have been reported.



R = Me, Et, ^iBu, Ph

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The structure of $Pb(S_2PMe_2)_2$ contains dimeric $[Pb(S_2PMe_2)_2]_2$ groups [93]. The Pb atoms in the dimer are anisobidentate-chelated by two dithiophosphinate ligands with the Pb–S bond lengths lying between 2.692(4) and 3.485(5) Å. Linking of the $Pb(S_2PMe_2)_2$ complexes into dimers occurs through a comparatively strong bridging bond Pb–S (2.918(4) Å). The dimers, in their turn, are linked into polymer chains through Pb. . .S interactions at 3.298(4) Å. The coordination polyhedron of the Pb atom in the structure of $Pb(S_2PMe_2)_2$ is a distorted ψ-pentagonal bipyramid with a vacant equatorial position, suggesting the presence of the stereochemically active LP. Attributing the rather long Pb. . .S distances (3.298(4), 3.485(5) Å) to secondary bonds, the coordination polyhedron can be approximated as type **II** (Table 4).

The crystal structure of $Pb(S_2PEt_2)_2$ contains three monomeric complexes $[Pb(S_2PEt_2)_2]$ linked by Pb. . .S interactions into polymer chains [94]. Each Pb atom is coordinated in an anisobidentate fashion by two diethyldithiophosphinate ligands giving rise to pyramidal PbS_4 groups with the S atoms in the basal plane and the Pb atom in the vertex. One of the ligands chelates asymmetrically (Pb(1)–S(1) 2.749(5), Pb(1)–S(2) 3.196(8) Å), while the second one is bonded to the Pb(1) atom more symmetrically (Pb(1)–S(3) 2.749(7), Pb(1)–S(4) 2.909(8) Å). A similar situation takes place at the Pb(2) atom. The chelate Pb–S bonds formed by the ligands with the Pb(3) atom are slightly asymmetric (Table 4). Aside from the bonds with the S atoms of their own diethyldithiophosphinate ligands, each metal atom forms two bonds with the S atoms of adjacent complexes, resulting in formation of a polymer chain. The coordination polyhedra of the Pb ions can be described as pentagonal bipyramids with an empty coordination site in the equatorial plane. According to the VSEPR model, the coordination environment can be thought of as type **II** with the vacant position in the equatorial plane occupied by the stereochemically active LP (Table 4).

The structure of $Pb(S_2PPh_2)_2$ consists of monomeric $[Pb(S_2PPh_2)_2]$ complexes linked through secondary Pb. . .S interactions into a supramolecular structure [95]. Both ligands in the monomer form anisobidentate-chelate bonds giving rise to a distorted tetragonal PbS_4 pyramid with the S atoms in the base and the Pb atom in the apical vertex. Through the intermolecular Pb. . .S interaction at 3.270 Å, the monomers are linked into symmetric dimers $\{Pb(S_2PPh_2)_2\}_2$. In addition, each Pb atom in the dimer forms longer intermolecular contacts (3.448 Å) with the S atoms of adjacent dimers resulting in a weak polymeric structure. The Pb atom is surrounded by six S atoms can be described as either a distorted octahedron or, taking into account the stereochemically active LP, as a ψ-capped octahedron. The geometry of the Pb atom's primary coordination sphere (without taking into account intermolecular Pb. . .S interactions) can be represented, within the scope of the VSEPR model, as type **II** (Fig. 16).

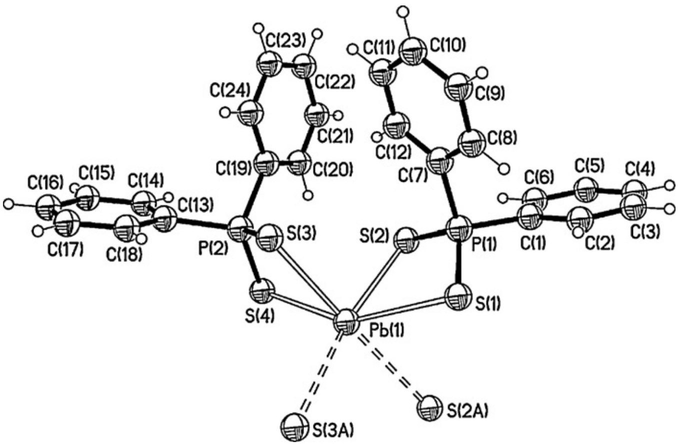


Fig. 16. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(S_2PPh_2)_2$.

The crystal structures of two modifications α- and β-$Pb(S_2P^iBu_2)_2$ are composed of monomeric complexes $[Pb(S_2P^iBu_2)_2]$ [96]. The structure of β-$Pb(S_2P^iBu_2)_2$ contains two crystallographically independent molecules, while that of α-$Pb(S_2P^iBu_2)_2$ has four. The molecular complexes α- and β-$Pb(S_2P^iBu_2)_2$ have identical type **II** structures (Table 4).

5.2.1. Mixed ligand dialkyldithiophosphinates

The crystal structures of lead(II) mixed ligand diisobutyldithiophosphinates with N-donor ligands L = phen, bpy and 4,4′-bpy were investigated [97,98]. The compounds $Pb(S_2P^iBu_2)_2(phen)$ and $Pb(S_2P^iBu_2)_2(bpy)$ [97] have similar structures built from $[Pb(S_2PR_2)(L)]$ molecular units linked by intermolecular interactions into dimers. In $Pb(S_2P^iBu_2)_2(phen)$ the complexes are crystallographically equivalent, while $Pb(S_2P^iBu_2)_2(bpy)$ contains two crystallographically independent molecules. Both complexes have virtually the same structure with only slight differences.

The coordination environment of the Pb atom in $Pb(S_2P^iBu_2)_2(phen)$ includes two N atoms of the bidentate phen with comparatively short bond lengths (2.534(3) and 2.656(3) Å) and four S atoms of two diisobutyldithiophosphinate ligands. One of the ligands forms slightly asymmetric chelate bonds (2.955(1), 3.040(1) Å), while the second is anisobidentate (2.993(1), 3.206(1) Å). The coordination sphere of the Pb atom also contains the bridging S atom of the adjacent complex (Pb. . .S(3A) 3.364(1) Å), which is responsible for dimer formation. The resulting coordination polyhedron (CN 7) has the pentagonal bipyramid configuration with N(2F) and S(3A) in the axial positions and the S atoms and N(1F) in the equatorial plane. The bridging S(3A) atom can be considered as a secondary atom. If one neglects this interaction, the coordination polyhedron of the Pb atom can be represented as a ψ-pentagonal bipyramid (**IV**) with an axial position occupied by the stereochemically active LP (Fig. 17). The N atom having the shortest Pb–N bond distance is located in the axial position of the ψ-pentagonal bipyramid, while the equatorial plane is formed by the second N atom from the phen ligand and four S atoms from the two diisobutyldithiophosphinate ligands. The complex $Pb(S_2P^iBu_2)_2(bpy)$ has the same ψ-pentagonal bipyramidal (type **IV**) structure (Table 4).

The structure of $Pb(S_2P^iBu_2)_2$(4,4′-bpy) is composed of $Pb(S_2P^iBu_2)_2$ molecules linked by the bridging 4,4′-bpy molecules into linear polymer chains [98]. The Pb atom is coordinated asymmetrically by four S atoms from the two bidentate dithiophosphinate ligands (Pb–S range: 2.812(2)–3.093(2) Å). It is also bonded by two N atoms in *trans*-position from two bidentate bridging 4,4′-bpy molecules. Besides the bonds from four S atoms of the two diisobutyldithiophosphinate ligands, the Pb atom also forms a rather weak bond with a S atom belonging to the adjacent polymer chain (Pb. . .S 3.295(2) Å), which results in formation

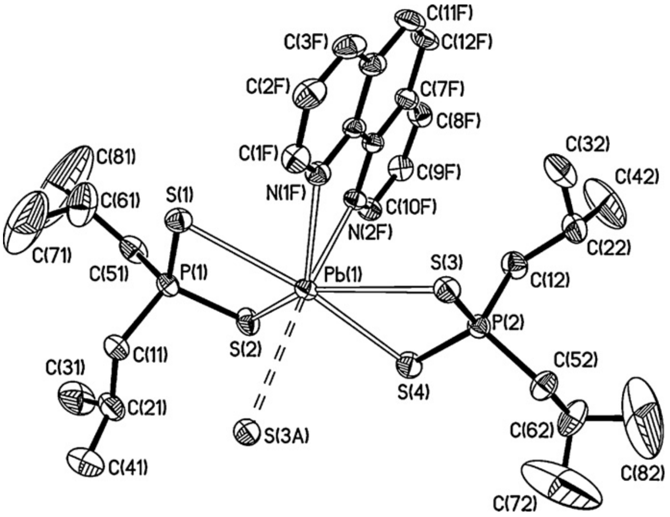
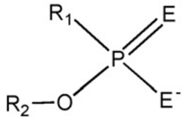


Fig. 17. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(S_2P^iBu_2)_2(phen)$.

of supramolecular columns. Taking into account the bridging S atom, the coordination polyhedron of the Pb atom is described as a pentagonal bipyramid. In accordance with the VSEPR model, the coordination polyhedron in $Pb(S_2P^iBu_2)_2$(4,4′-bpy) corresponds to a ψ-pentagonal bipyramid (type **V**) with the N atoms in the apical positions (<N–Pb–N 177.0(1)°) and four S atoms in the equatorial plane. The fifth vertex of the equatorial plane is vacant and occupied by the stereochemically active LP.

5.3. Alkyl(aryl)phosphonodithio(seleno)ates

Phosphonodithio(seleno)ates can be considered as derivatives of dithio(seleno)phosphates, in which one alkyl(aryl)oxy group is substituted by an organic radical (**32**). The crystal structures of six such compounds were determined. The structure of $Pb\{Fc(EtO)PS_2\}_2$ (Fc = ferrocenyl) contains molecular units in which the Pb resides above the center of a distorted square pyramid 1.25 Å from the basal plane formed by four anisobidentate-coordinated S atoms [99]. One of the ligands is bidentate chelating (2.740(2) vs. 3.008 (2) Å), while the second one is bridging (Pb–S(21) 2.737(2), Pb–S(22) 2.854(2) Å). The Pb–S(22) bond involves the S(22) bridging atom.



E = S, R_1 = Fc, p(MeO)Ph; R_2 = Et, ^{i}Pr
E = Se, R_1 = Ph, R_2 = Me, Et

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The coordination polyhedron of the Pb atom in the dimeric structure of $Pb\{Fc(EtO)PS_2\}_2$ has a ψ-trigonal-bipyramidal geometry with the atoms S(21) and S(1) and the LP in the equatorial plane (<S(21)–Pb–S(1) 92.45(5)°) and the atoms S(22) and S(2) (<S(22)–Pb–S(2) 154.19(4)°) in the axial positions. The S(22A) atom belonging to the adjacent unit of the dimer and located in the LP area forms a secondary bond with the Pb atom (Table 4).

Unlike the dimeric structure of $Pb\{Fc(EtO)PS_2\}_2$, the structure of bis[(isopropoxy)ferrocenylphosphonodithioato]lead(II), $Pb\{Fc(^iPrO)PS_2\}_2$ is polymeric [100] and similar to that of $Pb(Et_2dtp)_2$ [86]. The structure is built up of molecular units having the configuration of a distorted tetragonal pyramid with the apical Pb atom located 1.41 Å above the basal plane formed by four S atoms. As in the structure of $Pb\{Fc(EtO)PS_2\}_2$, the two $Fc(^iPrO)PS_2^-$ ligands are anisobidentate with the distances Pb–S falling into the range 2.721(3)–2.950(3) Å (Table 4). The geometry of the Pb atom coordination polyhedron is ψ-trigonal-bipyramidal.

The polymeric chain structure of $Pb\{(p\text{-}MeO)Ph(EtO)PS_2\}_2$ [101] is different from the previously considered polymer chain structures with the exception of $Pb(Me_2dtp)_2$ [90], in which the chain formation occurs by secondary comparatively weak Pb. . .S interactions. Each Pb atom is bonded to four S atoms contributed from four different phosphonodithioate ligands with formation of a distorted ψ-trigonal-bipyramidal polyhedron in accordance with the VSEPR model. The polyhedra are linked by rather strong Pb. . .S interactions at distances 3.133 Å. The structure of $Pb\{(p\text{-}MeO)Ph(EtO)PS_2\}_2$ is similar to that of $Pb(Me_2dtp)_2$ not only in terms of the polymer chain structure, but also in terms of virtually equal lengths of both primary and secondary bonds (Table 4).

Unlike $Pb\{(p\text{-}MeO)Ph(EtO)PS_2\}_2$, $Pb\{(p\text{-}MeO)Ph(^iPrO)PS_2\}_2$ exhibits a dimeric structure [101]. In each monomeric building unit one of the ligands, as in the structure of $Pb\{Fc(EtO)PS_2\}_2$ [99], is bidentate-chelating (Pb–S(1) 2.7363(11), Pb–S(2) 2.8954(12) Å), while the second ligand with the same Pb–S bond lengths is bonded via three atoms to the two Pb ions. The intermolecular secondary distance Pb. . .$S(2^{ii})$ is 3.45(1) Å. The coordination polyhedron is a distorted pyramid with the Pb atom located above the basal S_4 plane at a distance of 1.30 Å. As in $Pb\{Fc(EtO)PS_2\}_2$ [99], the geometry is type **II** with the atoms $S(2,2^i)$ in the axial positions (<S(2)–Pb–$(S2^i)$ 150.21(3)°) and S(1), its symmetry equivalent (<S(1)–Pb–$S(1^i)$ 95.18(3)°) and the stereochemically active LP in the equatorial plane (Table 4).

The crystal structures of two lead(II) phosphonodiselenoates having different dimeric structures are known. In $Pb\{Ph(EtO)PSe_2\}_2$ the lead center is chelated by two $Ph(EtO)PSe_2^-$ ligands [102]. One of the ligands forms virtually equal bonds (2.9249(12), 2.9335(9) Å), while the other ligand is anisobidentate (2.8522(9) vs. 3.2235(10) Å). The geometry of the coordination polyhedron is described as distorted trigonal-bipyramidal with a vacant position in the equatorial plane, in accordance with the VSEPR model. The monomer units can be considered to be linked into dimers through much longer Pb. . .Se bonds (3.390(1) Å) and these are linked in a three-dimensional network by weaker secondary Pb. . .Se interactions (Pb. . .Se 3.778 and 3.823 Å).

$Pb\{Ph(MeO)PSe_2\}_2$ [102] has a somewhat different structural motif as compared to that of $Pb\{Ph(EtO)PSe_2\}_2$. This structure is built around a central Pb_2Se_2 ring. Both unique Pb atoms are bound to two different types of ligands. One of the ligands is terminal and forms anisobidentate-chelate bonds (2.8757(5) vs. 3.0652(5) Å). The second ligand is bonded to two Pb atoms (Pb–Se(1) 2.8296(6) and Pb–Se(2A) 3.1327(5) Å), which gives rise to the central Pb_2Se_2 ring. The secondary Pb. . .Se(2) interactions forming the dimeric structure are slightly shorter than in $Pb\{Ph(EtO)PSe_2\}_2$, and their distance is 3.2689(5) Å (Table 4). The coordination polyhedron, as for $Pb\{Ph(EtO)PSe_2\}_2$, has a ψ-trigonal-bipyramidal geometry with the atoms Se(4) and Se(2A) (<Se(4)–Pb–Se(2A) 153.16(1)°) in the axial positions and the atoms Se(1) and Se(3) (<Se(1)–Pb–Se(3) 86.09(1)°) and the stereochemically active LP in the equatorial plane (Fig. 18; Table 4). The structural dimers are linked together by weak Pb. . .Se and Se. . .Se interactions.

5.4. Imidodithio(seleno)phosphinates

Three complexes of Pb(II) with imidodithio(seleno)phosphinate ligands (**33**) were investigated. The structure of $Pb\{(SPPh_2)_2N\}_2$ is built up of discrete $Pb\{(SPPh_2)_2N\}_2$ molecules [103]. The Pb atom is chelate-, anisobidentate-coordinated by the S atoms from both ligands giving rise to a trigonal bipyramid (type **II**) with a vacant equatorial position, in accordance with the VSEPR model. The S(2) atoms are located in the axial positions (Pb–S(2) = 2.943(4) Å,

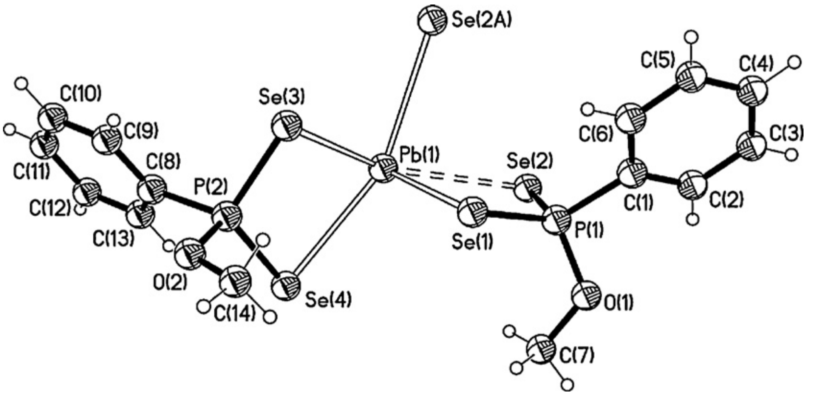
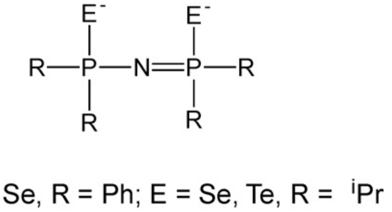


Fig. 18. ORTEP drawing of the coordination environment of the Pb(II) atom in Pb{Ph(MeO)PSe_2}$_2$.

<S(2)–Pb–S(2^i) = 176.4(1)°), while the S(1) atoms are found in the equatorial plane (Pb–S(1) = 2.695(4) Å, <S(1)–Pb–S(1^i) = 86.4(1)°). The third vertex in the equatorial plane is vacant, indicative of the presence of the stereochemically active LP. Secondary Pb. . .S bonds are absent in the molecular structure of Pb{$(SPPh_2)_2N$}$_2$, making it substantially distinct from the other dithiophosphate [86,87] and dithiophosphinate complexes [93–95], where supramolecular associations are built through secondary Pb. . .S bonds with formation of dimer or polymer structures (Table 4).



E = S, Se, R = Ph; E = Se, Te, R = ^{i}Pr

33

The discrete molecular complexes Pb{$(SePPh_2)_2N$}$_2$ are present in the structure of the selenium analog [104]. As in Pb{$(SPPh_2)_2N$}$_2$, in the structure of Pb{$(SePPh_2)_2N$}$_2$ the Pb atom is coordinated by the Se donor atoms of both bidentate ligands with formation of a distorted ψ-trigonal-bipyramidal coordination geometry with a vacant equatorial position. The Pb–Se bond lengths in the chelate ring are slightly asymmetric (2.874(3), 2.997(2) Å); however, this asymmetry is substantially lower than in the structure of the corresponding thiolate complex. In the structure of Pb{$(SePPh_2)_2N$}$_2$, as in the structure of Pb{$(SPPh_2)_2N$}$_2$, secondary Pb. . .Se interactions are absent.

In Pb{$(SeP^iPr_2)_2N$}$_2$ the Pb–Se bonds lie within the range 2.777(1)–3.099(1) Å [105], similar to those of the phenyl derivative Pb{$(SePPh_2)_2N$}$_2$ (Table 4). In contrast to monomeric Pb{$(SePPh_2)_2N$}$_2$, Pb{$(SeP^iPr_2)_2N$}$_2$ contains C_2-symmetric dimers formed via secondary Pb. . .Se(3A) (3.574(2) Å) interactions. The authors describe the coordination geometry around Pb(II) as square pyramidal with the LP on the vacant octahedral site; however, this description includes rather long intermolecular Pb. . .Se contacts, which based on the interatomic separations can be assigned to secondary bonds. According to the VSEPR model, the coordination polyhedron of the primary coordination sphere of the Pb(II) atom in Pb{$(SeP^iPr_2)_2N$}$_2$, as in the case of the phenyl analogue, can be presented as a ψ-trigonal-bipyramid (Fig. 19; Table 4). The bridging Se(3A) atoms involved in secondary bonding are located in the area of the Pb^{2+} LP.

In addition to Pb{$(SeP^iPr_2)_2N$}$_2$, the structure of the tellurium analog, Pb{$(TeP^iPr_2)_2N$}$_2$ has been described [105]. The Pb–Te distances range from 2.946(1) to 3.308(1) Å and are slightly larger than the corresponding Pb–Se bonds in the isostructural Se compound as expected due to the larger ionic radius of Te^{2-}. The molecular units are associated into dimers through secondary Pb. . .Te interactions (3.597(1) Å). As with Pb{$(SeP^iPr_2)_2N$}$_2$, the coordination polyhedron of the Pb(II) atom is a ψ-trigonal-bipyramid (Table 4).

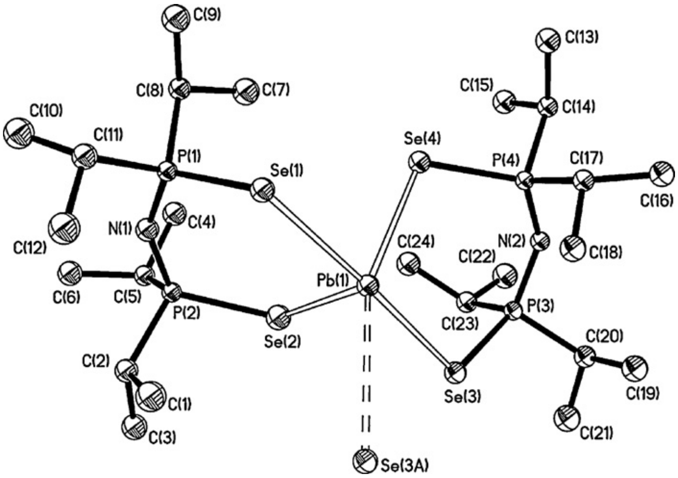
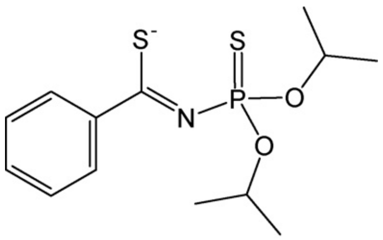


Fig. 19. ORTEP drawing of the coordination environment of the Pb(II) atom in Pb{$(SeP^iPr_2)_2N$}$_2$.

The structure of bis{(diisopropoxythiophosphoryl)thiobenzamido}lead(II), Pb{PhC(S)NP(S)$(O^iPr)_2$}$_2$ (**34**) [106] is similar to that of the earlier described Pb(II) imidodithio(seleno)phosphinates [103,104]. The Pb atom in the structure has a ψ-trigonal-bipyramidal coordination geometry with a vacant equatorial position. Two axial positions are occupied by the thiophosphoryl S atoms (Pb–S 2.834(2), 3.005(2) Å) and two equatorial positions—by the thioamide S atoms (Pb–S 2.698(1), 2.701(2) Å) (Table 4). The structure of Pb{PhC(S)NP(S)$(O^iPr)_2$}$_2$ is pseudo-dimeric. The length of the Pb. . .S contact (3.732 Å) linking monomers into a dimer is rather long and close to the sum of the van der Waals radii of Pb and S atoms [23].



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6. Conclusions

One of the most intriguing problems of the coordination chemistry of the heavy main group elements having a lone pair of electrons is the elucidation of the coordination polyhedron geometry, which has important implications on the stability and properties of these complexes. In many cases the identification of the coordination geometry in such complexes is difficult because of the irregular shape of the polyhedron as well as possible secondary interactions, which are longer than the sum of covalent radii but shorter than the sum of van der Waals radii [107]. While some of these distances may seem long, the solid state structures would not exist as they do without significant interactions between the Pb^{2+} ions and the ligands. The geometry of molecules and complexes of different elements, including those with a LP, can be determined by the valence shell electron-pair repulsion (VSEPR) model, which has been successfully used for more than 50 years to rationalize and predict coordination environments [20]. We successfully applied this model for description of the stereochemistry of lead(II) complexes with oxygen donor ligands [19].

In this review the description of the stereochemistry of structurally investigated Pb–S(Se) complexes is based on the analysis of the Pb–S(Se) bond lengths and S(Se)–Pb–S(Se) angles of the first coordination sphere of the Pb atom with using the VSEPR model. In all the studied structures of Pb–S(Se) complexes, with a few exceptions, the lone pair of electrons is stereochemically active and has an influence on the coordination geometry of the central atom. For complexes with the central atoms coordination numbers in the range from (3+*E*) to (6+*E*), the VSEPR model assigns the following coordination polyhedra: ψ-tetrahedron (**I**), ψ-trigonal bipyramid (**II**), ψ-octahedron (**III**), and ψ-pentagonal bipyramid with an axial (**IV**) or equatorial (**V**) vacant position. The data shown in both the text and the Tables 1–4 enable one to obtain information on the composition and structure of the primary coordination sphere of the Pb atom and the whole ligand surrounding of the central atom in these compounds.

In the structures of aliphatic monothiocomplexes, including those of a majority of mixed ligand thiourea complexes, the Pb atoms have mostly a ψ-trigonal-bipyramidal coordination geometry (type **II**). Unlike the structures of aliphatic monothiocomplexes, in the crystal structures of aromatic monothio(seleno)complexes, bis{benzenethio(seleno)lates, including those of mixed ligand bis(benzenethiolates) with a few exceptions, only the ψ-tetrahedral coordination geometry of the Pb atoms (type **I**) is realized (Table 1). In the latter group of Pb complexes, different types of crystal structures are seen—from monomers to polymers.

In the series of lead(II) polythio(seleno) complexes, the most exhaustive structural studies were performed for those of lead(II) dithio(seleno)late complexes, whose stereochemistry is characterized by a ψ-trigonal-bipyramidal coordination geometry of the first coordination sphere of the central atom. Among the 12 reported lead(II) dithio(seleno)late structures (13 types of Pb atoms), only in one of the compounds does the Pb atom have a ψ-tetrahedral geometry (Pb(mnt) [58]), while one of the non-equivalent (Pb(1)) atoms in the structure of $[Pb_2(Bmm^{Me})_5](ClO_4)_4 \cdot H_2O$ [61] demonstrates a unique ψ-octahedral coordination geometry (Table 2).

In the structures of all of the reported lead(II) dialkyldithio(seleno)carbamates, alkylxanthates, dialkyl(aryl)dithiophosphates, dialkyl(aryl)dithiophosphinates, alkyl(aryl)phosphonodithio(seleno)-ates and imidodithio(seleno)phosphinates, except the respective mixed ligand complexes, the central atom of the primary coordination sphere has a ψ-trigonal-bipyramidal coordination geometry (type **II**, Tables 3 and 4).

In the series of lead(II) dialkyldithiocarbamates containing equivalent Pb atoms, increasing the size of an alkyl substituent of the N atom results in a regular reduction of the average length of

Table 5
The polyhedra of the Pb atoms in the crystal structures of lead(II) complexes with S(Se)– and O-donor atom ligands.

Pb(II) complexes	Number of structures	Number of Pb(II) atoms	The number of polyhedra **I–V** of the primary coordination sphere of the Pb(II) atoms				
			ψ-tetrahedron (**I**)	ψ-trigonal bipyramid (**II**)	ψ-octahedron (**III**)	ψ-pentagonal bipyramid (axial) (**IV**)	ψ-pentagonal bipyramid (equatorial) (**V**)
Pb(II) complexes and mixed ligand complexes with S(Se)-donor atom ligands	101(7)*	126(7)	27	86	8	4	1
Pb(II) complexes with O-donor atom ligands	98	126	13	62	27	6	18

* The number in parentheses indicate Pb(II)Se complexes.

equatorial Pb–S bonds from 2.779 to 2.658 Å (see Table 3). Some reduction is also observed for the lengths of axial bonds in the above series; however, it does not correlate as well as the equatorial Pb–S bonds lengths.

As in the structures of lead(II) dialkyldithiocarbamates, the three structures of neutral Pb(II) alkylxanthates each show chelation by two xanthate ligands with asymmetric Pb–S bonds and have the type **II** structure. The monomeric alkylxanthate complexes are linked into polymeric chains by weak Pb. . .S interactions (the average value 3.378 Å).

The averages of the primary Pb–S equatorial and axial bond lengths for the reported lead(II) dialkyl(aryl)dithiophosphates are 2.792 and 3.008 Å, respectively, which is somewhat larger than the corresponding bond lengths (2.714 and 2.879 Å) in the structures of lead(II) dialkyldithiocarbamates with the same coordination geometry of the central atom, indicating formation of stronger chelate bonds in the latter structures.

The coordination geometry of the central atom and the supramolecular association of the polyhedra in the structures of dialkyl(aryl)dithiophosphinates, alkyl(aryl)phosphonodithio(seleno)-ates and imidodithio(seleno)phosphinates is identical to that in the structures of Pb(II) dialkyl(aryl)dithiophosphates. Similar values characterize the average lengths of both primary and secondary Pb–S bonds in these compounds: for example, 2.772, 2.949 and 3.321 Å in the structures of dithiophosphinates and 2.714 and 2.879 and 3.319 Å in those of dithiophosphates. In the structures of Pb(II) 1,1-diselenolate complexes the lengths of primary Pb–Se bonds are larger by ∼0.1 Å than the corresponding Pb–S bonds.

The surveys of the structural data available for Pb–S(Se) and Pb–O complexes have pointed out to important similarities as well as some distinct features in the coordination modes and Pb(II) polyhedra adopted by complexes with analogous composition, but different donor atoms, as well as compounds with similar donor atom sets. The most common coordination geometry of the first coordination sphere of Pb(II) atoms for both Pb–S(Se) and Pb–O [19] complexes is ψ-trigonal-bipyramidal (type **II**) (86 and 62 examples, respectively; Table 5). The coordination polyhedra of types **III**–**V** are common for Pb–O complexes, but they represent only a very rare occurrence in the case of Pb–S(Se) compounds and are exclusively characteristic for mixed ligand complexes. As far as type **I** polyhedra are concerned, they are found more frequently among Pb–S(Se) complexes (27 vs. 13).

It is interesting to compare the Pb–S(Se) and Pb–O [19] complexes with similar donor sets of atoms and coordination modes. For instance, the pair of Pb(II) complexes with (dimethylamino)thiosquarate and (dimethylamino)squarate ligands ($Pb(Me_2NC_4O_2S)_2(dmf)$ [28] and $Pb(Me_2NC_4O_3)_2(H_2O)_2$ [108]) forms type **II** polyhedra around Pb(II) and both compounds display polymeric chain structures. Similarly, a comparison between Pb(II) dithio(seleno)late complexes, including dithiocarbamate, xanthate, phosphor-1,1-dithiolate complexes and Pb(II) β-diketonates [19], Pb(II) phosphinates ($Pb\{(C_6H_5)_2PO_2\}_2$ [109], $Pb\{(^tBu)_2PO_2\}_2$ [110]), aminophosphonates ($Pb\{NH(CH_2PO_3H)_2\}$ [111], $Pb\{CH_3N(CH_2PO_3H)_2\}$ [112]) reveals that Pb(II) polyhedra in all these complexes have the type **II** structure; monomers, dimers and polymers form depending on the number of secondary S(Se) atoms and/or O atoms involved in interactions. In contrast, the coordination polyhedra of Pb atoms in thio(seleno)phenolate and nitrophenolate complexes differ, despite similarities in the coordination modes (cf. $Pb(SC_6H_5)_2$ [40], $[Pb\{Se(C_6H_2)(CF_3)_3\}_2]_2\cdot 3tol$ [43] and $Pb\{O(C_6H_4)NO_2\}_2$ [113], $Pb\{O(C_6H_3)(NO_2)_2\}_2$ [114]). The Pb–S(Se) complexes adopt the type **I** Pb(II) polyhedra, while the corresponding Pb–O complexes are type **II**. The complexes $Pb(SC_6H_5)_2$, $Pb\{O(C_6H_4)NO_2\}_2$ and $Pb\{O(C_6H_3)(NO_2)_2\}_2$ have polymeric chain structures, while $Pb\{Se(C_6H_2)(CF_3)_3\}_2]_2\cdot 3tol$ is dimeric.

The survey of the crystal structures of Pb(II) complexes with S- and Se-donor atoms revealed two distinct features of the stereochemistry of this class of compounds compared to Pb(II) complexes with O-donor ligands: (i) LP of the Pb(II) atoms is stereochemically active virtually in all the structurally investigated Pb–S(Se) complexes; (ii) this class of compounds (except mixed ligand complexes) displays two preferred geometries of the Pb(II) first coordination sphere—ψ-tetrahedral (**I**) and ψ-trigonal-bipiramidal (**II**). These distinctive features are caused by different donor ability of the S(Se) and O atoms, respectively, and by the ability of Pb(II) to form predominantly chelate bonds with bidentate dithio(seleno)-ligands.

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