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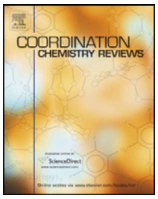

Review

Stereochemistry of lead(II) complexes with oxygen donor ligands

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Abbreviations: VSEPR, valence shell electron-pair repulsion; CN, coordination number; LP, *E*, lone pair of electrons; **I**, ψ-T, ψ-tetrahedron, tetrahedron with a vacant vertex; **II**, ψ-TBP, ψ-trigonal bipyramid, trigonal bipyramid with a vacant vertex in the equtarial 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; CSD, Cambridge Structural Database; CCDC, Cambridge Crystallographic Data Centre; DFT, density functional theory; MOCVD, metal–organic chemical vapour decomposition; dmso, dimethylsulfoxide; dmf, *N,N*-dimethylformamide; dma, *N,N*-dimethylacetamide; dmam, dimethylamine; Hac, acetic acid; Hhtno, heptanoic acid; Hcrot, (*E*)-2-butenoic acid; Hglyc, hydroxyacetic acid; Hdmac, 2-methylpropanoic acid; Hpiv, 2,2-dimethylpropanoic acid; H_2odac, oxydiacetic acid; Hval, 2-amino-3-methylbutanoic acid; H_2malo, malonic acid; H_2male, maleic acid; H_2azel, azelaic acid; H_2suc, succinic acid; H_2chdc, 1,4-cyclohexanedicarboxylic acid; H_2asp, aspartic acid; H_2glyglu, *N*-glycylglutamic acid; H_3cit, citric acid; $tmhd^-$, 2,2,6,6-tetramethylheptane-3,5-dionate; $acac^-$, 2,4-pentanedionate; pta^-, 1,1,1-trifluoro-5,5-dimethylhexa-2,4-dionate; $thfbd^-$, 1-(2-thienyl)-4,4,4-trifluorobutene-1,3-dionate; dbm^-, 1,3-diphenylpropane-1,3-dionate, dibenzoylmethanide; $dmfod^-$, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dione; hfa^-, hexafluoroacetylacetonate; H_2squ, 3,4-dihydroxy-3-cyclobutene-1,2-dione; Hmsqu, 3-(dimethylamino)-4-hydroxycyclobut-3-ene-1,2-dione; Hesqu, 3-(diethylamino)-4-hydroxycyclobut-3-ene-1,2-dione; Hamsqu, 3-amino-4-hydroxycyclobut-3-ene-1,2-dione; H_2pcp, methylenebis(phenylphosphinic) acid; H_2amdph, azanediylbis(methylene)diphosphonic acid; H_2aedp, 1-aminoethane-1,1-diyldiphosphonic acid; H_2phca, 2-(phosphonomethylamino)acetic acid; H_3caeph, 3-phosphonopropanoic acid; H_2pbmp, *N,N′*-piperazinebis(methylenephosphonic) acid; H_3sip, 5-sulfoisophthalic acid; Hhmsul, hydroxymethanesulfonic acid; H_2sal, 2-hydroxybenzoic acid; H_3dhb, 2,6-dihydroxybenzoic acid; H_2hca, 4-hydroxylcinnamonic acid; H_2nsal, *p*-nitrosalicylic acid; H_2dnsal, 2,4-dinitro-5-hydroxybenzoic acid; H_2sb, 4-sulfonatobenzoic acid; H_3ssa, 2-hydroxy-5-sulfobenzoic acid; Hamb, 4-aminobenzoic acid; Hnb, 2-nitrobenzoic acid; Hdnb, 3,5-dinitrobenzoic acid; Hino, isonicotinic acid N-oxide; H_2fa, fumaric acid; H_3btc, 1,3,5-benzenetricarboxylic acid; Hhmpyr, 3-hydroxy-1,2-dimethylpyridin-4(*1H*)-one; Hpa, phenoxyacetic acid; Hpda, phenoxydimethylacetic acid; Hmcpa, 2-(4-chloro-2-metylphenoxy)acetic acid; H_2(*o*-pht), *o*-phtalic acid; H_2(*m*-pht), *m*-phtalic acid; H_2(p-pht), *p*-phtalic acid; nmp, 1-methylpyrrolidin-2-one; H_2napdc, naphthalene-1,4-dicarboxylic acid; H_2dpa, 1,1′-biphenyl-2,2′-dicarboxylic acid; H_2dthb, 2,2′-disulfanediyldibenzoic acid; H_3btc, benzene-1,3,5-tricarboxylic acid; H_4bttc, benzene-1,2,3,4-tetracarboxylic acid; Hnph, 4-nitrophenol; Hdnph, 2,4-dinitrophenol; Hpic, picric acid; H_2styph, 2,4,6-trinitro-1,3-benzenediol; Hbzgly, *N*-benzoylglycine; Hfuoac, 5-fluorouracil-1-acetic acid; Hvnl, 4-hydroxy-3-methoxybenzaldehyde; Htrop, 2-hydroxy-2,4,6-cycloheptatrien-1-one; Hnorf, 1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid.

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Dedicated to the 50th anniversary of the VSEPR model.

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ABSTRACT

This review discusses the coordination number (CN) and the coordination geometry of the first coordination sphere of Pb(II) atoms in crystal structures of 98 lead(II) complexes with O-donor ligands and the stereochemically active lone pair of electrons (LP, *E*) in the terms of the valence shell electron-pair repulsion (VSEPR) model. The CN of Pb(II) atoms of the first coordination sphere has values falling into the range (3 + *E*) to (6 + *E*). The following coordination polyhedra—ψ-tetrahedron (**I**), ψ-trigonal bipyramid (**II**), ψ-octahedron (**III**), ψ-pentagonal bipyramid with an axial (**IV**) or equatorial (**V**) vacant position are formed. For the investigated structures of the Pb(II) complexes, the formula of each compound, the overall CN of the Pb(II) atom considered as the sum of the CN in the first coordination sphere and the number of secondary bonds, the polyhedron shape, the Pb–O bond lengths, and O–Pb–O bond angles in the first coordination sphere, secondary bond lengths, references and REFCODEs are presented in the comprehensive Tables. The quantum chemical investigations performed using density functional theory (DFT) method have confirmed the stereochemical activity of the LP of Pb(II) atoms in the studied structures of lead(II) complexes with O-donor ligands.

1. Introduction

Throughout human history lead and its compounds have known various applications, ranging from water pipes and projectiles to additives for wines and fuels. Lead was regarded by the ancients as the father of all metals and different civilizations used it extensively [1]. It is widespread, easy to extract, dense, highly malleable and stable to corrosion. However, with more evidence of lead toxicity and its adverse effects on human health, many of its applications were discontinued. One of the most notorious is the rise and decline of tetraethyllead as an antiknocking agent in gasoline during the 20th century. Once a common additive to gasoline, tetraethyllead usage was largely discontinued because of its high toxicity and disadvantageous effects on catalytic converters. Nowadays, lead use is mostly restricted to the manufacture of batteries, metal alloys, glasses, ceramic and radiation shielding materials as well as some pigments and paint additives [1]. Recently, an increasing interest has emerged in synthesis and study of the properties of lead(II) compounds motivated partly by the necessity of understanding the Pb(II) binding preferences for the design of selective chelation therapy agents [2–6] and remediation of waters and soils [3,7,8]. Another topic of interest is associated with the occurrence in Pb(II) compounds of a stereochemically active lone pair of electrons (LP, *E*) and its effect on the stereochemistry and properties of solid-state lead(II)-containing materials [9–12].

1.1. Previous reviews

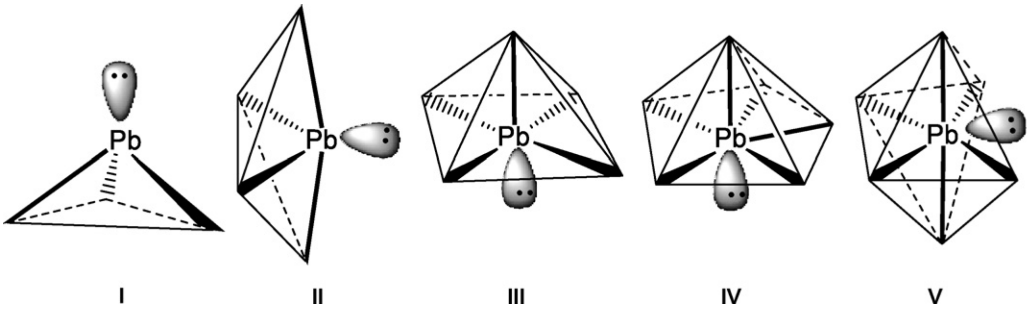
Despite the resurgence of interest in the structural chemistry and stereochemistry of Pb(II) complexes, there is a lack of systematic studies on this important class of compounds. The first review devoted to structural chemistry of Pb(II) compounds was published in 1976 by Harrison [13]. Along with the structures of Ge(II) and Sn(II) compounds, the review discusses the structures of some Pb(II) inorganic compounds. In a more complete form the crystal structures of Pb(II) compounds are presented in the review by the same author, published in *Comprehensive Coordination Chemistry* [14].

A detailed review of lead coordination and organometallic compounds is presented in a rather detailed work by Holloway and Melnik [15], in which more than 360 compounds were examined. About 20% are organometallic Pb(IV) compounds. The compounds are divided into subgroups based on their nuclearity. The tables of crystallographic and structural data, presented in [15] for each coordination number (CN) of the Pb atom, are of special interest. The same authors have also reviewed the crystallographic and structural data of lead oxyacids and halide compounds [16] as well as heterometallic lead coordination and organometallic compounds [17].

Parr published a brief review of the coordination chemistry of Pb(II) in 1997 [18], followed by a more extensive review on Pb complexes the *Comprehensive Coordination Chemistry II* [19]. In a detailed review by Claudio et al. [3], devoted to the fundamental coordination chemistry, environmental chemistry, and biochemistry of Pb(II), one of the sections describes structural investigations on Pb(II) complexes. The stereochemistry of Pb(II) complexes with aminopolycarboxylate ligands and the role of LP for this class of compounds were reviewed recently [20].

1.2. Hemidirected vs. holodirected

The electron configuration of Pb^{2+}, $[Xe]4f^{14}5d^{10}6s^2$, contains the $6s^2$ electron pair, which can be either stereochemically active or inactive in Pb(II) compounds. Based on the structural data presented in the Cambridge Structural Database (CSD) and *ab initio* molecular orbital optimizations, Shimoni-Livny et al. [21] investigated the role of the LP on the coordination geometry of the lead(II) ion. Based on the disposition of ligands around the metal ion, the authors [21] assigned the terminology described as "*holodirected, in which the bonds to ligand atoms are directed throughout the surface*



Scheme 1. Coordination polyhedra in Pb(II) complexes with O-donor ligands.

of an encompassing globe" and "*hemidirected*, *in which the bonds to ligand atoms are directed throughout only part of the globe*, *that is*, *there is an identifiable void (or gap) in the distribution of bonds to the ligands*".

Lead(IV) compounds exhibit a *holodirected* coordination geometry of the Pb atom, which is not surprising, taking into account that Pb(IV) has no LP. The crystal structures of lead(II) compounds presented in the CSD adopt both *holodirected* and *hemidirected* coordination geometry around the Pb atom. The geometry seems to strongly depend on the CN of Pb(II) and steric repulsion of the ligands. Thus, Pb(II) complexes with CN from 2 up to 5 usually have a *hemidirected* geometry of the Pb atom, while all Pb(II) compounds with high CNs (9–10) adopt, according to [21], a *holodirected* geometry of Pb(II). Both types of coordination geometry were detected in Pb(II) complexes with intermediate CN (from 6 to 8). A valuable part of the work by Shimoni-Livny et al. [21] is the quantum-chemical investigation, which confirmed the *holodirected* and *hemidirected* geometries of Pb(II) atom in four-coordinate gas-phase model compounds.

We would note that the concepts of stereochemically active and inactive lone pairs, that arises from the application of VSEPR model [22] to the lighter elements, breaks down for their heavier congeners as the s-orbitals become less involved in bonding. Consequently, an inert pair of electrons, i.e. the lone pair, will primarily reside in an orbital that is largely spherically symmetrical. The disposition of the ligands may then arise from the directional nature of the p-orbitals involved in bonding, rather than from a localized position for a LP. Regardless of the fine points of the orbital structures of the heavy metal complexes, the concept of stereochemical activity of a lone pair is still useful for describing structures and continues in common usage, in spite of its semantic limitations. The concepts of VSEPR model provide relatively good starting points for describing and classifying the structural types. Not surprisingly, it is common to find exceptions, or perhaps difficult to classify structures, for this class of compound.

The above-mentioned review papers present the structures of numerous Pb(II) compounds; however, in many cases the geometry of the Pb coordination polyhedra is not discussed. The number of publications dealing with crystal structures of Pb(II) complexes continues to increase every year. In most cases, however, the details about the geometry of the Pb atom are not presented.

1.3. *The VSEPR model*

The valence shell electron-pair repulsion (VSEPR) model [22] that enables one to predict and determine the geometry of molecules and complexes of different metals, including those with a LP, has received an extensive application to describe the stereochemistry of metal complexes. This model has been successfully applied for the last 50 years and found further development in the ligand–ligand repulsion and ligand close-packing models as well as in analysis of electron densities that serves as its physical basis [23]. For molecules and complexes containing the central atom A, ligand donor atoms X_n and the lone pair of electrons, the VSEPR model describes a geometry depending on the number of X as follows [24].

The molecules and complexes of composition AX_3E (CN A $(3+E)$) (E: lone pair of electrons) have a trigonal-pyramidal geometry with the metal atom in the apical vertex. The coordination polyhedron of the A atom is predicted to have a ψ-tetrahedral configuration (**I**) with the X–Pb–X angle less than an ideal tetrahedral angle of 109.5° (Scheme 1).

In the complexes AX_4E (CN A $(4+E)$) the A atom has a disphenoidal geometry (ψ-trigonal bipyramidal (**II**) with the lone pair of electrons in the equatorial plane) (Scheme 1).

For molecules and complexes of the AX_5E type with six electron pairs in the valence shell (one of them is a lone pair, CN A $(5+E)$), the VSEPR model describes the configuration of a square bipyramid (ψ-octahedron (**III**)) with E occupying one of the bipyramid axial vertices (Scheme 1). The characteristic feature of such configuration resulting from the presence of the stereochemically active lone pair and its interaction with bonding electron pairs is a shortening of A–X distance located in *trans*-position in regard to the E, as compared to the A–X distances in the bipyramid basal plane, and a decrease in the bond angles X_{ax}–Pb–X_{eq}, as compared to an ideal value of 90°.

For complexes with composition AX_6E (CN A $(6+E)$) the VSEPR model suggests the shape of a pentagonal bipyramid with the lone pair occupying the axial position (**IV**) (Scheme 1).

Pentagonal bipyramidal complexes with a vacant axial position (**IV**) were found in the crystal structure of isostructural compounds $(NH_4)_3Sb(C_2O_4)_3{\cdot}4H_2O$ and $K_3Sb(C_2O_4)_3{\cdot}4H_2O$ [25]. In the structure of lead(II) *O,O*′-diisopropylphosphorodithiolate [26] the Pb coordination geometry is an irregular pentagonal bipyramid in which the lone pair occupies an equatorial position (**V**) (Scheme 1). As will be shown in the present work, the Pb(II) coordination compounds with CN $6+E$ have both types of coordination polyhedra.

1.4. *Scope*

This review paper represents the first of a series of contributions on stereochemistry of Pb(II) complexes with O-, N-, S- as well as mixed donor ligands and is devoted exclusively to Pb(II) complexes with O-donor ligands and a stereochemically active LP. The main approach used to examine the coordination geometry of the Pb atom in lead(II) complexes with O-donor ligands is based on the VSEPR model [22,23]. The selection of the crystal structures for analysis (98 compounds, 126 types of Pb atoms) was made using the Cambridge Structural Database (version 5.28, August 2007) as well as scientific journals published before December 1, 2007. Preference was given to publications which appeared in press during the last decade, even though a number of the crystal structures examined (∼1/5 of the total number) were published earlier. The structures of the compounds in which the O donor atoms are coordinated to Pb(II) and form additional bonds with atoms of other metals (heterometallic complexes) were not examined.

For each compound, structural data from the original papers were used, with further analysis of the data using calculations by *PLATON* [27]. If the structural data were missing in a publication, the data from the CIF-files deposited in the Cambridge Crystallographic Data Centre (CCDC, ConQuest version 1.9) were used. The geometry of the Pb atom in each structure was also analyzed using the program *Mercury* [28]. Selected structural data for the crystal structures of the Pb(II) complexes with O-donor ligands are presented in tables that contain the coposition of each compound, overall CN of the Pb atom presented as the sum of the Pb(II) CN in the first coordination sphere and the number of secondary bonds, the form of the polyhedron, the Pb–O bond lengths (primary and secondary), O–Pb–O bond angles in the first coordination sphere, references and REFCODEs.

According to Bondi [29], the sum of the van der Waals radii of Pb and O is equal to 3.54 Å. In the present work the limiting value for a Pb–O bond is considered as 3.30 Å. The Pb· · ·O interactions which are longer than 3.30 Å were omitted from the discussion. The primary coordination sphere of the Pb(II) atom can be limited to the Pb–O distance of 2.70 Å. The present review examines the crystal structures of Pb(II) complexes with O-donor atoms. The organic ligands fall into to two general classes—aliphatic and aromatic compounds. Since among the O-donor ligands the organic carboxylates are represented the most extensively, the review first deals with the crystal structures of Pb(II) carboxylates and then with those of Pb(II) complexes with other O-donor ligands. The list of complexes under discussion is presented in Table 1.

Note about abbreviations: The abbreviations for the various ligands are based primarily upon the common names for those ligands. For carboxylic acids, we define the abbreviation by including the acidic protons in front of the shortened name. For example, salicylic acid is abbreviated as H_2sal, indicating that there are two acidic protons (the carboxylate and the phenol). Thus Hsal$^-$ refers to the ligand with the carboxylate proton removed, and sal^{2-} as the fully deprotonated ion.

Table 1
Pb(II) complexes with O-donor ligands covered in this review.

No.	Compound
Pb(II) aliphatic monocarboxylates	
I	$Pb(O_2CH)_2$
II	$Pb(ac)_2 \cdot 3H_2O$
III	$Pb(ac)_2 \cdot 3H_2O$
IV	$Pb(ac)_2(18\text{-crown-}6) \cdot 3H_2O$
V	$Pb(htno)_2$
VI	$Pb(crot)_2$
VII	$Pb(glyc)_2$
VIII	$Pb_6(dmac)_{12} \cdot 4H_2O$
IX	$Pb(ac)_2 \cdot 2Pb(piv)_2 \cdot 3Hpiv$
X	$Pb_4(odac)_3(NO_3)_2 \cdot H_2O$
XI	$Pb_3(O_2CCCl_3)_6 \cdot 3H_2O$
XII	$Pb(Hval)_2(NO_3)_2(H_2O)_2$
Pb(II) aliphatic polycarboxylates	
XIII	Pb(malo)
XIV	Pb(male)
XV	Pb(azel)
XVI	Pb(suc)
XVII	$Pb(chdc) \cdot H_2O$
XVIII	$Pb_2(chdc)_2 \cdot dmam$
XIX	$Pb(Hasp)(NO_3)$
XX	$Pb_2(Hglyglu)_2(ClO_4)_2 \cdot H_2O$
XXI	$Pb(Hcit) \cdot H_2O$
Pb(II) diketonates	
XXII	$Pb(tmhd)_2$
XXIII	$Pb(tmhd)_2$
XXIV	$Pb(acac)_2$
XXV	$Pb(pta)_2$
XXVI	$Pb(thfbd)_2$
XXVII	$Pb(dbm)_2$
XXVIII	$Pb(dmfod)_2$
XXIX	$Pb(hfa)_2(diglyme)$
XXX	$Pb(hfa)_2(diglyme)$
Pb(II) squarates and aminosquarates	
XXXI	$Pb(squ)(H_2O)_2 \cdot 2H_2O$
XXXII	$Pb(msqu)_2(H_2O)_2 \cdot H_2O$
XXXIII	$Pb(esqu)_2(H_2O)$
XXXIV	$Pb(amsqu)_2(H_2O)_2$
Pb(II) phosphonates and aminophosphonates	
XXXV	$Pb\{(Ph)_2PO_2\}_2$
XXXVI	$Pb(O_2P^tBu_2)_2$
XXXVII	Pb(pcp)
XXXVIII	Pb(amdph)
XXXIX	$Pb\{MeN(CH_2PO_3H)_2\}$
XL	$Pb(H_2aedp) \cdot H_2O$
XLI	Pb(phca)
XLII	$Pb_3(caeph)_2$
XLIII	$Pb_3(caeph)_2$
XLIV	$Pb_5(caeph)_2(Hcaeph)_2$
XLV	$Pb_4(pbmp)(sip)_2(H_2O)_4 \cdot 2H_2O$
Pb(II) sulfoxide Complexes	
XLVI	$Pb(dmso)_3(ClO_4)_2$
XLVII	$Pb(dmso)_5(ClO_4)_2$
XLVIII	$Pb(hmsul)_2(H_2O)$
Pb(II) aromatic monocarboxylates	
XLIX	Pb(sal)
L	$Pb(Hsal)_2(H_2O)$
LI	$Pb\{(4\text{-}HOC_6H_4CO_2)_2(H_2O)\} \cdot H_2O$
LII	$Pb_2(H_2dhb)_4 \cdot 3H_2O$
LIII	$Pb(Hhca)_2(dmf) \cdot dmf$
LIV	$Pb(Hnsal)_2(H_2O)$
LV	$Pb(dnsal)(H_2O) \cdot 0.25H_2O$
LVI	$Pb(sb)(H_2O)_2$
LVII	$Pb(sb)(H_2O)_2$ (4,4·-bpy)
LVIII	$Pb(sb)(H_2O)_2$ (4,4′-bpy)
LIX	$Pb(H_2ssa)_2(H_2O)$
LX	$Pb(amb)_2$
LXI	$Pb(nb)_2(H_2O)$
LXII	$Pb(dnb)_2(H_2O)$

2. Lead(II) aliphatic carboxylates

2.1. Monocarboxylates

Among Pb(II) complexes with O-donor ligands, the carboxylates, which in most cases display polymeric structures, are the best structurally characterized compounds.

The crystal structure of lead(II) formate, $Pb(O_2CH)_2$, is a three-dimensional polymer [30]. The oxygen atoms of the carboxylate groups of both ligands form bridging bonds between two different Pb atoms; consequently, each formate ligand is coordinated to four Pb atoms. The authors describe the octa-coordination polyhedron as a distorted octahedron, in which one of the axial positions is occupied by a "tripod" of three oxygen atoms. Three Pb–O bonds are relatively short, 2.47, 2.53 and 2.57 Å, while the bonds to the remaining five atoms are significantly longer (Pb–O 2.71–2.85 Å). According to the VSEPR model, the Pb polyhedron in $Pb(O_2CH)_2$ can be presented as a distorted ψ-tetrahedron (**I**) formed by three shorter Pb–O bonds with a vacant vertex. Five longer Pb–O distances form secondary bonds (Table 2).

The crystal structure of $Pb(ac)_2 \cdot 3H_2O$ (Hac = acetic acid, $MeCO_2H$) was determined independently and almost simulta-

Table 1 (*Continued*)

No.	Compound
Pb(II) nicotinates	
LXIII	$\{Pb(ino)_2\}_2 \cdot 7H_2O$
LXIV	$Pb(ino)_2 \cdot nH_2O$
LXV	$Pb_4(OH)_4(ino)_4 \cdot nH_2O$
LXVI	$Pb(ino)(fa)_{0.5}$
LXVII	$Pb_2(ino)(btc)(H_2O)$
LXVIII	$Pb(hmpyr)_2 \cdot 7H_2O$
Pb(II) phenoxyacetates	
LXIX	$Pb(pa)_2 \cdot 0.5H_2O$
LXX	$Pb(pa)_2 \cdot 0.5H_2O$
LXXI	$Pb(pda)_2 \cdot H_2O$
LXXII	$Pb(mcpa)_2 \cdot H_2O$
Pb(II) aromatic di- and polycarboxylates	
LXXIII	Pb(*o*-pht)(H_2O)
LXXIV	Pb(*m*-pht)
LXXV	Pb(*p*-pht)(H_2O)
LXXVI	Pb(*p*-pht)(dma)
LXXVII	Pb(*p*-pht)(nmp)
LXXVIII	$Pb_2(OH)_2$(*p*-pht)
LXXIX	Pb(napdc)(dmf)
LXXX	Pb(ndc)(dma)
LXXXI	$Pb(dthb)(dmf)_2$
LXXXII	$Pb_6(dpa)_4(O_2)$
LXXXIII	$Pb_3(btc)_2 \cdot H_2O$
LXXXIV	$Pb_2(Hbtc)_2(H_2O)_4 \cdot H_2O$
LXXXV	$Pb_2(Hbtc)_2(H_2O)_4 \cdot H_2O$
LXXXVI	$Pb_2(bttc)$
Pb(II) Nitrophenolates	
LXXXVII	$Pb(nph)_2$
LXXXVIII	$Pb(dnph)_2$
LXXXIX	$Pb(pic)_2 \cdot 2dmso$
XC	Pb(styph)(H_2O)
Pb(II) complexes with other O-donor ligands	
XCI	Pb(bzgly-*O*)$_2(H_2O)_2 \cdot 2H_2O$
XCII	$Pb(fuoac)_2$
XCIII	$Pb_2(vnl)_2(H_2O)_2(ClO_4)_2$
XCIV	$Pb(trop)_2$
XCV	$Pb(trop)(CF_3SO_3)(H_2O)$
XCVI	$Pb_3(trop)_4(ClO_4)_2$
XCVII	$Pb_2(trop)_2(NO_3)_2$
XCVIII	$Pb(Hnorf)(NO_3)_2$

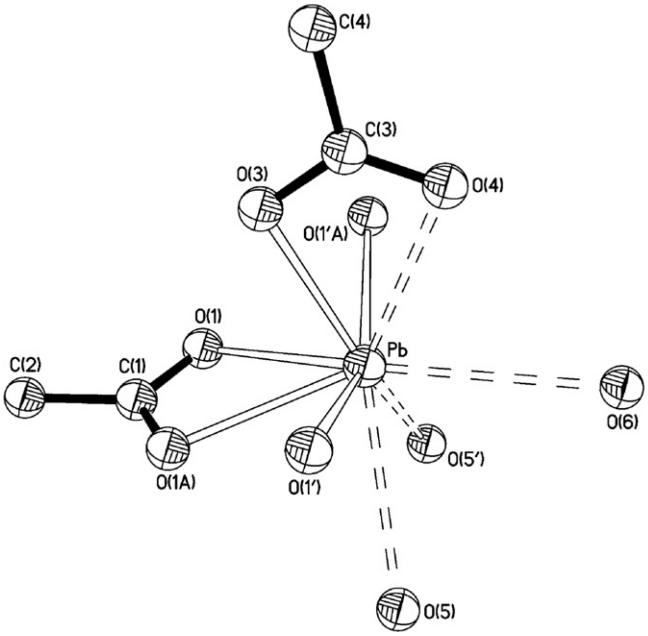


Fig. 1. ORTEP drawing of the coordination environment of the Pb(II) atom in $Pb(ac)_2 \cdot 3H_2O$.

neously by three groups of authors [30–32]. While structural data correlate well with each other, the conclusions about the structure of the Pb(II) coordination polyhedron are different. The $Pb(ac)_2 \cdot 3H_2O$ complex has a polymeric chain structure formed by bidentate–chelate carboxylate groups. The carboxylate group C(1)O(1)O(1A) forms symmetric Pb–O bonds (Pb–O 2.59(1) × 2 Å, [32]), while the second group is coordinated to Pb(II) asymmetrically (Pb–O 2.45(1) and 2.74(1) Å, [32]) (Fig. 1, Table 2). The symmetric chelate carboxylate group is a bridging one. Both O atoms of this carboxylate group bridge inversion-related Pb atoms binding them into polymeric chains along the *b* axis. According to [30], the Pb coordination polyhedron in $Pb(ac)_2 \cdot 3H_2O$ represents a distorted pentagonal bipyramid, in which one of the axial positions is occupied by the symmetrical chelating acetate group while in [31] the polyhedron is described as a strongly distorted monocapped square antiprism. The VSEPR model describes the Pb coordination polyhedron in $Pb(ac)_2 \cdot 3H_2O$ as a ψ-octahedron (**III**).

In the crystal structure of $Pb(ac)_2(18\text{-crown-}6) \cdot 3H_2O$ the monomeric complex is found with the Pb atom being bidentate–chelate coordinated by two acetate ligands [33]. It forms virtually symmetric bonds with O atoms of one carboxylate group (Pb–O 2.457(6) and 2.495(7) Å), and asymmetric bonds with the carboxylate atoms of the second group (Pb–O 2.375(7) and 2.745(6) Å). In addition to these bonds, there are relatively weak interactions between Pb and the six O donor atoms of the crown ether (Table 2). The H_2O-molecules are involved in hydrogen bonds with O atoms of both ligands. The Pb(II) primary coordination sphere can be represented as a ψ-tetrahedron (**I**) (Table 2).

The structure of $Pb(htno)_2$ (Hhtno = heptanoic acid) is formed by two-dimensional layers parallel to the *bc* plane [34]. Each Pb atom is surrounded by seven O atoms, which belong to four different carboxylate groups. One carboxylate group of one of the ligands [C(11^i)O(11^i)O(12^i)] is asymmetrically bidentate–chelated to the Pb atom and performs a doubly bridging function as well as binding adjacent Pb atoms along the *b* direction (Fig. 2). The carboxylate group of the second heptanoate ligand [C(21)O(21)O(22)] is bidentate-chelating and has shorter Pb–O bond lengths (Table 2). The authors [34] describe the coordination geometry of the Pb atom as a distorted octahedron with a stereochemically active LP. Analysis of interatomic distances and angles in $Pb(htno)_2$ in accordance with VSEPR model enables one to represent the Pb coordination

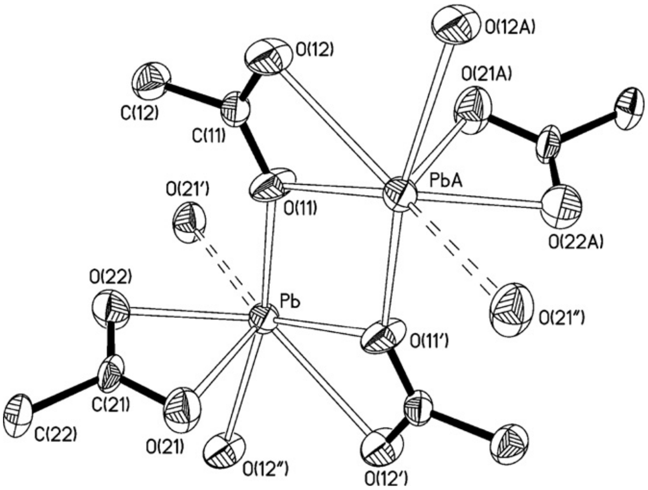


Fig. 2. ORTEP view of the coordination environment around the Pb(II) atom in $Pb(htno)_2$. Only one C atom of the C6 chain is shown.

Table 2
Stereochemistry of Pb(II) complexes with aliphatic carboxylic acid ligands.

Compound	Overall CN	Shape of the polyhedron	Pb–O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
Pb(II) aliphatic monocarboxylates								
$Pb(O_2CH)_2$	8 $(3+E)+5$	ψ-T **I**	2.47 O(2) 2.53 O(9) 2.57 O(5)		60.4 61.7 68.0		2.71 O(1) 2.72 $O(1^{i})$ 2.74 $O(5^{i})$ 2.845 $O(2^{i})$ 2.85 $O(9^{i})$	[30], BIYLAW
$Pb(ac)_2 \cdot 3H_2O$	9 $(5+E)+4$	ψ-OC **III**	2.47(3) O(1)	2.62(4) O(3) 2.62(4) $O(3)^{i}$ 2.62(4) $O(3)^{ii}$ 2.62(4) $O(3)^{iii}$	75(1) 75(1) 80(1) 80(1)	51(1) 64(1) 64(1) 149(1) $\Sigma = 328(1)$	2.75(4) $O(4)^{ii}$ 2.75(4) $O(4)^{iii}$ 2.85(5) O(2) 3.09(4) $O(5)^{iv}$	[31], PBACTH10
$Pb(ac)_2 \cdot 3H_2O$	9 $(5+E)+4$	ψ-OC **III**	2.45(1) O(3)	2.59(1) O(1) 2.59(1) O(1A) 2.64(1) $O(1^{i})$ 2.64(1) $O(1^{i}A)$	77.7(3) 77.7(3) 75.37(18) 75.37(18)	63.8(2) 63.8(2) 49.6(3) 150.7(2) $\Sigma = 327.8$	2.74(1) O(4) 2.97(1) O(5) 2.97(1) $O(5^{i})$ 3.11(1) O(6)	[32], PBACTH02
$Pb(ac)_2(18\text{-crown-}6) \cdot 3H_2O$	10 $(3+E)+7$	ψ-T **I**	2.375(7) O(9) 2.457(6) O(8) 2.497(7) O(7)		82.5(2) 52.6(2) 81.0(2)		2.745(6) O(10) 2.867(7) O(4) 2.929(7) O(1) 2.990(7) O(5) 3.008(7) O(2) 3.066(7) O(3) 3.148(7) O(6)	[33], LAPPEX
$Pb(htno)_2$	7 $(6+E)+1$	ψ-PBP_{eq} **V**	2.410(9) O(22) 2.583(8) $O(11^{i})$	2.451(8) O(21) 2.567(7) O(11) 2.620(7) $O(12^{ii})$ 2.735(8) $O(12^{i})$	118.7(3)	70.9(3) 77.2(3) 91.1(3) 113.4(3) $\Sigma = 352.6$	2.994(9) $O(21^{i})$	[34], QILWEN
$Pb(crot)_2$	6 $(6+E)$	ψ-PBP_{ax} **IV**	2.350(6) O(11)	2.512(6) O(22) 2.554(7) O(12) 2.578(6) O(22B) 2.634(6) O(21A) 2.635(7) O(21)	77.8(2) 53.1(2) 85.1(2) 83.9(2) 77.4(2)	49.5(2) 64.7(3) 68.1(2) 82.8(3) 86.7(3) $\Sigma = 351.8$		[35], DUPKAA
$Pb(glyc)_2$	8 $(4+E)+4$	ψ-TBP **II**	2.397(9) O(1) 2.633(10) O(6)	2.460(10) O(3) 2.597(10) O(4)	132.1(3)	73.9(3)	2.724(10) $O(4^{i})$ 2.778(10) O(2a) 2.793(10) O(5a) 3.079(9) O(1a)	[36], PASBAM
$Pb_6(dmac)_{12} \cdot 4H_2O$								[37], REXBAX
Pb(1)	7 $(4+E)+3$	ψ-TBP **II**	2.488(20) O(3) 2.499(16) O(9)	2.368(24) O(2) 2.397(20) O(4)	121.1(6)	75.2(7)	2.696(22) O(13) 2.710(22) O(1) 2.905(17) O(6d)	
Pb(2)	8 $(6+E)+2$	ψ-PBP_{ax} **IV**	2.462(20) O(10)	2.528(24) O(5) 2.568(16) O(9) 2.578(18) O(7) 2.671(17) O(6) 2.683(22) O(14)	75.8(7) 52.4(6) 66.5(7) 78.6(6) 88.7(7)	50.5(6) 70.8(6) 74.1(6) 76.8(5) 80.7(6) $\Sigma = 352.9$	2.728(20) O(4) 2.94(2) O(1c)	

Table 2 (*Continued*)

Compound	Overall CN	Shape of the polyhedron	Pb–O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial/equatorial)	Equatorial		
Pb(3)	8 $(4+E)+4$	ψ-TBP **II**	2.552(11) O(6) 2.507(21) O(12)	2.381(26) O(8a) 2.510(22) O(11)	134.5(7)	79.6(8)	2.720(18) O(7a) 2.832(19) O(10b) 2.90(2) O(3c) 2.967(18) O(7)	
$Pb(ac)_2\cdot 2Pb(piv)_2\cdot 3Hpiv$								[38], TUCPEM
Pb(1)	8 $(4+E)+4$	ψ-TBP **II**	2.56(2) O(2a) 2.58(2) O(3)	2.38(1) O(4) 2.46(1) O(1b)	119.1(6)	80.4(6)	2.81(2) O(7) 2.85(1) O(1a) 2.88(1) O(10a) 3.06(2) O(13)	
Pb(2)	8 $(4+E)+4$	ψ-TBP **II**	2.51(2) O(6) 2.65(2) O(2)	2.32(2) O(8) 2.53(1) O(5)	123.5(6)	78.0(7)	2.72(1) O(4) 2.91(2) O(7) 3.01(1) O(12) 3.06(2) O(7a)	
Pb(3)	8 $(5+E)+3$	ψ-OC **III**	2.37(2) O(9)	2.41(2) O(11) 2.54(2) O(10) 2.58(2) O(12) 2.70(1) O(15)	79.2(7) 51.4(6) 86.5(7) 82.9(7)	51.6(5) 72.0(6) 76.7(6) 130.5(6) $\Sigma = 330.7$	2.85(1) O(5) 2.98(2) O(3a) 3.11(1) O(2)	
$Pb_4(odac)_3(NO_3)_2\cdot H_2O$								[39], LIVKEG
Pb(1)	7 $(3+E)+4$	ψ-T **I**	2.464(13) O(2) 2.464(13) O(2^{i}) 2.51(3) O(9)		70.5(5) 72.2(8) 72.2(8)		2.798(14) O(2^{ii}) 2.798(14) O(2^{iii}) 2.890(13) O(3^{i}) 2.890(13) O(3)	
Pb(2)	8 $(4+E)+4$	ψ-TBP **II**	2.467(13) O(3) 2.493(12) O(4)	2.487(17) O(7) 2.549(13) O(1)	124.7(5)	83.4(5)	2.732(14) O(8) 2.78(2) O(11^{i}) 2.86(2) O(10) 2.87(2) O(11)	
$Pb_3(O_2CCCl_3)_6\cdot 3H_2O$								[40], QOZBIQ
Pb(1)	8 $(4+E)+4$	ψ-TBP **II**	2.507(11) O(1) 2.667(10) O(3)	2.379(9) O(1W) 2.529(12) O(2W)	143.5(4)	80.6(4)	2.735(10) O(3^{i}) 2.755(10) O(4) 2.862(10) O(8^{ii}) 3.006(10) O(10^{ii})	
Pb(2)	7 $(6+E)+1$	ψ-PBP$_{eq}$ **V**	2.543(9) O(7) 2.564(12) O(2)$^{\#2}$	2.496(9) O(5) 2.568(9) O(6) 2.633(9) O(4)$^{\#2}$ 2.638(9) O(9)	142.3(4)	51.3(3) 66.9(3) 78.7(3) 161.2(3) $\Sigma = 357.9$	2.956(11) O(8)	
Pb(3)	7 $(6+E)+1$	ψ-PBP$_{eq}$ **V**	2.443(12) O(11) 2.527(10) O(3W)	2.543(10) O(10) 2.550(10) O(10)$^{\#3}$ 2.622(8) O(5) 2.649(10) O(9)	142.1(4)	49.8(3) 63.6(3) 65.3(3) 157.7(3) $\Sigma = 336.1$	2.830(8) O(12)	
$Pb(Hval)_2(NO_3)_2(H_2O)_2$	10 $(3+E)+7$	ψ-T **I**	2.36(1) O(3) 2.44(1) O(1) 2.50(1) O(12)		76.5(3) 88.2(4) 79.6(4)		2.78(1) O(8a) 2.85(2) O(9a) 2.87(1) O(4) 2.89(1) O(11) 2.95(1) O(10) 3.19(1) O(8b) 3.275(15) O(2)	[41], ESAPET

Pb(II) aliphatic polycarboxylates								
Pb(malo)	8 (5 + *E*) + 3	ψ-OC **III**	2.41(1) O(1)	2.47(1) O(4^{i}) 2.48(1) O(1^{i}) 2.55(1) O(3) 2.70(1) O(3^{i})	79.2(4) 72.0(4) 68.6(3) 68.7(4)	74.5(3) 74.7(3) 74.7(4) 111.5(3) Σ = 335.4	2.86(1) O(4^{ii}) 2.96(1) O(2^{ii}) 2.99(2) O(2^{i})	[42], BOPZOV10
Pb(male)	8 (6 + *E*) + 2	ψ-PBP$_{eq}$ **V**	2.423(6) O(4) 2.688(6) O(4^{i})	2.453(6) O(1) 2.524(7) O(2) 2.619(7) O(3) 2.741(7) O(1^{i})	141.8(2)	48.5(2) 73.4(2) 79.8(2) 126.4(2) Σ = 328.1	2.860(8) O(3^{i}) 3.139(8) O(2^{i})	[43], VATYUL
Pb(azel)	7 (4 + *E*) + 3	ψ-TBP **II**	2.543(6) O(3A) 2.543(6) O(3B)	2.382(9) O(2) 2.453(7) O(1)	164.0(3)	52.1(2)	2.677(5) O(3C) 2.677(5) O(3D) 2.868(7) O(1E)	[44], IPAMER
Pb(suc)								[40], QOZBAI
Pb(1)	8 (5 + *E*) + 3	ψ-OC **III**	2.47(1) O(7)$^{\#1}$	2.54(1) O(5) 2.57(1) O(4)$^{\#4}$ 2.66(1) O(1) 2.67(1) O(3)$^{\#3}$	88.1(4) 87.4(4) 85.4(4) 67.3(4)	47.4(4) 63.0(4) 90.2(4) 144.1(4) Σ = 344.7	2.75(1) O(2) 2.79(1) O(4) 2.91(1) O(2)$^{\#4}$	
Pb(2)	8 (5 + *E*) + 3	ψ-OC **III**	2.44(1) O(1)	2.52(1) O(5) 2.55(1) O(8)$^{\#3}$ 2.55(1) O(3) 2.71(1) O(8)	66.5(4) 87.2(4) 88.4(4) 82.8(4)	67.6(4) 88.5(4) 90.4(4) 111.1(4) Σ = 357.6	2.79(1) O(7) 2.81(1) O(6) 2.980(1) O(6)$^{\#3}$	
Pb(chdc)·H$_2$O	7 (5 + *E*) + 2	ψ-OC **III**	2.285(4) O(3)	2.429(4) O(1) 2.625(5) O(W1) 2.636(4) O(2^{1}) 2.736(4) O(2)	75.30(15) 81.12(16) 82.58(15) 79.03(14)	50.24(12) 66.34(13) 91.86(13) 143.45(15) Σ = 351.9	2.814(5) O(4) 2.915(5) O(1^{ii})	[45], JEYZUJ
Pb$_2$(chdc)$_2$·dmam								[45], YICRIM
Pb(1)	6 (6 + *E*)	ψ-PBP$_{eq}$ **V**	2.564(11) O(1) 2.737(8) O(6)$^{\#2}$	2.397(9) O(4) 2.464(11) O(2) 2.565(9) O(3) 2.638(9) O(7)$^{\#1}$	168.9(3)	52.8(3) 68.0(3) 86.6(3) 120.5(3) Σ = 327.9		
Pb(2)	6 (4 + *E*) + 2	ψ-TBP **II**	2.547(8) O(6)$^{\#1}$ 2.563(10) O(2)$^{\#2}$	2.372(10) O(8)$^{\#1}$ 2.404(9) O(5)$^{\#1}$	124.5(3)	84.3(4)	2.840(10) O(7)$^{\#1}$ 2.889(10) O(7)$^{\#2}$	
Pb(Hasp)(NO$_3$)	9 (4 + *E*) + 5	ψ- TBP **II**	2.536(12) O(4)$^{\#2}$ 2.706(12) O(1)$^{\#1}$	2.493(12) O(3) 2.500(11) O(2)$^{\#1}$	127.6(3)	91.4(4)	2.730(17) O(5) 2.743(10) O(1)$^{\#3}$ 2.904(16) O(7b) 2.913(16) O(5b) 3.229(13) O(1h)	[46], XARQAI
Pb$_2$(Hglyglu)$_2$(ClO$_4$)$_2$·H$_2$O	8 (6 + *E*) + 2	ψ-PBP$_{ax}$ **IV**	2.451(6) O(11)$^{\#1}$	2.571(8) O(10)$^{\#1}$ 2.576(19) O(13)$^{\#2}$ 2.593(7) O(15) 2.657(8) O(14) 2.734(19) O(13)	51.3(4) 77.2(6) 82.1(3) 78.8(3) 81.9(6)	48.2(3) 69.6(3) 71.6(3) 89.5(3) 74.2(3) Σ = 353.1	2.801(8) O(10)$^{\#3}$ 3.023(12) O(7)	[47], OHETEA
Pb(Hcit)·H$_2$O	9 (4 + *E*) + 5	ψ-TBP **II**	2.510(6) O(5c) 2.527(6) O(3)	2.397(7) O(5) 2.416(7) O(1^{i})	127.7(2)	80.9(3)	2.805(1) O(4a) 2.847(1) O(2^{i}) 2.883(1) OW(b) 3.216(1) OW 3.271(1) O(4c)	[48], MAKZON

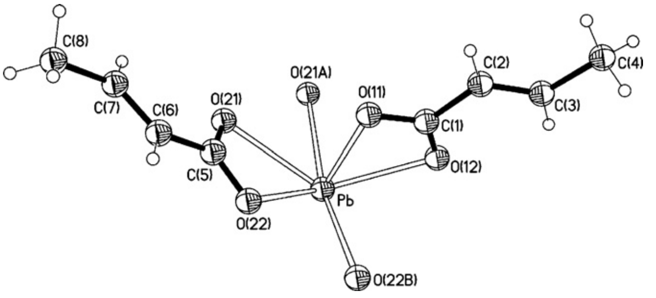
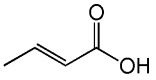


Fig. 3. ORTEP diagram of the coordination environment of the Pb(II) atom in $Pb(crot)_2$.

polyhedron as a ψ-pentagonal bipyramid with a vacant position for the LP in the equatorial plane (**V**).

In the polymeric chain structure of $Pb(crot)_2$ [Hcrot = (*E*)-2-butenoic acid (crotonic acid), **1**] each Pb atom is coordinated by two chelating ligands, one of which forms bonds that are substantially asymmetric [35]. The oxygen atoms of the more symmetrically coordinated carboxylate group [C(5)O(21)O(22)] are doubly bridging, binding the Pb atoms into polymeric chains (Fig. 3). The coordination geometry of the Pb atom can be described as a ψ-pentagonal bipyramid with a vacant axial site (**IV**). The Pb atom is located below the basal plane of the bipyramid by 0.262(1) Å.



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The structure of $Pb(glyc)_2$ [Hglyc = hydroxyacetic acid (glycolic acid)] contains dimeric units $[Pb_2(glyc)_4]$ that are bonded by bridging carboxylate ligands and hydrogen bonds into a three-dimensional polymeric network [36]. Each Pb atom is surrounded by eight O atoms with four relatively short Pb–O distances (Pb–O 2.397(9)–2.633(10) Å) and four longer bonds (Pb–O 2.724(10)–3.079(9) Å). The glycolate ligands are coordinated to the Pb atom via the hydroxyl oxygen and one carboxylate oxygen atom. Considering the four closest O atoms, the Pb(II) atom adopts a ψ-trigonal bipyramidal shape (**II**) (Table 2).

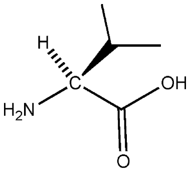
In contrast to the structure of the polymeric Pb(II) acetate [30–32], $Pb_6(dmac)_{12}\cdot 4H_2O$ [Hdmac = 2-methylpropanoic acid (dimethylacetic acid)] contains hexanuclear $[Pb_6(dmac)_{12}\cdot 4H_2O]$ units, formed by four Pb atoms coordinated by identical bridging O atoms of chelating carboxylate groups and with some of these O atoms also bridging to two "terminal" Pb atoms [37]. The molecular units were shown to contain pairs of Pb atoms with CN 6 (Pb(1)), CN 7 (Pb(2)) and CN 5 (Pb(3)) [37]. The Pb(1) and Pb(3) atoms have a similar geometry in the first coordination sphere (ψ-trigonal bipyramidal) with similar geometric characteristics (Table 2). There is a difference between the Pb(1) and Pb(3) atoms regarding the number and the length of secondary Pb–O bonds. In contrast to Pb(1) and Pb(3), the Pb(2) atom is chelated by two carboxylate groups that simultaneously bridge to the adjacent Pb(1) and Pb(3) atoms. Additionally, the Pb(2) atom is bonded to a water molecule. According to the VSEPR model, the coordination geometry of the Pb(2) atom has a pentagonal bipyramidal geometry with a vacant axial position (**IV**) occupied by the LP.

The solid state structure of the mixed acetate–pivalate Pb(II) complex, $Pb_3(ac)_2(piv)_4\cdot 3Hpiv$ [Hpiv = 2,2-dimethylpropanoic acid (pivalic acid)], which can be considered to be comprised of one $Pb(ac)_2$, three Hpiv and two $Pb(piv)_2$ units, is formed by means of bridging oxygen atoms [38]. There are three crystallographically independent Pb atoms. The Pb(1) atom forms slightly asymmetric chelate bonds with the oxygen atoms of both acetate groups. In addition, the Pb(1) atom forms four weaker bridging bonds with the O atoms of the ligands from adjacent complexes and Hpiv molecules (Table 2). Compared to Pb(1), the Pb(2) and Pb(3) atoms form chelate bonds only with the carboxylate oxygen atoms of the pivalate ligands. The overall CN for each of the three Pb atoms is 8. The coordination polyhedra of Pb(1) and Pb(2) atoms can be represented, according to the VSEPR model, as having a ψ-trigonal bipyramidal configuration with a vacant site in the equatorial plane occupied by the LP. The coordination polyhedron of the Pb(3) atom has a ψ-octahedral geometry (Table 2). All three Pb atoms form secondary Pb–O bonds (Pb–O 2.72(1)–3.11(1) Å) with bridging functions.

The 3D polymeric structure of $Pb_4(odac)_3(NO_3)_2\cdot H_2O$ (H_2odac = oxydiacetic acid, $HO_2CCH_2OCH_2CO_2H$) includes three crystallographically independent lead atoms with CN 7, 8 and 9 [39]. The environment of the seven-coordinated Pb(1) atom includes O atoms of four oxydiacetate anions and a water molecule. Two $odac^{2-}$ anions are coordinated to Pb(1) in a bidentate–chelate mode, while the other two anions are monodentate. The analysis of the polyhedron enabled the authors to conclude that the LP of Pb(II) is stereochemically active with the open site oriented opposite to the three short Pb–O bonds. According to the VSEPR model, the Pb(1) polyhedron can be represented as a ψ-tetrahedron (**I**) (CN 3 + *E*) formed by three short Pb(1)–O distances. Four relatively long distances should be considered as secondary bonds (Table 2). The Pb(2) atoms are coordinated by two $odac^{2-}$ ligands in tridentate and bidentate modes. The coordination polyhedron of Pb(2) can be represented as a ψ-trigonal bipyramid (**II**) (Table 2). The geometry of the Pb(3) atom (CN 9) is not discussed because its LP is stereochemically inactive.

The polymeric layered structure of lead(II) trichloroacetate trihydrate, $Pb_3(O_2CCCl_3)_6\cdot 3H_2O$ includes three crystallographically independent Pb atoms [40]. The VSEPR model suggests a ψ-trigonal bipyramidal environment for Pb(1). The geometry of Pb(2) was presented as a distorted pentagonal-based bipyramid in which the LP resides in one of the equatorial sites (**V**), which is in agreement with the VSEPR model. For Pb(3), as in the case of Pb(2), the CN is equal to 7. The geometries of the coordination polyhedra of Pb(3) and Pb(2) are similar.

Burford et al. have described the structure of $Pb(Hval)_2(NO_3)_2(H_2O)_2$ [Hval = 2-amino-3-methyl-butanoic acid (valine), **2**], in which the Pb atom is coordinated by oxygen atoms of two valine ligands as an asymmetric chelate (Pb–O 2.36(1) and 2.87(1) Å) and one that is monodentate (Pb–O 2.44(1) Å) [41]. The Pb atom also forms bonds to two H_2O molecules. The octa-coordination is completed by three O atoms of two NO_3 groups. Analysis of the structure of $Pb(Hval)_2(NO_3)_2(H_2O)_2$ indicates that the LP of Pb(II) is stereochemically active, and, therefore, the Pb(II) atom has a *hemidirected* geometry. Taking into account only primary Pb–O bonds, the coordination polyhedron can be regarded as a ψ-tetrahedron (**I**). In the LP area there are seven additional O atoms, which form weaker secondary Pb–O bonds to account for an overall Pb CN of 10 (Table 2).



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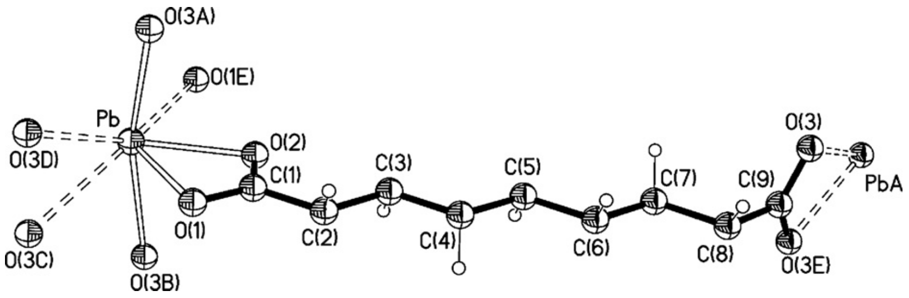
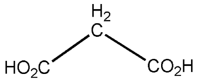


Fig. 4. ORTEP drawing of the coordination environment around the Pb(II) atom in Pb(azel).

2.2. Polycarboxylates

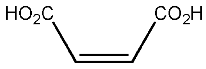
A number of crystal structures of Pb(II) complexes with the anions of aliphatic di- and tricarboxylic acids have been investigated.

In the crystal structure Pb(malo) (H_2malo = malonic acid, $HO_2CCH_2CO_2H$, **3**) there are no chelate interactions between the Pb(II) ion and the carboxylate oxygen atoms of the ligand [42]. The authors describe the Pb coordination polyhedron as a monocapped rectangular antiprism. According to the VSEPR model, the geometry of the coordination polyhedron in Pb(II) malonate should be a ψ-octahedron (**III**). Three oxygen atoms form secondary bonds with the Pb(II) ion (Table 2).



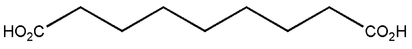
3

The crystal structure of Pb(male) (H_2male = maleic acid, *cis*-$HO_2CC(H) = C(H)CO_2H$, **4**) is lamellar and contains double polymer layers parallel to the *bc* plane of the unit cell [43]. The independent Pb atoms are bonded to seven oxygen atoms, which belong to four equivalent maleate ligands. Based on the character of carboxylate group binding, this crystal structure exhibits some similarities with the structure of Pb(II) aliphatic monocarboxylates. Both carboxylate groups of the ligand are somewhat asymmetrically chelated to Pb(II). The authors indicated that the coordination polyhedron around the Pb atom exhibits a strongly distorted *hemidirected* geometry. According to the VSEPR model, the Pb(II) coordination polyhedron in Pb(male) [43] can be represented as a distorted ψ-pentagonal bipyramid with a vacant vertex in the equatorial plane (**V**). In the LP area there are two additional O atoms, which form secondary bonds to Pb(II) (Table 2).



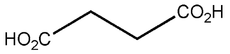
4

The structure of Pb(azel) (H_2azel = azelaic acid, $HO_2C(CH_2)_7CO_2H$, **5**) is a three-dimensional polymeric framework [44]. As in the crystal structure of Pb(male), both carboxylate groups of the ligand are coordinated to Pb in a bidentate–chelate mode (Fig. 4) and the Pb coordination polyhedron is a ψ-trigonal bipyramid (**II**) with the LP located in the vacant equatorial position (Table 2).



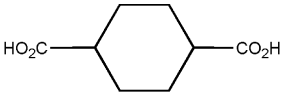
5

The asymmetric unit of the polymeric structure of Pb(suc) (H_2suc = succinic acid, $HO_2C(CH_2)_2CO_2H$, **6**) contains two crystallographically independent Pb atoms and two succinate ligands [40]. The coordination environment of each Pb atom is formed by eight oxygen atoms from both carboxylate groups, which adopt bidentate–chelate di-bridging modes. According to the VSEPR model, both types of Pb atoms have a ψ-octahedral geometry, formed by the oxygen atoms of the carboxylate groups of the ligand. For both Pb atoms, the bond angles between axial and equatorial atoms are less than 90° (Table 2), which is in agreement with the VSEPR model.



6

The crystal structures of a number of Pb(II) complexes with different dicarboxylic acids were investigated. The crystal structure of Pb(chdc)·H_2O (H_2chdc = 1,4-cyclohexanedicarboxylic acid, **7**) possesses a 2D network formed by Pb atoms and *trans*-chdc^{2-} ligands [45]. The Pb atoms in the structure are surrounded by six O atoms from different bidentate–chelate carboxylate groups and an oxygen atom of a coordinated water molecule (Fig. 5, Table 2). The coordination polyhedron of the Pb ion is described as a distorted tetragonal bipyramid with a vacant axial position (ψ-octahedron, **III**), in agreement with the VSEPR model.



7

The asymmetric unit of the complex $Pb_2(chdc)_2$·dmam (dmam = dimethylamine) contains two crystallographically independent Pb atoms, two *cis*-1,4-cyclohexanedicarboxylate ligands and a dimethylamine molecule [45]. The Pb(1) atoms are each coordinated by six oxygen atoms of the chdc^{2-} ligands. The coordination polyhedron of Pb(1) is described as a distorted ψ-pentagonal bipyramid with a vacant equatorial vertex (**V**) that is in agreement with the VSEPR model. The authors describe the Pb(2) coordination polyhedron as a distorted tetragonal pyramid PbO_4 with a stereochemically active LP. According to the VSEPR model, the Pb(2) coordination polyhedron should be a ψ-trigonal bipyramid (**II**) with a vacant equatorial position. A characteristic feature of the crystal structure of $Pb_2(chdc)_2$·dmam is the formation of octanuclear $[Pb_8(\textit{cis}\text{-chdc})_8]$ wheel-shaped clusters.

The crystal structures of a number of Pb(II) complexes with the anions of substituted dicarboxylic acids and their derivatives have been determined. Aspartic acid (**8**) is an amine-derivative of succinic acid. The crystal structure of Pb(Hasp)(NO_3) has a 3D framework, formed by polymeric chains oriented along the three crystallographic axes [46]. The Pb atoms are coordinated by six oxygen atoms, five from the carboxylate groups of the organic ligand

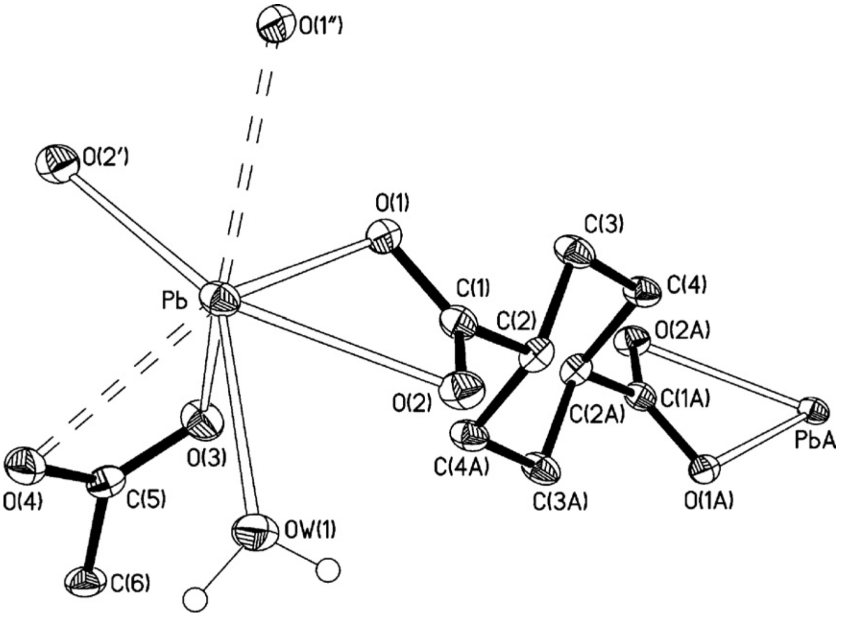
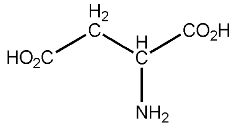


Fig. 5. ORTEP view of the coordination environment of the Pb(II) atom in Pb(chdc)·H_2O.

and one of the nitrate-ion. The coordination geometry of Pb was described as a distorted square pyramid with the oxygen atoms of the β-carboxylate group in the apical position. The Pb atom is located 0.13 Å above the basal plane of the pyramid, formed by four O atoms of four different ligands. According to the authors, such a geometry indicates that there is a void below the basal plane occupied by the Pb(II) LP. Taking into account the primary Pb–O bonds up to 2.70 Å, the coordination polyhedron of Pb can be described in terms of VSEPR model as a ψ-trigonal bipyramid (**II**). Five O atoms situated at 2.730(17)–3.229(13) Å from Pb form secondary Pb–O bonds (Table 2).

The structure of $Pb_2(Hglyglu)_2(ClO_4)_2\cdot H_2O$ (H_2glyglu = *N*-glycylglutamic acid, **9**) was determined by the same group of authors as the structure of Pb(Hasp)(NO_3) [47]. The Pb atoms are coordinated by the O atoms of two chelate carboxylate groups of symmetry equivalent ligands. One of the oxygen atoms of the α-carboxylate group is also involved in a bridging bond Pb–O (2.576(19) Å) with the adjacent Pb atom to build up a 2D network structure. The coordination environment of the Pb atom is completed by a water molecule (Pb–O 2.593(7) Å), which is bridging two symmetry related Pb atoms, allowing for formation of a 3D polymeric structure. The resulting coordination polyhedron of Pb (PbO_6) was described as a distorted square pyramid, in which the apical position is occupied by the oxygen atoms of one carboxylate group. The coordination geometry of the Pb atom is similar to that found in Pb(Hasp)(NO_3). The difference is in the position of the Pb atom relative to the basal plane; in $Pb_2(Hglyglu)_2(ClO_4)_2\cdot H_2O$ the Pb atom is located 0.42 Å below the basal plane, while in Pb(Hasp)(NO_3) the displacement is only 0.13 Å. According to the VSEPR model, the coordination polyhedron of the Pb atom in $Pb_2(Hglyglu)_2(ClO_4)_2\cdot H_2O$ is a pentagonal bipyramid with a vacant axial position (**IV**). Two secondary bonds with Pb–O distances 2.801(8) and 3.023(12) Å complete the overall CN 8 of Pb (Table 2).



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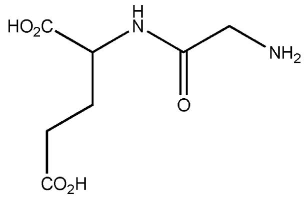
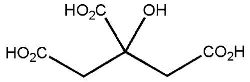


9

Kourgiantakis et al. have described the crystal structure of the lead(II) citrate complex Pb(Hcit)·H_2O (H_3cit = citric acid, **10**) [48]. This is one of the few publications devoted to the stereochemistry of Pb(II) complexes with O-donor ligands within the scopes of the VSEPR model. The Pb atoms in this structure have a trigonal bipyramidal geometry. The $Hcit^{2-}$ anions bridge the adjacent Pb atoms in rhombohedral Pb_2O_2 units, which form polymeric chains along the *a* axis. The chains are connected into a 3D network by means of secondary Pb–O bonds and hydrogen bonds formed by the OH groups of the ligand and H_2O molecules.



10

3. Lead(II) complexes with aliphatic oxoligands

3.1. Diketonates

The crystal structures of bis(acetylacetonate)lead(II) complexes were investigated in a number of publications [49–54] and were characterized in detail because of their possible use in the metal–organic chemical vapour decomposition (MOCVD) technique for the production of new materials.

The structural data of Pb(II) complexes with O-donor ligands containing four isolated Pb–O bonds are limited. In the crystal structure of $Pb(tmhd)_2$ ($tmhd^-$ = 2,2,6,6-tetramethylheptane-3,5-dionate, **11**) the Pb atom is chelated by four O atoms of two diketonate ligands with the formation of a monomeric complex

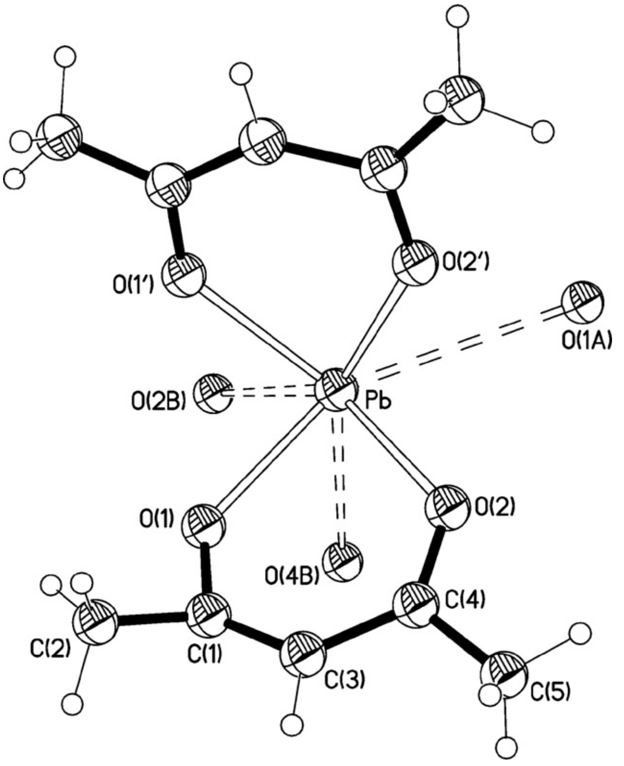
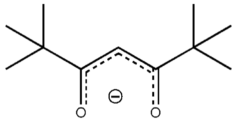


Fig. 6. ORTEP drawing of the coordination environment of the Pb(II) atom in Pb(acac)$_2$.

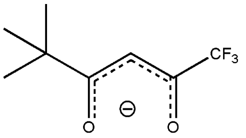
[49,50]. The Pb atom is located on the crystallographic twofold axis. The stereochemically active LP resides on the same axis. The geometry of the complex was described [49] as a square pyramid with oxygen atoms in the basal plane and the LP in the axial position that does not comply with the VSEPR model for the PbX$_4$*E* configuration. According to the VSEPR model, the geometry of the Pb atom in Pb(tmhd)$_2$ can be described as a ψ-trigonal bipyramid (**II**). In this structure there are no secondary Pb–O bonds with lengths up to 3.60 Å.



11

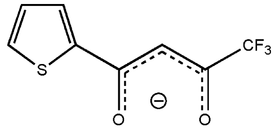
In the crystal structure of *bis*(acetylacetonate)lead(II), Pb(acac)$_2$, each Pb atom is also chelated by four O atoms of two acac$^-$ anions [51]. According to the VSEPR model, the coordination polyhedron of the Pb atom in the structure of Pb(acac)$_2$ is expected to be a ψ-trigonal bipyramid (**II**) (Fig. 6, Table 3).

The crystal structure of Pb(pta)$_2$ (pta$^-$ = 1,1,1-trifluoro-5,5-dimethylhexa-2,4-dionate, **12**) has also been investigated [52]. The Pb atoms in Pb(pta)$_2$ are coordinated by four O atoms from two β-diketonate ligands and its polyhedron has a ψ-trigonal bipyramidal geometry.



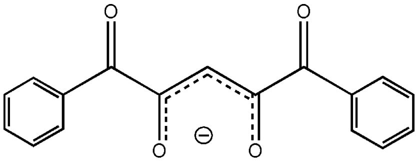
12

The crystal structure of Pb(thfbd)$_2$ (thfbd$^-$ = 1-(2-thienyl)-4,4,4-trifluorobutene-1,3-dionate, **13**), which contains the two different substituents: CF$_3$ and 2-thienyl [53], is similar to that of Pb(pta)$_2$. In both structures the Pb atom is coordinated by four O atoms of two bidentate ligands with the formation of molecular complexes bonded by bridging Pb–O bonds into polymeric chains. The coordination polyhedron of the Pb atom is a ψ-trigonal bipyramid (**II**).



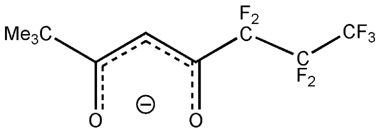
13

Compared to the above-mentioned crystal structures of the Pb(II) diketonates containing monomeric complexes, linked by means of Pb–O-Pb bonds into polymeric chains, the crystal structure of Pb(dbm)$_2$ (dbm$^-$ = 1,3-diphenylpropane-1,3-dionate, dibenzoylmethanide, **14**) is formed by [Pb$_2$(dbm)$_4$] dimers linked by close intermolecular contacts into zigzag chains [54]. The closest inner coordination sphere of the Pb atom in the Pb(dbm)$_2$ structure is formed by four O atoms of bidentate-coordinated dbm ligands with Pb–O distances in the range from 2.295(3) up to 2.458(3) Å (Fig. 7). The O(1) atom of one of the coordinated ligands bridges two adjacent Pb atoms (Pb–O(1^i) 2.713(3) Å), resulting in formation of centrosymmetric dimers. The authors mention that the shape of the dimers indicates a *hemidirected* coordination of the Pb(II) atom, suggesting the presence of a stereochemically active LP in this compound. The coordination geometry of the Pb atom coordinated by four O primary atoms is a ψ-trigonal bipyramid (**II**) (Table 3).



14

Dimeric complexes were also found in the structure of Pb(dmfod)$_2$ (dmfod$^-$ = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionate, **15**) [49]. Each Pb atom in the dimer is surrounded by four O atoms from two diketonate ligands with bond lengths Pb–O 2.272(6)–2.410(5) Å forming a ψ-trigonal bipyramidal coordination polyhedron. In addition to four primary Pb–O bonds, the Pb atoms also form two secondary bonds with the O atoms of the adjacent complex in the dimeric unit (Pb–O 3.084(6) and 3.179(6) Å) that are longer than the bridging Pb–O(1^i) bond (2.713(3) Å) in the dimeric structure of Pb(dmb)$_2$ [54] (Table 3).



15

The synthesis and the crystal structure of a volatile Pb(II) hexafluoroacetylacetonate complex Pb(hfa)$_2$(diglyme) (hfa$^-$ = hexafluoroacetylacetonate, **16**) has been described [55,56]. This compound was used as a precursor for the preparation of PbO films by MOCVD techniques. The structure is formed by a racemic pair of enantiomers, in which one oxygen atom of the diglyme ligand of one monomeric unit is oriented towards the lead atom of

Table 3
Stereochemistry of Pb(II) complexes with aliphatic oxoligands.

Compound	Overall CN	Shape of the polyhedron	Pb–O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial and equatorial)	Equatorial		
Pb(II) diketonates								
Pb(tmhd)$_2$	4 (4 + E)	ψ-TBP **II**	2.303(8) O(1^{i}) 2.303(8) O(1)	2.287(9) O(2) 2.287(9) O(2^{i})	121.3(3)	121.6(3)		[49], RIMHAW01
Pb(tmhd)$_2$	4 (4 + E)	ψ-TBP **II**	2.327(14) O(1a) 2.327(14) O(1)	2.297(14) O(2) 2.297(14) O(2a)	119.7(7)	123.0(7)		[50], RIMHAW
Pb(acac)$_2$	7 (4 + E) + 3	ψ-TBP **II**	2.351(5) O(2) 2.365(5) O(1^{i})	2.319(5) O(1) 2.375(4) O(2^{i})	123.1(2)	121.1(2)	3.013(5) O(4B) 3.159(6) O(2B) 3.264(6) O(1A)	[51], WAJQAZ01
Pb(pta)$_2$	6 (4 + E) + 2	ψ-TBP **II**	2.438(7) O(3) 2.447(7) O(4)	2.328(7) O(2) 2.341(7) O(1)	144.9(3)	84.5(3)	2.894(8) O(1a) 2.936(9) O(2b)	[52], YODNIO
Pb(thfbd)$_2$	6 (4 + E) + 2	ψ-TBP **II**	2.433(6) O(2) 2.433(6) O(2^{i})	2.335(5) O(1^{i}) 2.335(5) O(1)	151.3(3)	81.8(2)	2.889(4) O(1^{iii}) 2.889(4) O(1^{ii})	[53], WAJQON01
Pb(dbm)$_2$	5 (4 + E) + 1	ψ-TBP **II**	2.354(3) O(3) 2.458(3) O(2)	2.295(3) O(4) 2.308(3) O(1)	142.00(9)	83.14(10)	2.713(3) O(1^{i})	[54], IVEFIY
Pb(dmfod)$_2$	6 (4 + E) + 2	ψ-TBP **II**	2.400(6) O(2) 2.410(5) O(3)	2.272(6) O(1) 2.296(6) O(4)	138.6(2)	88.3(2)	3.084(6) O(3^{i}) 3.179(6) O(1^{i})	[49], YAGLAT01
Pb(hfa)$_2$(diglyme)	8 (4 + E) + 4	ψ-TBP **II**	2.48(1) O(4) 2.50(2) O(1)	2.44(2) O(3) 2.44(1) O(2)	128.0(6)	91.7(7)	2.69(2) O(7) 2.78(2) O(6) 2.90(1) O(5) 3.14(2) O(5^{i})	[55], ABUTEX
Pb(hfa)$_2$(diglyme)	8 (4 + E) + 4	ψ-TBP **II**	2.476(3) O(3) 2.497(3) O(2)	2.417(3) O(1) 2.444(3) O(4)	128.34(11)	90.45(13)	2.706(3) O(5) 2.759(3) O(6) 2.851(3) O(7) 3.021(3) O(7^{i})	[56], ABUTEX01
Pb(II) squarates and aminosquarates								
Pb(squ)(H$_2$O)$_2$·2H$_2$O	8 (6 + E) + 2	ψ-PBP$_{ax}$ **IV**	2.450(7) O(8)	2.48(2) O(1)$^{\#1}$ 2.621(7) O(7) 2.65(2) O(6)$^{\#2}$ 2.67(2) O(6) 2.74(2) O(1)	77.2(9) 76.8(3) 72.9(9) 80.1(7) 76.9(7)	63.7(6) 67.0(8) 68.7(6) 73.1(8) 76.7(9) $\Sigma = 349.2$	2.97(3) O(10) 2.98(2) O(9)	[57], NEFWEA
Pb(msqu)$_2$(H$_2$O)$_2$·H$_2$O	8 (4 + E) + 4	ψ-TBP **II**	2.560(10) O(1) 2.569(9) O(11)	2.435(10) O(21) 2.456(10) O(22)	147.1(3)	85.5(4)	2.791(9) O(1)$^{\#1}$ 2.873(10) O(6)$^{\#1}$ 2.873(10) O(11)$^{\#2}$ 2.903(10) O(20)$^{\#2}$	[57], NEFVUP
Pb(esqu)$_2$(H$_2$O)	8 (4 + E) + 4	ψ-TBP **II**	2.491(4) O(11A) 2.622(4) O(14A)	2.514(5) O(20) 2.578(4) O(1A)	149.4(2)	78.8(1)	2.736(4) O(1) 2.775(5) O(12) 2.853(5) O(2) 2.858(4) O(11)	[57], NEFWAW
Pb(amsqu)$_2$(H$_2$O)$_2$	8 (4 + E) + 4	ψ-TBP **II**	2.595(8) O(2^{ii}) 2.595(8) O(2^{i})	2.535(8) O(1) 2.535(8) O(1^{i})	144.9(3)	87.3(3)	2.756(8) × 2 O 2.798(8) × 2 O^{ii}	[58], HERDOX
Pb(II) phosphonates and aminophosphonates								
Pb{(Ph)$_2$PO$_2$}$_2$	4 (4 + E)	ψ-TBP **II**	2.430(6) O(2^{i}) 2.439(6) O(4^{ii})	2.232(7) O(1) 2.234(6) O(3)	167.6(2)	88.2(2)		[59], DPPOPB10

$Pb(O_2P^tBu_2)_2$	4 (4 + *E*)	ψ-TBP **II**	2.458(2) O(2) 2.458(2) O(2^{i})	2.208(4) O(1) 2.208(4) O(1^{i})	176.7(1)	89.5(2)		[60], NETCUK
Pb(pcp)	5 (5 + *E*)	ψ-OC **III**	2.297(10) O(1)	2.345(12) O(3) 2.401(10) O(2^{i}) 2.488(11) O(4^{i}) 2.678(11) O(1^{i})	85.2(4) 79.0(4) 80.5(4) 77.0(4)	75.4(4) 85.9(4) 92.6(4) 92.6(4) Σ = 353.7		[61], WACKUH
Pb(amdph)	8 (4 + *E*) + 4	ψ-TBP **II**	2.513(9) O(3) 2.550(8) O(4)	2.456(9) O(1) 2.476(9) O(6)	155.6(3)	74.3(3)	2.639(9) O(3^{i}) 2.922(9) O(5^{ii}) 3.045(9) O(1^{i}) 3.154(10) O(6^{ii})	[62], MUHPEK
$Pb\{MeN(CH_2PO_3H)_2\}$								[63], WULYOR
Pb(1)	5 (4 + *E*) + 1	ψ-TBP **II**	2.491(6) O(31)$^{\#1}$ 2.513(6) O(33)$^{\#2}$	2.288(6) O(21) 2.371(6) O(42)	160.3(2)	98.5(2)	2.893(6) O(43)$^{\#2}$	
Pb(2)	6 (4 + *E*) + 2	ψ-TBP **II**	2.538(6) O(13)$^{\#3}$ 2.588(6) O(12)$^{\#4}$	2.284(6) O(43) 2.302(6) O(23)	175.2(2)	86.5(2)	2.910(6) O(21)$^{\#5}$ 3.289(6) O(1^{i})	
$Pb(H_2aedp)\cdot H_2O$	7 (5 + *E*) + 2	ψ-OC **III**	2.409(5) O(3)$^{\#1}$	2.501(5) O(4) 2.567(5) O(5)$^{\#2}$ 2.569(5) O(3)$^{\#3}$ 2.589(5) O(4)$^{\#1}$	80.53(17) 76.84(17) 71.46(19) 73.15(16)	71.92(16) 72.38(16) 89.92(16) 111.49(15) Σ = 345.71	2.738(5) O(1) 2.908(8) O(6)	[64], KICYUR
Pb(phca)	7 (5 + *E*) + 2	ψ-OC **III**	2.325(13) O(1)	2.495(13) O(3) 2.546(12) O(1^{i}) 2.623(12) O(2) 2.651(13) O(4)	74.4(5) 73.4(4) 73.4(5) 85.4(4)	72.1(3) 74.9(4) 80.9(4) 116.4(4) Σ = 344.4	2.827(13) O(5) 3.124(14) O(5^{i})	[62], MUHPAG
$Pb_3(caeph)_2$								[65], DINDUZ
Pb(1)	6 (3 + *E*) + 3	ψ-T **I**	2.267(15) O(2) 2.313(15) O(6h) 2.414(15) O(8a)		83.0(5) 83.9(5) 76.6(6)		2.853(19) O(7a) 2.870(15) O(4) 3.17(2) O(10j)	
Pb(2)	7 (4 + *E*) + 3	ψ-TBP **II**	2.561(15) O(5h) 2.563(17) O(7h)	2.311(19) O(9i) 2.445(13) O(3)	165.6(5)	78.9(5)	2.719(16) O(5c) 2.830(14) O(1h) 3.089(16) O(4h)	
Pb(3)	8 (3 + *E*) + 5	ψ-T **I**	2.391(14) O(1) 2.412(15) O(4) 2.502(15) O(3g)		80.3(5) 74.6(5) 72.9(5)		2.738(15) O(6h) 2.83(2) O(10i) 2.836(16) O(8f) 2.862(14) O(2g) 3.025(15) O(5h)	
$Pb_3(caeph)_2$								[66], DINDUZ01
Pb(1)	6 (3 + *E*) + 3	ψ-T **I**	2.26(2) O(3) 2.36(3) O(8) 2.51(4) O(4b)	2.27(4) O(10a) 2.59(3) O(1)	85.8(9) 83.5(12) 79.8(11)		2.77(4) O(5b) 2.96(3) O(7f) 3.19(4) O(9h)	
Pb(3)	7 (4 + *E*) + 3	ψ-TBP **II**	2.52(3) O(6) 2.59(4) O(5e)		166.2(12)	71.1(13)	2.62(2) O(6c) 2.76(3) O(2e) 2.98(3) O(7)	

Table 3 (*Continued*)

Compound	Overall CN	Shape of the polyhedron	Pb–O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial and equatorial)	Equatorial		
Pb(2)	8 (3 + *E*) + 5	ψ-T **I**	2.35(3) O(7) 2.44(3) O(2e) 2.53(3) O(1)		75.5(10) 74.6(9) 73.8(10))		2.77(2) O(8e) 2.87(4) O(9d) 2.89(3) O(4b) 2.98(3) O(3) 3.15(3) O(6e)	
Pb$_5$(caeph)$_2$(Hcaeph)$_2$								[66], EXAHAM
Pb(1)	9 (4 + *E*) + 5	ψ-TBP **II**	2.66(1) O(9) 2.69(1) O(2)	2.40(1) O(3) 2.44(1) O(8)	158.9(3)	77.1(4)	2.72(1) O(6) 2.74(1) O(1) 2.86(1) O(10) 2.99(1) O(7^{i}) 3.16(1) O(6^{i})	
Pb(2)	7 (4 + *E*) + 3	ψ-TBP **II**	2.48(1) O(6) 2.67(1) O(5)	2.30(1) O(7) 2.40(1) O(2)	152.4(4)	85.0(4)	2.86(1) O(9) 2.88(1) O(3) 2.98(1) O(1)	
Pb$_4$(pbmp)(sip)$_2$(H$_2$O)$_4$ 2H$_2$O								[67], CEJXIZ
Pb(1)	7 (6 + *E*) + 1	ψ-PBP$_{eq}$ **V**	2.556(7) O(1)$^{\#3}$ 2.690(8) O(23)$^{\#4}$	2.335(7) O(12)$^{\#1}$ 2.529(7) O(3)$^{\#2}$ 2.625(7) O(13) 2.660(8) O(4)	154.4(3)	73.2(2) 80.3(2) 88.2(3) 114.7(3) $\Sigma = 356.4$	3.175(10) O(22)$^{\#4}$	
Pb(2)	9 (4 + *E*) + 5	ψ-TBP **II**	2.459(8) O(11)$^{\#5}$ 2.713(8) O(2W)	2.599(8) O(1W) 2.636(8) O(2)$^{\#6}$	126.9(3)	82.7(3)	2.751(8) O(23) 2.784(9) O(13)$^{\#7}$ 2.787(7) O(1)$^{\#6}$ 2.928(7) O(12)$^{\#7}$ 2.955(8) O(2)$^{\#8}$	
Pb(II) sulfoxide complexes								
Pb(dmso)$_3$(ClO$_4$)$_2$								
Pb(1)	6 (3 + *E*) + 3	ψ-T **I**	2.30(2) O(12) 2.31(2) O(13) 2.37(1) O(11)		83.2(6) 88.7(6) 79.2(5)		2.78(2) O(111) 2.79(2) O(112) 3.04(3) O(121)	[68], LAMJAK
Pb(2)	8 (3 + *E*) + 5	ψ-T **I**	2.25(1) O(23) 2.31(1) O(22) 2.42(1) O(21)		80.6(5) 78.8(4) 86.0(5)		2.79(1) O(21) 2.81(1) O(222) 2.86(4) O(211) 2.89(3) O(212) 3.12(2) O(221)	
Pb(dmso)$_5$(ClO$_4$)$_2$	7 (5 + *E*) + 2	ψ-OC **III**	2.348(6) O(1)	2.406(7) O(3) 2.433(7) O(4) 2.516(7) O(5) 2.531(7) O(2)	78.5(3) 83.0(3) 76.3(3) 84.3(2)	84.4(3) 84.5(3) 88.3(3) 97.3 (3) $\Sigma = 354.5$	3.08(2) O(11) 3.21(2) O(12)	[68], LAMHUC
Pb(hmsul)$_2$(H$_2$O)	9 (6 + *E*) + 3	ψ-PBP$_{eq}$ **V**	2.542(3) O(12) 2.589(3) O(21^{i})	2.547(3) O(3) 2.592(3) O(42^{i}) 2.660(3) O(11) 2.691(3) O(22^{i})	141.3(1)	66.1(1) 68.5(1) 72.1(1) 149.5(1) $\Sigma = 356.2$	2.794(3) O(41^{i}) 2.944(3) O(22^{ii}) 3.122(4) O(32^{ii})	[69], PEFDAF

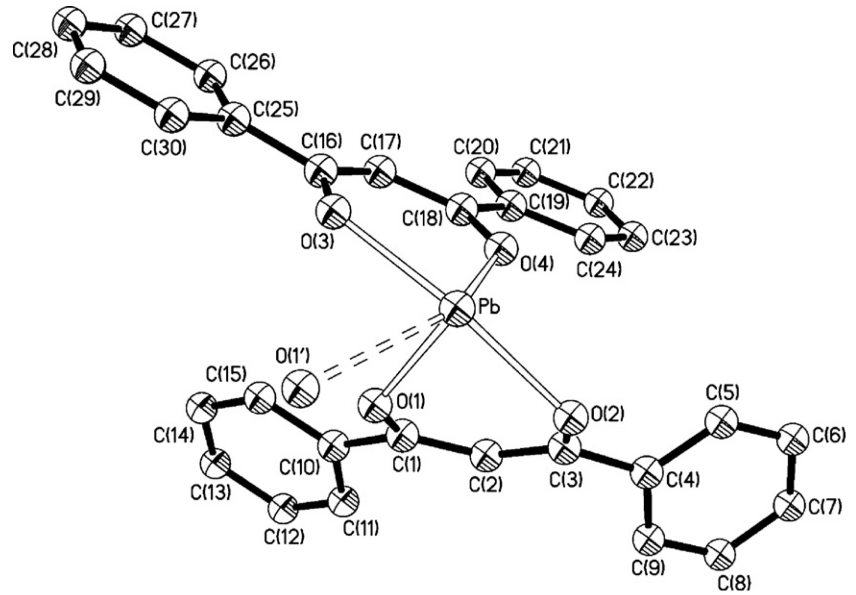
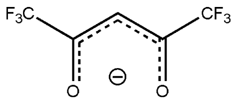


Fig. 7. ORTEP diagram of the coordination environment of the Pb(II) atom in $Pb(dbm)_2$.

the other unit. In each monomeric unit the Pb atom is coordinated by two hfa^- ligands with Pb–O bond lengths ranging from 2.417(3) to 2.497(3) Å, which are slightly longer than the corresponding bonds in $Pb(tmhd)_2$ [49] and $Pb(dmfod)_2$ [49] (Table 3). Both hfa^- ligands are located on the same side of Pb atom while the diglyme ligand is situated on the other side. The distribution of donor atoms around the Pb atom did not allow the authors [56] to describe the Pb coordination using a typical polyhedron for the eight-coordinate geometry. The authors mention that there is a void in the coordination sphere of Pb, which suggests a stereochemically active LP. If only the O atoms of the hfa^- ligands are taken into account, the Pb coordination polyhedron can be described as a ψ-trigonal bipyramid (**II**). The geometric characteristics of the Pb polyhedron are in full agreement with this model.



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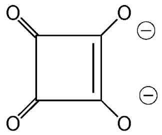
3.2. Squarates and aminosquarates

The squarate and aminosquarate anions are interesting ligands because they display a large variety of coordination modes in metal complexes: monodentate, bidentate, *cis*-1,2- or μ-1,3-*bis*-monodentate bridging, in some cases with a co-existence of these modes in the same complex.

The asymmetric unit of the crystal structure of lead(II) squarate tetrahydrate, $Pb(squ)(H_2O)_2{\cdot}2H_2O$ (squ = $C_4O_4^{2-}$, **17**) [57] contains one formula unit. The squarate ligand is coordinated to Pb(II) by means of the two oxygen atoms, which bridge neighboring Pb atoms forming Pb_2O_2 rings. These rings, which contain almost symmetric bridging bonds (Pb–O(6, $6^{\#2}$) 2.67(2) and 2.65(2) Å), and substantially asymmetric Pb–O(1, $1^{\#1}$) bonds (Pb–O(1, $1^{\#1}$) 2.74(2) and 2.48(2) Å), are bonded to each other to form zigzag polymeric ribbons. Two water molecules form bonds with the Pb atom (Pb–O 2.621(7) and 2.450(7) Å). Two other H_2O molecules are located at distances 2.97(3) and 2.98(2) Å from the Pb atom. The Pb coordination polyhedron can be described as a ψ-pentagonal bipyramid with a vacant axial position (**IV**). Two secondary Pb–O bonds complete the overall CN 8 for Pb(II) (Table 3).



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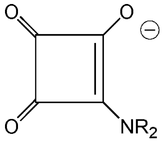
In order to study the effect of the alkyl substituents in amine-derivatives of squaric acid on the structure of Pb(II) complexes with these ligands, Hall et al. [57] also synthesized lead(II) 1-aminosquarate complexes containing *N*-methyl and *N*-ethyl substituents and investigated their crystal structures. In the structure of $Pb(msqu)_2(H_2O)_2{\cdot}H_2O$ ($msqu^-$ = (dimethylamino)squarate, **18**, *R* = Me) each $msqu^-$ ligand forms bidentate–chelate bonds with Pb. One of the two coordinated O atoms of each of the ligands bridges adjacent Pb atoms into centrosymmetric planar Pb_2O_2 units that form polymeric chains. According to [57], the CN of the Pb atom in $Pb(msqu)_2(H_2O)_2{\cdot}H_2O$ is equal to 8 while its geometry was described as a slightly distorted square antiprism. If the VSEPR model is applied, the Pb(II) geometry can be represented as ψ-trigonal bipyramidal (Table 3). The polymeric crystal structure of $Pb(esqu)_2(H_2O)$ ($esqu^-$ = $Et_2NC_4O_3$, **18**, R = Et) [57], containing an ethyl substituent on the amino-group is similar to the $Pb(msqu)_2(H_2O)_2{\cdot}H_2O$ structure [57]. As in the case of $Pb(msqu)_2(H_2O)_2{\cdot}H_2O$, the geometry of the Pb(II) coordination polyhedron in $Pb(esqu)_2(H_2O)$ can be described in terms of the VSEPR model as a ψ-trigonal bipyramid (**II**) (Table 3).



(R = Me, Et, H)

18

The structure of $Pb(amsqu)_2(H_2O)_2$ ($amsqu^-$ = aminosquarate, **18**, R = H) [58] is formed by parallel chains, containing one formula as the repeating unit. The Pb atoms are eight-coordinate and are

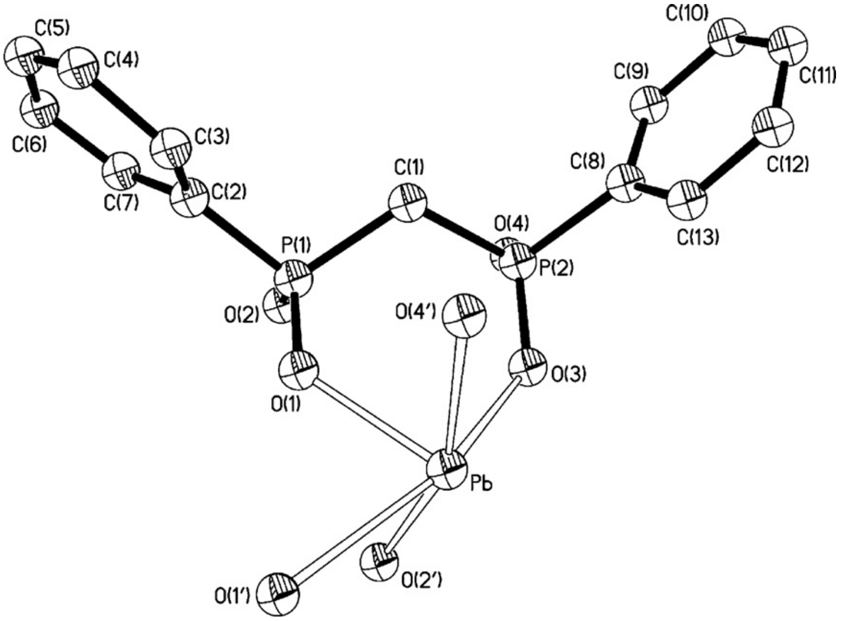


Fig. 8. ORTEP view of the coordination environment around the Pb(II) atom in Pb(pcp).

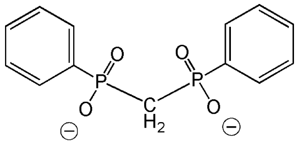
described as having a distorted square antiprismatic coordination. Each Pb atom in the structure is connected to two neighboring Pb atoms by means of four bridging aminosquarate ligands. In a similar fashion, each Pb atom forms bridging bonds with its two neighbors by means of four water molecules. According to the VSEPR model, the Pb coordination polyhedron in Pb(amsqu)$_2$(H$_2$O)$_2$ should be a ψ-trigonal bipyramid (**II**). The O atoms of four H$_2$O molecules are located in the vicinity of the LP and form secondary Pb–O bonds (Table 3).

3.3. Phosphonates, aminophosphonates and carboxyphosphonates

Hybrid organic/inorganic metal phosphonates and phosphinates are being intensively studied recently in relation to their possible applications as molecular sieves, selective catalysts, absorbers, ionic exchangers, and matrices for electric and magnetic devices [61]. A number of Pb(II) organo-phosphonates and organo-phosphinates have been synthesized and structurally investigated.

The lead(II) bis phosphinates Pb(Ph$_2$PO$_2$)$_2$ [59] and Pb(O$_2$P^{t}Bu$_2$)$_2$ [60] have similar crystal structures, containing polymeric chains in which the Pb atoms are doubly bridged by the phosphinate ligands. In both structures the Pb coordination polyhedra have a ψ-trigonal bipyramidal configuration with the LP located at one site of the bipyramid's equatorial plane (Table 3). The lengths of the axial and equatorial Pb–O bonds in Pb(O$_2$P^{t}Bu$_2$)$_2$ are close to the corresponding values in Pb(O$_2$PPh$_2$)$_2$. In both structures the values of the bond angles are also similar (Table 3).

The Pb atoms in Pb(pcp) (pcp^{2-} = P,P^{i}-diphenylmethylenediphosphinate, **19**) [61] have a pentacoordinate geometry and are surrounded by five O atoms from four pcp^{2-} ligands (Fig. 8). The coordination geometry of the Pb atom was described as square pyramidal (ψ-octahedral) with a vacant coordination site in agreement with the VSEPR model. The O(1) atom is located in the axial position of the ψ-octahedron and forms the shortest Pb–O distance in the polyhedron (2.297(10) Å). The equatorial plane of the ψ-octahedron consists of four O atoms with Pb–O distances from 2.345(12) up to 2.678(11) Å (Table 3). The indication of the presence of the stereochemically active LP is the displacement of the Pb atom by 0.41 Å from the equatorial plane towards the vacancy.



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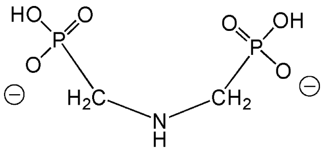
In the structure of Pb(amdph) (amdph^{2-} = aminodiphosphonate, NH(CH$_2$PO$_3$H)$_2$$^{2-}$, **20**) the Pb atoms have a pseudo-octahedral arrangement of five O atoms, with Pb–O lengths falling in the range from 2.456(9) up to 2.639(9) Å, and a LP [62]. According to the VSEPR model, the coordination polyhedron of the Pb atom should have a ψ-trigonal bipyramidal configuration with a vacant equatorial vertex. In addition to the primary Pb–O bonds (2.456(9)–2.550(8) Å), the Pb atom forms four longer secondary bonds in the range 2.639(9)–3.154(10) Å (Table 3).



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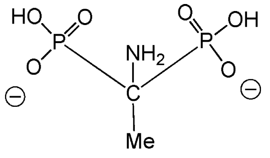
The structure of Pb{MeN(CH$_2$PO$_3$H)$_2$}, containing the *N*-methyl derivative of amdph^{2-}, contains two crystallographically independent Pb atoms [63]. Each is coordinated, as in the Pb(amdph) structure, by five phosphonate oxygen atoms of four different ligands. The authors describe the coordination geometry of the Pb atoms as a distorted trigonal-bipyramid or distorted octahedron with a vacant vertex occupied by the LP of the Pb^{2+} ion. The VSEPR model suggests that the coordination polyhedra of the lead atoms in the *N*-methyl derivative [63] and Pb(amdph) [62] are best considered as ψ-trigonal bipyramidal (**II**) (Table 3).

The Pb atoms in the layered polymeric structure of Pb(H$_2$aedp)·H$_2$O (H$_2$aedp^{2-} = 1-aminoethylidenephosphonate,

21) [64] are hexacoordinate, being ligated by six oxygen atoms from four equivalent diphosphonate ligands. According to the VSEPR model the coordination polyhedron of the Pb atom in Pb(H_2aedp)·H_2O is a ψ-octahedron (**III**) (Table 3).



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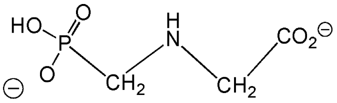
The Pb atom in the structure of Pb(phca) (phca^{2-} = phosphonecarboxylate, $^{-}O_3PCH_2NH_2CH_2COO^{-}$, **22**) forms a distorted pentagonal bipyramid in which the Pb atom is surrounded by six oxygen atoms and a LP [62]. The carboxylate group of the ligand is chelated by both oxygen atoms to the Pb atom. Two O atoms of the phosphonate groups form bonds with one Pb atom while one O atom bridges to an adjacent Pb atom. The Pb_2O_{10} dimers are linked by the $(O_3PCH_2NH_2CH_2CO_2)^{2-}$ anions into layers. As in the structure of Pb(pcp) [61], the coordination geometry of the Pb atom in Pb(phca) is a ψ-octahedron **(III)** (Table 3).



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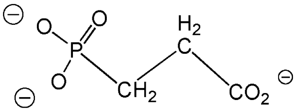
The crystal structure of $Pb_3(caeph)_2$ (caeph^{3-} = carboxyethylphosphonate, $^{-}O_2CCH_2CH_2PO_3{}^{2-}$, **23**) [65] contains three crystallographically independent Pb atoms with different coordination geometries. The crystal structure of $Pb_3(caeph)_2$ was re-determined by powder X-ray diffraction and compared, using soft constraints, with the single-crystal data [66]. The structural model obtained from powder diffraction data is in good agreement with the single-crystal experiment (Table 3). The geometry of the Pb(1) atoms is presented in [65] as a ψ-tetrahedron (**I**) (ψ-PbO_3), that of Pb(3) as a ψ-trigonal bipyramid (**II**) (ψ-PbO_4) and that of Pb(2) as a ψ-octahedron (**III**) (ψ-PbO_5) with the LPs on the fourth, fifth or sixth position in the polyhedron. Using *PLATON*, full geometric characteristics of all three Pb atoms were determined (Table 3). As described in [65], the coordination polyhedron of Pb(1) atom is a ψ-tetrahedron (**I**). The configuration of the coordination polyhedron of the Pb(3) atom can be represented as a ψ-tetrahedron (**I**) as well, with three primary Pb(3)–O bonds (2.391(14)–2.502(15) Å) and five secondary Pb(3)–O bonds (2.738(15)–3.025(15) Å) (Table 3). The coordination polyhedron of the Pb(2) atom should have a ψ-trigonal bipyramidal geometry according to the VSEPR model. Three secondary Pb(2)–O bonds complete the hepta-coordinate environment of Pb(2) atom (Table 3).



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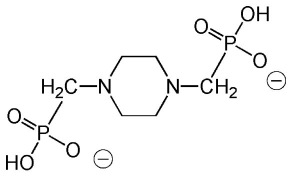
The synthesis and structure of $Pb_5(caeph)_2(Hcaeph)_2$ with a pillared, layered framework has been reported. There are three independent Pb atoms in the structure [66]. The coordination polyhedra of the Pb(1) and Pb(2) atoms can be described as ψ-trigonal bipyramids (**II**) if the Pb–O distances less than 2.69(1) Å are considered (Table 3). The Pb(3) atoms are each surrounded by eight O atoms with bond lengths 2.53(1)–2.85(1) Å. The LP of the Pb(3) atom, which is situated on a special position in the unit cell, is stereochemically inactive.

In order to examine materials with open-framework and porous structures, Du et al. carried out the synthesis and structure determination of a hybrid phosphonate complex, $Pb_4(pbmp)(sip)_2(H_2O)_4{\cdot}2H_2O$, (pbmp^{2-} = *N*,*N*′-piperazinebis(methylenephosphonate), **24**; sip^{3-} = 5-sulfoisophthalate, **25**) [67]. The complex contains three different coordinating functional groups: phosphonate, carboxylate and sulfonate. There are two independent Pb atoms. The Pb(1) atoms are coordinated by two phosphonate oxygen atoms from two phosphonate anions and four oxygen atoms from four sip^{3-} anions. The coordination polyhedron of the Pb(1) atom was described as a distorted octahedron. According to the VSEPR model, the coordination polyhedron of Pb(1) corresponds to a pentagonal bipyramid with a vacant vertex in the equatorial plane (**V**), occupied by the LP. The Pb(2) atom in $Pb_4(pbmp)(sip)_2(H_2O)_4{\cdot}2H_2O$ is penta-coordinated by one phosphonate oxygen atom of one of the pbmp^{2-} ligands, two oxygen atoms from two sip ligands and two coordinated H_2O molecules. The authors describe the coordination polyhedron of Pb(2) as a slightly distorted ψ-PbO_5 with the LP of Pb^{2+} ion in the vacant position. Taking into account the stereochemically active LP, the coordination polyhedron of the Pb(2) atom can be represented in terms of VSEPR model as a ψ-trigonal bipyramid (**II**) (Table 3).



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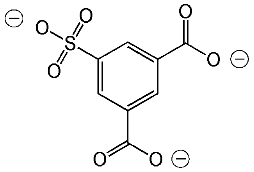

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3.4. Sulfoxides

In this section the crystal structures of the Pb(II) alkyl sulfonate complexes, in which the coordination polyhedra contains only Pb–O bonds, are considered. Harrowfield et al. describe the crystal structures of two $Pb(ClO_4)_2$ adducts with dimethylsulfoxide (dmso): $Pb(dmso)_3(ClO_4)_2$ and $Pb(dmso)_5(ClO_4)_2$ [68]. The asymmetric unit of the $Pb(dmso)_3(ClO_4)_2$ structure contains two non-equivalent Pb atoms, each forming dimeric $[Pb_2(dmso)_6(ClO_4)_4]$ units with similar composition, but different bridging ligands. The dimers formed by Pb(1) contain bridging $ClO_4{}^{-}$ions, while the dimers formed by Pb(2) atoms have bridging dmso molecules. The authors assigned CN 6 to the Pb(1) atom with a coordination polyhedron intermediate between that of a distorted octahedron and a trigonal prism, while for Pb(2) a CN 8 was suggested. The VSEPR model assigns similar geometries to the coordination polyhedra for Pb(1) and Pb(2) in $Pb(dmso)_3(ClO_4)_2$, namely **I** (CN 3 + *E*) (Table 3). The difference in the surrounding of the Pb(1) and Pb(2) atoms is in the number of the secondary Pb–O bonds: 3 for Pb(1) and 5 for Pb(2).

The structure of $Pb(dmso)_5(ClO_4)_2$ [68] consists of isolated $[Pb(dmso)_5(ClO_4)]^+$ cations and ClO_4^- anions. The coordinated dmso molecules act as monodentate ligands toward Pb(II) with Pb–O distances 2.348(6)–2.531(7) Å. The Pb atom also forms two additional weak contacts with O atoms of the perchlorate ion (Pb–O 3.08(2) and 3.21(2) Å), which in this case acts as a bidentate ligand. The authors represent an alternative interpretation of the geometry of the central atom in $Pb(dmso)_5(ClO_4)_2$ as octahedral or pentagonal-bipyramidal with a stereochemically active LP directed towards the bidentate perchlorate ion. If the secondary bonds are omitted, the geometry of the primary coordination sphere in $Pb(dmso)_5(ClO_4)_2$ can be thought of as a ψ-octahedron (**III**) (Table 3).

The compound $Pb(hmsul)_2(H_2O)$ ($hmsul^- = HOCH_2SO_3^-$) has Pb atoms coordinated by nine oxygen atoms—one from a water molecule and the remaining eight from five different hydroxymethanesulfonate ligands [69]. The oxygen atoms are located 2.547(3)–3.122(4) Å from the central atom and form an irregular polyhedron. The VSEPR model predicts the coordination polyhedron of the Pb atom to be a ψ-pentagonal bipyramid with a vacant position in the equatorial plane (**V**) (Table 3).

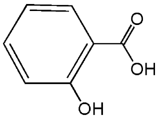
4. Lead(II) aromatic carboxylates

4.1. Monocarboxylates

No data are available on crystal structures of Pb(II) complexes with benzoic acid, but the crystal structures of a number of complexes with benzoic acid derivatives containing OH, NH_2, NO_2 and SO_3H groups have been determined. The structures with hydroxyl derivatives of benzoic acid are the most numerous. Depending on the relative hydroxyl group position, one can distinguish *o*-, *m*- and *p*-hydroxybenzoic acids. The crystal structures of Pb(II) complexes with all three types of oxybenzoic acids have been determined while in the case of *o*-hydroxybenzoic acid (salicylic acid) the structures of Pb(II) complexes with anions of both mono-deprotonated and completely deprotonated acid have been investigated.

4.2. Hydroxybenzoates

In the crystal structure of Pb(sal) [H_2sal = 2-hydroxybenzoic acid (salicylic acid), **26**] the Pb atom is coordinated by five O atoms each from four completely deprotonated salicylic acid ligands with Pb–O lengths falling into the range 2.318(16)–2.605(15) Å [70]. Besides, the Pb atom also forms one weak bond with the oxygen atom of the adjacent complex. The coordination geometry around the Pb atom is described as being intermediate between a square-pyramid and a trigonal-bipyramid. Based on the lengths of primary bonds and values of the angles around the Pb atom, its coordination polyhedron can be described, in accordance with the VSEPR model, as a ψ-octahedron (**III**) (Table 4).



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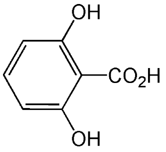
The structure of $Pb(Hsal)_2(H_2O)$ [71] is composed of polymeric helices located around a twofold screw axis. The Pb atoms form asymmetric bonds with the O atoms of the carboxylate groups of both crystallographically non-equivalent $Hsal^-$ anions with Pb–O lengths equal to 2.40(3)–2.88(3) Å. According to the authors [71], the Pb coordination sphere also includes the oxygen atom of a coordinated H_2O-molecule (Pb–O_W 2.45(4) Å), and the O^i atom of the $OH(2)^*$-group of the organic ligand of the adjacent complex. Taking into account the four shortest Pb–O bonds (Pb–O 2.40(3)–2.64(4) Å), the coordination polyhedron of the Pb atom in the crystal structure of $Pb(Hsal)_2(H_2O)$ can be described, in accordance with the VSEPR model, as a ψ-trigonal bipyramid (**II**) (Table 4).

Unlike the crystal structure of Pb(sal) [70], whose salicylate ligand has both carboxylate and hydroxyl groups deprotonated, for $Pb(Hsal)_2(H_2O)$ and $Pb\{(4\text{-}HOC_6H_4CO_2)_2(H_2O)\}\cdot H_2O$ only the carboxylate groups are deprotonated. The OH-group of the ligand is not included into the Pb coordination sphere and participates only in formation of H-bonds with H_2O-molecules and OH-group of the adjacent ligand. In the structure of the aquabis(*p*-hydroxybenzoato)lead(II) monohydrate [72], as in the structure of Pb(sal) [70], the geometry of the primary coordination sphere of the Pb atom comprises a ψ-octahedron (**III**) (Table 4).

2,6-Dihydroxybenzoic acid (H_3dhb, **27**) is a convenient organic ligand for forming complexes with metal ions. The polymeric crystal structure of $Pb_2(H_2dhb)_4\cdot 3H_2O$ includes two types of Pb atoms [73]. The Pb(1) atoms are each chelated by the carboxylate groups of two dihydroxybenzoate ligands. The coordination environment of the Pb(1) atom is supplemented by a coordinated H_2O-molecule and two phenolic oxygen atoms. The overall geometry around Pb(1) is described as a heavily distorted pentagonal bipyramid. Taking into account only the shortest Pb(1)–O bonds, the coordination polyhedron of the Pb(1) atom in the crystal structure of $Pb_2(H_2dhb)_4\cdot 3H_2O$, has a ψ-trigonal bipyramidal configuration (Table 4) in accord with the VSEPR model. The Pb(2) atoms in the crystal structure of $Pb_2(H_2dhb)_4\cdot 3H_2O$ form dimeric units bridged by two water molecules at distances of 2.592(6) and 2.612(6) Å. The eight-coordinated geometry of the Pb(2) polyhedron is presented in [73] as a distorted square antiprism. According to the VSEPR model, the Pb(2) coordination polyhedron in $Pb_2(H_2dhb)_4\cdot 3H_2O$ can be described as a ψ-pentagonal bipyramid with a vacant position in the equatorial plane (**V**) (Table 4).



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The crystal structure of the Pb(II) complex with an aromatic hydroxymonocarboxylic acid containing a carboxyl group in the side chain has been investigated. The 2D crystal structure of the lead(II) compound with 4-hydroxylcinnamonic acid (H_2hca, **28**), $Pb(Hhca)_2(dmf)\cdot dmf$, is composed of neutral $[Pb(Hhca)_2(dmf)]$ units and lattice dmf molecules [74]. Each Pb atom in the structure is coordinated by two chelating $Hhca^-$ anions and a dmf molecule. The authors mentioned that the Pb atom is seven-coordinate and that the LP is directed approximately opposite to the short Pb–O chelate bonds. Analysis of the interatomic distances and angles in the crystal structure (Table 4) enables one to conclude that the coordination geometry of the Pb atom is a ψ-octahedron (**III**) when considering only the shortest Pb–O contacts.

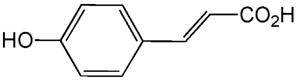

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Table 4
Stereochemistry of Pb(II) complexes with monoaromatic carboxylate ligands.

Compound	Overall CN	Shape of the polyhedron	Pb–O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial and equatorial)	Equatorial		
Pb(II) aromatic monocarboxylates								
Pb(sal)	6 (5 + *E*) + 1	ψ-OC **III**	2.318(16) O(3^{i})	2.437(15) O(2) 2.465(14) O(2^{ii}) 2.499(15) O(3) 2.605(15) O(1^{iii})	89.5(5) 82.6(5) 71.9(6) 80.4(5)	64.5(5) 69.0(5) 101.7(5) 119.7(5) $\Sigma = 354.9$	2.947(18) O(1^{ii})	[70], MENHET
Pb(Hsal)$_2$(H$_2$O)	7 (4 + *E*) + 3	ψ-TBP **II**	2.40(4) O(2), 2.64(4) O(4)	2.40(3) O(3) 2.45(4) O$_w$	129.3(14)	75.4(14)	2.88(3) O(1) 2.99(4) O^{i}(OH(2))* 3.18 O(1^{ii})	[71], FUFWEI
Pb{(HOC$_6$H$_4$CO$_2$)(H$_2$O)}·H$_2$O	8 (5 + *E*) + 3	ψ-OC **III**	2.39(4) O(4)	2.50(3) O(3) 2.52(5) O(5) 2.61(4) O(8) 2.65(4) O(3)*	79.43(3) 51.52(3) 70.70, 73.75	85.73(3) 72.94(3) 65.25(3) 103.40(4) $\Sigma = 327.3$	2.82(3) O(8)* 2.83(5) O(5)* 2.89(3) O(4)*	[72], AQOHPB
Pb$_2$(H$_2$dhb)$_4$·3H$_2$O								[73], LAJDOP
Pb(1)	7 (4 + *E*) + 3	ψ-TBP **II**	2.353(7) O(21) 2.654(7) O(12)	2.354(7) O(W1) 2.423(7) O(11)	123.0(2)	87.3(3)	2.724(8) O(23^{iii}) 2.968 (7) O(22)	
Pb(2)	8 (6 + *E*) + 2	ψ-PBP$_{eq}$ **V**	2.591(6) O(W3) 2.592(7) O(W2)	2.510(7) O(41) 2.612(6) O(W3^{i}) 2.666(6) O(42) 2.696(6) O(31)	143.9(2)	49.5(2) 68.53(19) 75.6(2) 167.4(2) $\Sigma = 361.0$	3.062(7) O(14^{ii}) 2.775(7) O(13) 2.892(6) O(44)	
Pb(Hhca)$_2$(dmf)·dmf	8 (5 + *E*) + 3	ψ-OC **III**	2.404(2) O(4)	2.524(2) O(1) 2.567(2) O(2) 2.583(2) O(5) 2.620(2) O(1^{i})	76.25(9) 78.96(8) 52.25(8) 75.11(8)	51.30(7) 66.41(8) 74.19(8) 124.14(8) $\Sigma = 334.86$	2.774(3) O(7) 2.785(2) O(2^{i}) 3.193(3) O(3c)	[74], YEXVUT
Pb(Hnsal)$_2$(H$_2$O)	7 (4 + *E*) + 3	ψ-TBP **II**	2.428(5) O(6) 2.691(4) O(2)	2.419(4) O(11) 2.452(4) O(1)	133.9(2)	74.2(1)	2.727(5) O(7) 2.872(5) O(7^{ii}) 3.084(5) O(5^{i})	[75], TEJZUD
Pb(dnsal)(H$_2$O)·0.25H$_2$O	10 (6 + *E*) + 4	ψ-PBP$_{eq}$ **V**	2.576(4) O(3d) 2.62(5) O(2c)	2.450(4) O(2e) 2.55(12) O(8) 2.633(4) O(1) 2.646(4) O(1g)	142.24(12)	66.54(13) 73.3(3) 84.54(12) 129.0 (3) $\Sigma = 353.38$	2.995(4) O(3e) 3.020(4) O(7) 3.017(4) O(7h) 2.097(4) O(6h)	[76], JEGTIZ
Pb(sb)(H$_2$O)$_2$	9 (6 + *E*) + 3	ψ-PBP$_{ax}$ **IV**	2.400(4) O(1)	2.562(4) O(1w) 2.580(4) O(2) 2.618(4) O(3^{i}) 2.670(4) O(2w) 2.733(4) O(2w^{ii})	78.9(2) 52.2(1) 84.3(2) 76.8(1) 76.0(1)	64.73(12) 68.19(13) 71.94(12) 72.03(13) 73.91(14) $\Sigma = 350.8$	2.960(4) O(4a) 3.155(5) O(6f) 3.209(4) O(5e)	[77], PECZUT
Pb(sb)(H$_2$O)$_2$(4,4-bpy)	8 (4 + *E*) + 4	ψ-TBP **II**	2.549(4) O(6) 2.567(4) O(2)	2.492(3) O(7) 2.504(3) O(1)	113.72(12)	105.00(11)	2.654(3) O(2^{i}) 2.749(4) O(3^{ii}) 2.856(3) O(3^{iii}) 3.112(4) O(5^{iii})	[78], NEVLAC

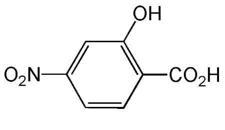
Table 4(*Continued*)

Compound	Overall CN	Shape of the polyhedron	Pb–O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial and equatorial)	Equatorial		
$Pb(sb)(H_2O)_2(4,4\text{-bpy})$	8 (4 + *E*) + 4	ψ-TBP **II**	2.561(8) O(1W) 2.572(7) O(4)$^{\#1}$	2.492(7) O(2W) 2.492(6) O(5)$^{\#1}$	113.8(2)	104.7(2)	2.647(7) O(4)$^{\#2}$ 2.744(6) O(2) 2.840(7) O(2^{iii}) 3.106(9) O(3^{iii})	[79], NEVLAD
$Pb(H_2ssa)_2(H_2O)$	7 (5 + *E*) + 2	ψ-OC **III**	2.407(4) O(1W)	2.561(3) O(51A) 2.561(3) O(51A^{d}) 2.580(3) O(51B^{b}) 2.580(3) O(51B^{c})	73.31(8) 73.31(8) 72.31(8) 72.31(8)	82.05(9) 82.05(9) 88.27(9) 87.55(9) $\Sigma = 339.92$	2.675(4) O(52A^{a}) 2.717(4) O(52B)	[80], PIKCAO
$Pb(amb)_2$	6 (4 + E) + 2	ψ-TBP **II**	2.519(22) O(4) 2.521(18) O(1)	2.370(20) O(2) 2.399(21) O(3)	111.5(7)	88.4(7)	2.658(22) O(1^{i}) 2.842(19) O(2^{ii})	[81], ABZORB
$Pb(nb)_2(H_2O)$	8 (4 + *E*) + 4	ψ-TBP **II**	2.558(4) O(2)$^{\#1}$ 2.631(5) O(6)	2.421(4) O(1) 2.531(5) O(5)	131.08(14)	77.09(17)	2.670(3) O(1)$^{\#2}$ 2.676(5) O(9) 2.790(4) O(2) 3.037(6) O(8)$^{\#3}$	[40], QOZBOW
$Pb(dnb)_2(H_2O)$	8 (5 + *E*) + 3	ψ-OC **III**	2.358(2) O(1)	2.520(3) O(7) 2.543(3) O(8) 2.577(2) O(2)$^{\#1}$ 2.660(3) O(1W)	77.63(9) 84.58(8) 77.16(7) 80.11(10)	51.80(8) 74.73(8) 80.44(11) 145.28(10) $\Sigma = 352.25$	2.799(2) O(1)$^{\#2}$ 2.815(3) O(2) 3.012(3) O(10)$^{\#3}$	[40], QOZBUC
Pb(II) nicotinates								
$\{Pb(ino)_2\}_2\cdot 7H_2O$	8 (3 + *E*) + 5	ψ-T **I**	2.456(2) O(4) 2.459(2) O(5) 2.464(2) O(1)		70.17(7) 78.93(6) 88.88(6)		2.650(2) O(2) 2.670(2) O(1)$^{\#1}$ 2.779(2) O(6) 2.836(2) O(3) 2.8563(18) O(2d)	[82], CEZZEN
$Pb(ino)_2\cdot nH_2O$	8 (4 + *E*) + 4	ψ-TBP **II**	2.499(4) O(1) 2.499(4) O(1)$^{\#3}$	2.381(4) O(2) 2.381(4) O(2)$^{\#3}$	156.0(2)	75.1(2)	2.863(4) O(1)$^{\#4}$ 2.863(4) O(1)$^{\#5}$ 2.983(6) O(3) 2.983(6) O(3)$^{\#3}$	[82], CEZZIR
$Pb_4(OH)_4(ino)_4\cdot nH_2O$	8 (5 + *E*) + 3	ψ-OC **III**	2.375(7) O(2)	2.405(4) O(2)$^{\#2}$ 2.405(4) O(2)$^{\#3}$ 2.68(1) O(3) 2.68(1) O(3)$^{\#4}$	73.1(2) 73.1(2) 74.7(3) 74.7(3)	69. 7(2) 88.0(3) 88.0(3) 96.5(4) $\Sigma = 342.2$	2.873(4) O(1)$^{\#1}$ 2.873(4) O(1)$^{\#5}$ 2.9366(9) O(3W)$^{\#2}$	[82], CEZZOX
$Pb(ino)(fa)_{0.5}$	8 (4 + *E*) + 4	ψ-TBP **II**	2.483(9) O(4) 2.586(8) O(6)	2.388(9) O(1) 2.518(8) O(3)	134.3(3)	82.3(3)	2.845(9) O(7) 2.851(9) O(6E) 2.915(9) O(3C) 3.044(9) O(7E)	[83], CIBQOU
$Pb_2(ino)(btc)(H_2O)$								[83], CIBQUA
Pb(1)	8 (4 + *E*) + 4	ψ-TBP **II**	2.623(7) O(6) 2.670(8) O(7h)	2.383(7) O(7) 2.459(7) O(2)	113.6(2)	88.8(3)	2.750(8) O(10) 2.754(8) O(10g) 2.880(7) O(3h) 2.901(7) O(8a)	

Pb(2)	7 (5 + *E*) + 2	ψ-OC **III**	2.362(7) O(1)	2.449(7) O(9e) 2.465(7) O(5c) 2.516(6) O(8e) 2.745(7) O(3i)	87.3(2) 87.2(2) 77.1(2) 78.1(2)	53. 1(2) 73.0(2) 75.4(2) 152.7(2) $\Sigma = 354.2$	2.972(7) O(4c) 2.987(7) O(5i)	
Pb(hmpyr)$_2$·7H$_2$O	6 (4 + *E*) + 2	ψ-TBP **II**	2.370(5) O(2A) 2.544(5) O(1)	2.300(5) O(2) 2.358(5) O(1A)	141.6(2)	90.6(2)	2.684(5) O(2A^{i}) 3.199(6) O(6B)	[84] MALFUA
Pb(II) phenoxyacetates								
Pb(pa)$_2$·0.5H$_2$O								[85], DEBGEW
Pb(1)	9 (4 + *E*) + 5	ψ-TBP	2.51(2) O(11)D 2.71(2) O(11)A[a]	2.34(2) O(10)B[b] 2.51(2) O(10)B	133.5(7)	65.8(6)	2.76(2) Ow 2.79(2) O(10)D 2.87(2) O(11)B[a] 2.96(2) O(7)B 3.10(2) O(11)C	
Pb(2)	8 (5 + *E*) + 3	ψ-OC **III**	2.48(2) O(10)C	2.50(2) O(11)C[a] 2.58(2) O(11)A 2.58(2) O(10)D 2.72(2) O(10)A	52.1(7) 81.3(7) 82.6(6) 83.9(7)	48.8(6) 74.4(6) 104.0(6) 118.0(6) $\Sigma = 345.2$	2.73(2) O(11)B 2.73(2) O(11)C 3.17(2) O(8)	
Pb(pa)$_2$·0.5H$_2$O								[86], ZOWQEH
Pb(1)	8 (5 + *E*) + 3	ψ-OC **III**	2.477(12) O(1)	2.487(8) O(2) 2.550(11) O(10) 2.558(9) O(4) 2.713(8) O(5)	52.4(3) 82.9(3) 81.1(3) 83.3(3)	48.4(3) 74.4(3) 104.7(3) 118.1(3) $\Sigma = 345.5$	2.720(12) O(7) 2.730(7) O(2^{i}) 3.155(10) O(3^{i})	
Pb(2)	9 (4 + *E*) + 5	ψ-TBP **II**	2.500(10) O(8) 2.695(10) O(4^{i})	2.387(9) O(8^{i}) 2.547(11) O(11)	122.8(3)	76.1(3)	2.723(8) O(13) 2.829(10) O(10^{ii}) 2.925(10) O(7) 2.945(9) O(9$^{i)}$ 3.105(9)O(2^{i})	
Pb(pda)$_2$·H$_2$O	8 (6 + *E*) + 2	ψ-PBP$_{eq}$ **V**	2.493(4) O(6A) 2.698(4) O(5A)	2.394(4) O(6) 2.505(3) O(3) 2.637(5) O(2) 3.685(4) O(1)	154.9(1)	75.2(1) 50.6(1) 76.3(1) 142.4(2) $\Sigma = 344.5$	2.796(4) O(7A) 2.931(5) O(5D)	[86], ZOWQIL
Pb(mcpa)$_2$·H$_2$O	7 (5 + *E*) + 2	ψ-OC **III**	2.419(5) O(3)	2.507(5) O(13) 2.613(5) O(2) 2.649(4) O(3)$^{\#1}$ 2.657(5) O(12)	77.42(16) 51.51(15) 66.61(17) 74.53(16)	50.29(15) 72.44(15) 74.95(17) 112.14(14) $\Sigma = 309.84$	2.717(4) O(13)$^{\#2}$ 2.774(6) O(4)	[87], MURZOO

4.3. Nitrohydroxybenzoates

The coordination polyhedron of the Pb atom in the structure of Pb(Hnsal)$_2$(H$_2$O) (H$_2$nsal = *p*-nitrosalicylic acid-*O,O*, **29**) [75] is characterized by the same ψ-trigonal bipyramid (**II**) with close values of primary Pb–O bonds lengths as that in the structure of Pb(Hsal)$_2$(H$_2$O) [71] (Table 4). An insignificant difference is observed only in the lengths of secondary bonds.



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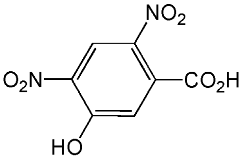
The Pb(II) complex Pb(dnsal)(H$_2$O)·0.25H$_2$O (H$_2$dnsal = 2,4-dinitro-5-hydroxybenzoic acid, **30**) has a supramolecular structure composed of one-dimensional lead-oxide chains [76]. The Pb atom in the structure is surrounded by six oxygen atoms and a coordinated H$_2$O-molecule. The Pb–O bonds lengths fall into the range 2.450(4)–2.662(5) Å. According to the VSEPR model, the coordination polyhedron of the Pb atom should be a ψ-pentagonal bipyramid with a vacant vertex in the equatorial plane (**V**) (Table 4).



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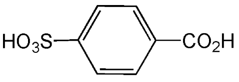
4.4. Sulfonatobenzoates and sulfonatosalicylates

The crystal structures of a number of Pb(II) complexes with sulfobenzoic and sulfosalicylic acids have been determined. A ψ-pentagonal-bipyramidal coordination of the Pb atom with a vacant axial vertex (**IV**) occupied by the stereochemically active LP has been established in the crystal structure of Pb(sb)(H$_2$O)$_2$ (H$_2$sb = 4-sulfonylbenzoic acid, **31**) [77]. The Pb atom in the structure chelates the carboxylate group of the ligand and forms monodentate coordination bonds with one of the oxygen atoms of the sulfonate group and an oxygen atom of the H$_2$O-molecule. The Pb–O bonds lengths in the structure are in the range 2.400(4)–2.733(4) Å (Table 4).



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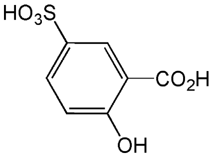
The crystal structure of the adduct diaqua(4-sulfonatobenzoato)lead(II) with 4,4′-bipyridine, Pb(sb)(H$_2$O)$_2$(4,4′-bpy), was independently and simultaneously investigated by two groups [78,79]. The results are in very good agreement. The bpy molecule is not coordinated by the Pb atom. The composition of the [Pb(sb)(H$_2$O)$_2$] unit in the structures of Pb(sb)(H$_2$O)$_2$ [77] and Pb(sb)(H$_2$O)$_2$(4,4′-bpy) [78,79)] are identical. Analysis of the values of primary bonds lengths and angles enables one to represent, in accordance with the VSEPR model, the Pb coordination polyhedron in the crystal structure of Pb(sb)(H$_2$O)$_2$ as a ψ-pentagonal bipyramid with a vacant axial position (**IV**) and in Pb(sb)(H$_2$O)$_2$(4,4′-bpy) as a ψ-trigonal bipyramid (**II**) (Table 4).

Unlike Pb(sb)(H$_2$O)$_2$ [77] and Pb(sb)(H$_2$O)$_2$(4,4′-bpy), where both sulfonyl and carboxyl groups of the ligand are deprotonated, in Pb(H$_2$ssa)$_2$(H$_2$O) (H$_3$ssa = 2-hydroxy-5-sulfobenzoic acid, **32**), deprotonation occurs only at the sulfonyl groups [80]. The carboxyl and hydroxyl groups are involved in formation of hydrogen bonds that unite the helical polymeric ribbons into a three-dimensional framework. The Pb atom forms monodentate coordination bonds with the H$_2$O molecule and six separate sulfonate oxygen donor atoms. The Pb–O lengths fall into the range 2.407(4)–2.717(4) Å. The resulting PbO$_7$-polyhedron has an irregular shape. According to the VSEPR model, the coordination polyhedron should be a ψ-octahedral configuration (Table 4).



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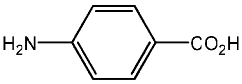
4.5. Aminobenzoates and nitrobenzoates

The crystal structure of Pb(amb)$_2$ (Hamb = *p*-aminobenzoic acid, **33**) is composed of one-dimensional polymeric chains [81]. Two crystallographically non-equivalent amb$^-$ anions chelate the central atom (Fig. 9). The ligand containing C(1)O(1)O(2) is bridging, providing both carboxylate O atoms for binding with adjacent Pb atoms. The second amb$^-$ anion containing C(8)O(3)O(4) forms only a chelate bond with the Pb atom (Pb–O(3) 2.399(21) and Pb–O(4) 2.519(22) Å). Two types of four-membered Pb$_2$O$_2$ and PbOCO rings are formed through bridging bonds. These two types alternate in polymeric chains. The Pb polyhedron can be represented as a distorted trigonal prism (CN 6). According to the VSEPR model, the coordination geometry of Pb atom corresponds to a ψ-trigonal bipyramid (**II**) formed by oxygen atoms of chelate carboxylate groups. The oxygen atoms O(4) and O(1) are located in the apical positions of the bipyramid while its equatorial plane is formed by the O(2) and O(3) atoms and the stereochemically active lone pair. The distances from the Pb to the bridging oxygen atoms O(1$^{\mathrm{i}}$) and O(2$^{\mathrm{ii}}$) should be considered as secondary bonds (Table 4). Theoretical studies of Pb(amb)$_2$ [109] have confirmed the four-coordinate geometry of the Pb atom in the structure and stereochemical activity of the Pb(II) lone pair in this compound. The electron population of the Pb^{2+} ion 6s orbital is equal to 1.88 and can be attributed to the stereochemical active lone pair of electrons in this compound.



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The crystal structures of a number of nitro derivatives of benzoic acid have been determined. The structure of Pb(nb)$_2$(H$_2$O) (Hnb = 2-nitrobenzoic acid, **34**), comprises a 1D coordination polymer, in which carboxylate oxygen atoms form a bridge between the Pb atoms [40]. The carboxylate groups of both ligands form chelate bonds with the Pb atom. One of the chelate-bonded carboxylate groups is simultaneously a bridge between adjacent Pb atoms forming Pb$_2$O$_2$ rings that are bonded into polymeric chains. Taking into account the Pb–O bonds lengths up to 3.0 Å, the Pb atom polyhedron is described in [40] as a grossly distorted edge-capped pentagonal pyramid where the axial sites are occupied by the carboxylate oxygen and the lead LP. According to the VSEPR model, the polyhedron of the Pb atom of the first coordination sphere should be a ψ-trigonal bipyramid (**II**) (Table 4).

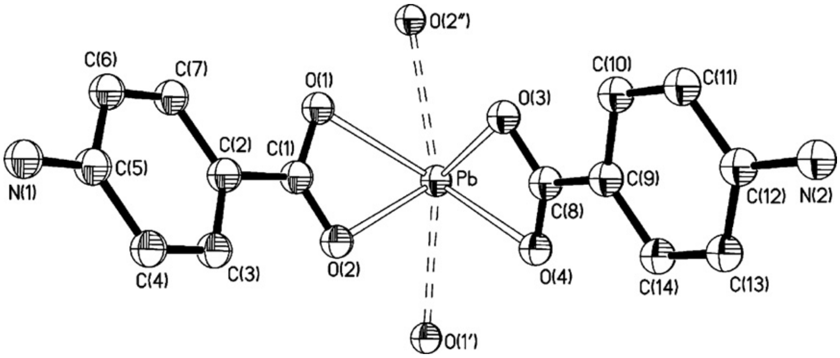
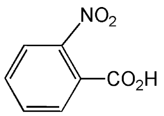
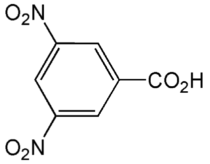


Fig. 9. ORTEP drawing of the coordination environment of the Pb(II) atom in Pb(amb)$_2$.



34

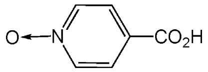
Similar to the structure of Pb(nb)$_2$(H$_2$O), Pb(dnb)$_2$(H$_2$O) (Hdnb = 3,5-dinitrobenzoic acid, **35**) is a 1D coordination polymer [40]. The coordination of the organic ligands is identical in both structures. The difference between the crystal structures lies in the different arrangement of the central atom's first coordination sphere. Unlike Pb(nb)$_2$(H$_2$O), where the Pb atom is a ψ-trigonal bipyramid (**II**), that for Pb(dnb)$_2$(H$_2$O) is a ψ-octahedron (**III**) (Table 4).



35

4.6. Nicotinates

The syntheses and crystal structures of three lead(II) complexes with isonicotinic acid N-oxide (Hino, **36**) with compositions {Pb(ino)$_2$}$_2$·7H$_2$O, Pb(ino)$_2$·nH$_2$O and Pb$_4$(OH)$_4$(ino)$_4$·nH$_2$O have been described [82].



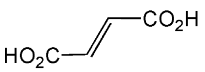
36

According to [82], the inner coordination sphere of the Pb atom in {Pb(ino)$_2$}$_2$·7H$_2$O is formed by five O atoms which are located at one side from the Pb atom. This supports the presence of a stereochemically active LP in the compound. The Pb coordination polyhedron in the structure of {Pb(ino)$_2$}$_2$·7H$_2$O is assigned by the authors [82] as a distorted square pyramid does not comply with the expected ψ-octahedron (**III**) predicted by the VSEPR model, since one of the axial-equatorial angles in the polyhedron is larger than 90° (96.18(6)°). The coordination geometry of the Pb atom in the structure of {Pb(ino)$_2$}$_2$·7H$_2$O corresponds, according to the VSEPR model, to a ψ-tetrahedron (**I**) (Table 4).

According to the data presented in [82], the Pb atom in the structure of Pb(ino)$_2$·nH$_2$O is hexa-coordinate, displaying a *hemidirected* pentagonal bipyramidal geometry. Both ino ligands are tridentate and bind three Pb atoms each through the monodentate O atom of the carboxylate group and the bridging oxygen atom of the N-oxide group. The coordination of the Pb atom has, in accordance with the VSEPR model, the configuration of a ψ-trigonal bipyramid (**II**) (Table 4).

In the structure of Pb$_4$(OH)$_4$(ino)$_4$·nH$_2$O every Pb atom is coordinated to three hydroxyl oxygen atoms of three bridging OH-groups. Every μ$_3$-OH-group makes a bridge to three Pb(II) atoms forming a M$_4$O$_4$ core with metal atoms in the distorted cubane core vertices. Every Pb$_4$O$_4$ group is bonded to four bridging O(1) oxygen atoms from the N-oxide ino-ligands with formation of inorganic metal-oxide polymeric chains. The coordination polyhedron of the Pb atom has a ψ-octahedral configuration (Table 4).

The tetra-coordinated Pb atoms in the structure of Pb(ino)(fa)$_{0.5}$ [H$_2$fa = *trans*-HO$_2$CC(H) = C(H)CO$_2$H (fumaric acid), **37**] form bonds with the oxygen atoms O(1) (Pb–O(1) 2.388(9) Å) and O(4) (Pb–O(4) 2.483(9) Å) from the N-oxide and carboxylate groups of one of the ino-ligands and two oxygen atoms of the carboxylate group C(2)O(3)O(6) (Pb–O(3) 2.518(8) and Pb–O(6) 2.586(8) Å) [83]. The coordination polyhedron of the Pb atom in the structure of Pb(ino)(fa)$_{0.5}$ comprises a ψ-trigonal bipyramid (**II**) with the O(4) and O(6) atoms in the axial positions (angle O(4)PbO(6) 134.3(3)°) and O(1) and O(3) atoms in the bipyramid equatorial vertices (angle O(1)PbO(3) 82.3(3)°) (Fig. 10). Four oxygen atoms located at distances 2.845(9)–3.044(9) Å from the central atom form secondary Pb–O bonds (Table 4).



37

Two crystallographically independent Pb centers are present in the crystal structure of Pb$_2$(ino)(btc)(H$_2$O) (H$_3$btc = 1,3,5-benzenetricarboxylic acid, **38**) [83]. The Pb(1) atom has an octahedral coordination geometry and is bonded to carboxylate oxygen atoms of three btc-ligands, one carboxylate oxygen atom of the ino-ligand and two oxygen atoms of two coordinated bridging H$_2$O-molecules. According to the VSEPR model, the Pb(1) coordination polyhedron should be a ψ-trigonal bipyramid (**II**) rather than an octahedron as stated in [83] (Table 4). Unlike the Pb(1) atom, the Pb(2) atom is a distorted square-pyramid formed by three carboxylate oxygen atoms from the btc^{3-} ligands, one carboxylate oxygen atom from the ino-ligand and one N-oxide oxygen atom from the same ino-ligand. These five oxygen atoms are located at one side of the Pb(2) atom indicating the presence of the stereochemically active lone electron pair on the Pb^{2+} ion.

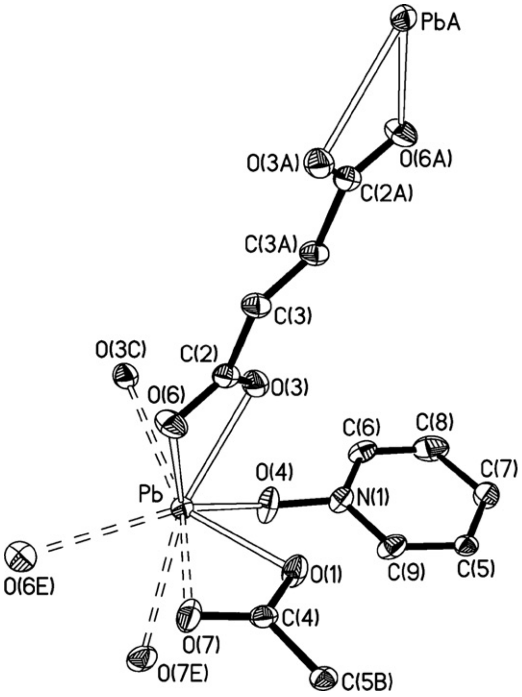
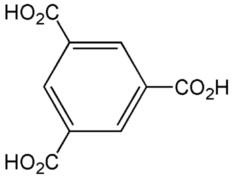
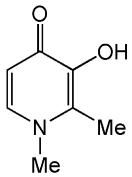


Fig. 10. ORTEP diagram of the coordination environment around the Pb(II) atom in Pb(ino)(fa)$_{0.5}$.



38

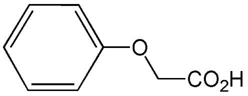
The crystal structure of Pb(hmpyr)$_2$·7H_2O (Hhmpyr = 3-hydroxy-1,2-dimethyl-4-pyridin-4(*1H*)-one, **39**) is composed of dimeric Pb_2(hmpyr)$_4$ units and lattice H_2O-molecules [84]. The coordination sphere of every Pb atom in the dimer includes five oxygen atoms. The location of oxygen atoms around the central atom suggests the presence of a LP that should be stereochemically active. The coordination geometry of the Pb atom in the structure of Pb(hmpyr)$_2$·7H_2O can be described, in accordance with the VSEPR model, as a ψ-trigonal bipyramid (**II**) (Table 4).



39

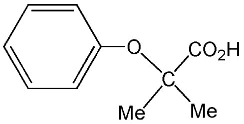
4.7. Phenoxyacetates

The crystal structures of a number of Pb(II) phenoxyacetates have been investigated. The polymeric layered structure of Pb(pa)$_2$·0.5H_2O (Hpa = phenoxyacetic acid, **40**) contains two crystallographically independent Pb atoms [85,86]. The coordination environment of the Pb(1) atom consists of eight oxygen atoms (Pb–O 2.34(2)–2.96(2) Å) forming an irregular Pb(1)O_8-polyhedron. The seven-coordinate Pb(2) atom is bound by two chelating carboxylate groups of phenoxyacetate ligands. The Pb(2) atom is also bound to an O atom of one of carboxylate groups attached to the symmetry-related Pb(2^i) atom (Pb(2^i)–O 2.73(2) Å). The coordination polyhedron of the Pb(1) (Pb(2) in [86]) atom is, taking into account the primary bonds in the range 2.34(2)–2.71(2) Å, a ψ-trigonal bipyramid (**II**) while the coordination polyhedron of the Pb(2) atom (Pb(1) in [86]) has a ψ-octahedral configuration (Table 4).



40

The crystal structure of Pb(pda)$_2$·H_2O (Hpda = phenoxydimethylacetic acid, **41**) was also studied [86]. Considering the six Pb–O distances less than 2.70 Å, the coordination environment can be described as a ψ-pentagonal bipyramid with a vacant position in the equatorial plane (**V**) (Table 4).



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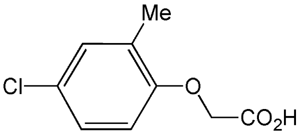
The compound Pb(mcpa)$_2$·H_2O [Hmcpa = 2-(4-chloro-2-methylphenoxy)acetic acid, **42**] has an infinite polymeric structure [87]. The Pb atoms in the structure are seven-coordinate with bonds to four O atoms from two chelate carboxylate groups, one O atom from the H_2O-molecule and two oxygen atoms from two symmetrically generated carboxylate groups of adjacent units, respectively. By using the bridging oxygen atoms, adjacent Pb atoms are united into dimeric Pb_2O_2 rings that are linked into polymeric chains in a *spiro* arrangement. Taking into account all seven O atoms surrounding the metal atom, the geometry of the Pb coordination polyhedron is described in [87] as a mixed trigonal-tetragonal antiprism (4 + 3). The geometry of the primary coordination sphere of the Pb atom in the crystal structure of Pb(mcpa)$_2$·H_2O corresponds, according to the VSEPR model, to a ψ-octahedron (**III**) (Table 4).



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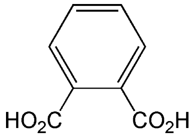
4.8. Dicarboxylates

Crystal structures of lead(II) complexes with three isomeric benzenedicarboxylic acids: *o*-phthalic acid [phthalic acid, H_2(*o*-pht), **43**], *m*-phthalic acid [isophthalic acid, H_2(*m*-pht), **44**] and *p*-phthalic acid [terephthalic acid, H_2(*p*-pht), **45**] have been investigated.



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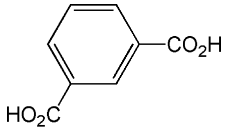

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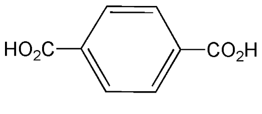

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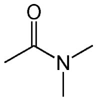
The crystal structure of Pb(*o*-pht)(H_2O) [88] comprises a two-dimensional polymer. Every phthalate anion is a tetradentate ligand binding four Pb atoms. The coordination surrounding of the Pb atom is formed by 7 oxygen atoms from three phthalate anions and the coordinated H_2O-molecule. The location of these atoms around the Pb atom suggests the presence of the stereochemically active LP in this compound. Analysis of the primary Pb–O bonds and the bond angles O–Pb–O (Table 5) enables one to represent the Pb polyhedron in the structure of Pb(*o*-pht)(H_2O), in accordance with the VSEPR model, as a ψ-trigonal bipyramid (**II**).

Unlike the crystal structure of Pb(*o*-pht)(H_2O) containing equivalent Pb atoms [88], a polymeric crystal structure of Pb(*m*-pht), [89] contains two crystallographically independent Pb atoms with CNs 6 and 7 and two crystallographically independent isophthalate ligands. The Pb(1) atom environment in the structure is formed by two chelate-bonded carboxylate groups belonging to two isophthalate ligands. Additionally, Pb(1) forms two bridging bonds with two oxygen atoms of two different ligands chelated to the Pb(2) atoms. The coordination polyhedron of the Pb(1) atom can be described, in accordance with the VSEPR model, as a ψ-pentagonal bipyramid with a vacant axial position (**IV**).

The coordination environment of the Pb(2) atom is formed by two carboxylate groups belonging to two isophthalate dianions that are chelate-coordinated to the Pb(2) atom by different carboxylate units. Besides, the Pb(2) atom forms three bridging monodentate bonds with the O atoms of chelate-bonded carboxylate groups of adjacent complexes. The coordination polyhedron of the Pb(2) atom inside the primary coordination sphere comprises a ψ-trigonal bipyramid (**II**) (Table 5).

The Pb(II) complex with terephthalate anion Pb(*p*-pht)(H_2O) [90] has the same chemical composition as the Pb(II) complex with *o*-phthalate anion; however, the crystal structures differ significantly [88]. Unlike Pb(*o*-pht)(H_2O), where both carboxylate groups of the ligand are bidentate–chelate bonded to the Pb atom, in the structure of Pb(*p*-pht)(H_2O) one of the carboxylate groups of the ligand forms a bidentate–chelate bond with the Pb atom, while another is monodentate. Both carboxylate groups also serve as bridges. The CN of the Pb atom in Pb(*p*-pht)(H_2O) is reported to be 7 [90], but according to the calculations performed with *PLATON*, the CN of the Pb atom in the structure of Pb(*p*-pht)(H_2O), just like that in the structure of Pb(*o*-pht)(H_2O) [88], is 8. Every Pb atom in the structure of Pb(*p*-pht)(H_2O) is bonded to four symmetry-related terephthalate anions: three of them are monodentate and the fourth is bidentate. Additionally, the Pb atom binds a H_2O molecule. As in the structure of Pb(*o*-pht)(H_2O), the coordination geometry of the Pb atom in the structure of Pb(*p*-pht)(H_2O) can be represented, in accordance with the VSEPR model and taking into account the primary Pb–O bonds, as a ψ-trigonal bipyramid (**II**) (Table 5).

In the crystal structure of the mixed Pb(II) terephthalate complex, Pb(*p*-pht)(dma) (dma = dimethylacetamide, **46**) the Pb atom is coordinated by five oxygen atoms from three benzenedicarboxylate ligands and the oxygen atom from the dimethylacetamide molecule [45]. Unlike the structure of Pb(*p*-pht)(H_2O), where one of the carboxylate groups of the ligand forms a bidentate–chelate bond to the Pb atom while another group is monodentate. Both carboxylate groups of the ligand in Pb(p-pht)(dma) are bidentate, chelating to the central atom. The coordination polyhedron of the Pb atom may be described as a tetragonal bipyramid with a vacant vertex (ψ-octahedron (**III**) in the VSEPR model) [45].



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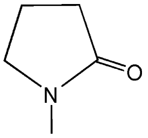
Unlike Pb(*p*-pht)(dma) which contains equivalent Pb atoms, the structure of the Pb(*p*-pht)(nmp) (nmp = 1-methylpyrrolidin-2-one, **47**) contains two crystallographically independent Pb atoms having different coordination environments [91]. The Pb(1) atoms are coordinated by five oxygen atoms: four from three carboxylate groups and one from the coordinated nmp ligand. The Pb(2) atoms are coordinated by six oxygen atoms: five of them belong to three carboxylate groups and one to the coordinated nmp. The coordination geometries of the Pb(1) and Pb(2) atoms are described as severely distorted pyramidal and severely distorted octahedral, respectively. From the VSEPR model the geometry of the Pb(1) coordination polyhedron can be described as a ψ-trigonal bipyramid (**II**), while the coordination polyhedron for the Pb(2) atom is a ψ-pentagonal bipyramid with a vacant vertex in the equatorial plane (**V**) (Table 5).



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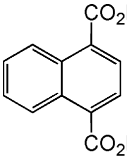
The structure of the hydroxy lead(II) terephthalate complex $Pb_2(OH)_2$(*p*-pht) is formed by ladder-type $Pb(OH)_{3/3}$ double chains, which are connected to a three-dimensional framework by terephthalate anions [92]. The seven-coordinated Pb atoms are each surrounded by three hydroxyl ions and four carboxylate O atoms from four different terephthalate anions. The coordination geometry of the Pb atom considering Pb–O bonds in the range up to 3.10 Å was described as a distorted monocapped trigonal prism. Considering only the primary Pb–O bonds (Pb–O 2.325(4)–2.567(4) Å), the Pb coordination polyhedron can be represented as a ψ-trigonal bipyramid (**II**).

The crystal structures of a number of other Pb(II) complexes with aromatic dicarboxylic acids have been investigated: Pb(napdc)(dmf) (H_2napdc = naphthalene-1,4-dicarboxylic acid, H_2ndc, **48**, dmf = *N*,*N*-dimethylformamide) [93], Pb(ndc)(dma) [45], $Pb(dthb)(dmf)_2$ (H_2dthb = 2,2-dithiodibenzoic acid, **49**) [94], $Pb_6(dpa)_4O_2$ (H_2dpa = 1,1′-biphenyl-2,2′-dicarboxylic acid, **50**) [95]. The structure of Pb(napdc)(dmf), a 3D coordination polymer, contains seven-coordinated Pb atoms, each bonded to the O atoms of carboxylate groups of five $napdc^{2-}$ ligands and the O atom of the coordinated dmf molecule. The authors suggested that the Pb coordination polyhedron is a tetragonal bipyramid with the carboxylate group and the dmf-molecule at its axial vertices. The coordination polyhedron according to the VSEPR model and taking into account only the primary Pb–O bonds lengths (2.349(5)–2.688(4) Å), is expected to be ψ-pentagonal bipyramid with a vacant vertex in the equatorial plane (**V**).

Table 5
Stereochemistry of Pb(II) complexes with aromatic polycarboxylate ligands.

Compound	Overall CN	Shape of the polyhedron	Pb–O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial and equatorial)	Equatorial		
Pb(II) aromatic di- and polycarboxylates								
Pb(*o*-pht)(H_2O)	8 (4 + E) + 4	ψ-TBP **II**	2.574(6) O(2) 2.616(7) O(5)	2.340(7) O(3^{i}) 2.474(6) O(1^{ii})	147.3(2)	73.4(2)	2.706(6) O(1) 2.745(7) O(4^{i}) 2.809(7) O(2^{iii}) 3.032(6) O(4^{iv})	[88], YIGZAQ
Pb(*m*-pht)								[89], WENRIR
Pb(1)	6 (6 + E)	ψ-PBP$_{ax}$ **IV**	2.365(6) O(6)	2.393(7) O(7^{i}) 2.565(6) O(8^{i}) 2.597(6) O(4^{ii}) 2.614(6) O(3^{iii}) 2.656(6) O(5)	80.8(2) 79.3(2) 85.1(2) 77.1(2) 52.1(2)	52.1(2) 68.4(2) 69.4(2) 78.5(2) 83.6(2) $\Sigma = 352.0$		
Pb(2)	7 (4 + E) + 3	ψ-TBP **II**	2.604(6) O(5) 2.639(6) O(8^{iv})	2.323(7) O(1) 2.553(6) O(3^{ii})	165.2(2)	80.7(2)	2.741(7) O(4^{ii}) 2.756(7) O(2) 2.842(7) O(2^{iv})	
Pb(*p*-pht)(H_2O)	8 (4 + E) + 4	ψ-TBP **II**	2.563(4) O(5) 2.650(4) O(4^{i})	2.434(4) O(3^{i}) 2.492(3) O(1)	118.47(11)	83.53(12)	2.731(4) O(1^{ii}) 2.751(4) O(3^{iii}) 2.759(4) O(5^{ii}) 2.882(4) O(4^{ii})	[90], INIZAG
Pb(*p*-pht)(dma)	8 (5 + E) + 3	ψ-OC **III**	2.439(4) O(3)	2.452(4) O(1) 2.498(4) O(4) 2.506(3) O(2A) 2.699(5) O(5)	70.66(13) 53.03(12) 74.63(12) 80.15(15)	82.29(15) 82.38(13) 82.53(13) 87.03(13) $\Sigma = 334.23$	2.786(3) O(2) 3.020(4) O(3A) 3.055(4) O(1A)	[45], YICREI
Pb(*p*-pht)(nmp)								[91], XILBAW
Pb(1)	8 (4 + E) + 4	ψ-TBP **II**	2.461(4) O(6) 2.486(4) O(3^{i})	2.381(4) O(2) 2.410(4) O(5)	125.39(13)	72.48(14)	2.633(5) O(9) 2.880(4) O(1) 3.119(4) O(4^{ii}) 3.185(4) O(7)	
Pb(2)	8 (6 + E) + 2	ψ-PBP$_{eq}$ **V**	2.495(4) O(4^{ii}) 2.657(5) O(10)	2.434(4) O(7) 2.456(4) O(8) 2.552(4) O(1) 2.660(4) O(3^{ii})	159.02(16)	53.45(13) 72.48(14) 78.39(13) 136.11(13) $\Sigma = 340.33$	2.971(4) O(2^{i}) 3.276(4) O(5^{i})	
$Pb_2(OH)_2$(*p*-pht)	7 (4 + E) + 3	ψ-TBP **II**	2.483(4) O(1^{ii}) 2.567(4) O(12)	2.325(4) O(1) 2.415(4) O(1^{i})	150.12(15)	73.97(15)	2.746(4) O(12^{i}) 2.982(5) O(11) 3.072(5) O(11^{i})	[92], YAPQUC
Pb(napdc)(dmf)	8 (6 + E) + 2	ψ-PBP$_{eq}$ **V**	2.349(5) O(2)$^{\#1}$ 2.688(5) O(1)	2.537(4) O(3)$^{\#2}$ 2.637(4) O(4)$^{\#3}$ 2.670(7) O(5) 2.689(4) O(4)$^{\#2}$	150.4(2)	50.4(1) 70.0(1) 91.7(2) 144.9(2) $\Sigma = 357.0$	2.713(4) O(3)$^{\#4}$ 3.262(5) O(1)$^{\#3}$	[93], LEKGOY
Pb(ndc)(dma)	8 (6 + E) + 2	ψ-PBP$_{eq}$ **V**	2.379(6) O(1) 2.696(5) O(2f)	2.504(7) O(5) 2.543(4) O(4g) 2.701(4) O(3c) 2.702(4) O(4a)	154.49(18)	73.70(13) 84.3(2) 86.9(2) 114.78(13) $\Sigma = 359.7$	2.769(4) O(3g) 3.270(6) O(2)	[45], YICRAE

Pb(dthb)(dmf)$_2$	7 (4 + E) + 3	ψ-TBP **II**	2.514(3) O(4b) 2.609(4) O(1)	2.444(4) O(3b) 2.459(5) O(2)	119.70(12)	87.09(14)	2.701(5) O(5) 2.846(5) O(6) 2.872(5) O(6c)	[94]
Pb$_6$(dpa)$_4$(O$_2$)								[95], XERSET
Pb(1)	6 (4 + E) + 2	ψ-TBP **II**	2.409(8) O(7)$^{\#1}$ 2.557(8) O(9)	2.281(7) O(10)$^{\#1}$ 2.393(7) O(10)	149.5(3) 136.5(3)	73.8(3) 78.9(2)	2.816(9) O(4)$^{\#2}$ 2.832(8) O(1)	
Pb(2)	6 (4 + E) + 2	ψ-TBP **II**	2.511(8) O(11) 2.616(8) O(3)	2.248(7) O(10) 2.447(8) O(2)	138.4(3)	94.4(3)	2.741(9) O(7)$^{\#1}$ 2.864(8) O(4)$^{\#3}$	
Pb(3)	6 (4 + E) + 2	ψ-TBP **II**	2.377(9) O(4) 2.609(9) O(9)	2.270(7) O(10) 2.411(9) O(8)			2.801(9) O(4)$^{\#3}$ 3.052(10) O(8d)	
Pb$_3$(btc)$_2$·H$_2$O								[96], XADLIX
Pb(1)	8 (4 + E) + 4	ψ-TBP **II**	2.519(6) O(2b) 2.531(6) O(4)	2.382(6) O(5a) 2.497(6) O(3)	122.6(2)	79.9(2)	2.704(6) O(3c) 2.888(6) O()7b) 2.910(6) O(1b) 2.974(7) O(13d)	
Pb(2)	7 (6 + E) + 1	ψ-PBP$_{eq}$ **V**	2.570(6) O(7) 2.711(6) O(12)	2.429(6) O(1) 2.550(6) O(8) 2.579(6) O(6e) 2.667(6) O(11f)	154.4(2)	67.1(2) 75.1(2) 76.0(2) 125.3(2) Σ = 343.5	2.902(6) O(9g)	
Pb(3)	7 (4 + E) + 3	ψ-TBP **II**	2.433(6) O(10) 2.661(6) O(8h)	2.412(6) O(9) 2.450(6) O(11j)	122.1(2)	97.1(2)	2.739(6) O(6i) 2.805(7) O(13k) 3.072(6) O(4h)	
Pb$_2$(Hbtc)$_2$(H$_2$O)$_4$·H$_2$O	9 (6 + E) + 3	ψ-PBP$_{eq}$ **V**	2.652(9) O(7) 2.745(6) O(1^{ii})	2.562(6) O(4^{i}) 2.617(6) O(1) 2.641(6) O(2) 2.702(6) O(3^{i})	139.6(3)	48.95(19) 49.5(2) 73.33(19) 150.9(2) Σ = 322.65	2.782(6) O(5^{iii}) 2.815(6) O(2^{iv}) 2.875(8) O(8)	[97], CERPOF
Pb$_2$(Hbtc)$_2$(H$_2$O)$_4$·H$_2$O	9 (6 + E) + 3	ψ-PBP$_{eq}$ **V**	2.658(4) O(1W) 2.752(3) O(5B)	2.568(3) O(2) 2.618(3) O(5A) 2.646(3) O(6A) 2.715(3) O(1)	139.60(11)	49.11(9) 49.49(9) 73.04(10) 150.91(10) Σ = 322.55	2.788(3) O(3A) 2.818(3) O(6B) 2.884(3) O(2W)	[98]
Pb$_2$(bttc)								[99]
Pb(1)	5 (5 + E)	ψ-OC **III**	2.382(6) O(8)$^{\#1}$	2.436(6) O(3)$^{\#2}$ 2.513(6) O(1) 2.604(6) O(6)$^{\#3}$ 2.609(6) O(7)$^{\#1}$	75.8(2) 81.4(2) 69.5(2) 52.09(19)	72.4(2) 79.5(2) 87.5(2) 93.7(2) Σ = 333.1		
Pb(2)	6 (6 + E)	ψ-PBP$_{eq}$ **V**	2.539(7) O(4)$^{\#2}$ 2.551(6) O(6)$^{\#4}$	2.379(6) O(2) 2.669(6) O(1) 2.742(6) O(5)$^{\#4}$ 2.760(6) O(5)$^{\#5}$	136.4(2)	51.18(19) 65.95(19) 67.86(18) 175.15(11) Σ = 360.14		



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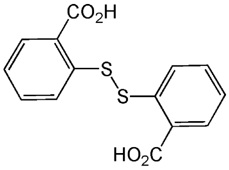

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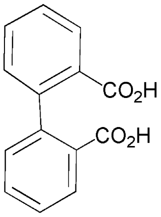


50

The mixed complex Pb(ndc)(dma) is isostructural to the compound Pb(napdc)(dmf) described above [45]. Similar to Pb(napdc)(dmf), the Pb coordination environment is a ψ-pentagonal bipyramid with a vacant vertex in the equatorial plane (**V**). As primary and as secondary bonds lengths have close values for both structures. Slight differences are observed only for the values of angles around the Pb atom in the bipyramid's equatorial planes, though their sum is close for both structures (Table 5).

In the structure of Pb(dthb)(dmf)$_2$ the Pb atom is coordinated by seven oxygen atoms: four atoms from two carboxylate groups of two dithiodibenzoate anions and three atoms from three dmf-ligands [94]. The carboxylate groups are bidentate–chelates. One of the dmf-ligands is monodentate while another one is bridging between two Pb atoms to form centrosymmetrical dimers. In accordance with the VSEPR model, the Pb coordination polyhedron can be represented as a ψ-trigonal bipyramid (**II**) (Table 5).

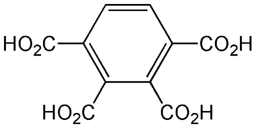
The one-dimensional chain crystal structure of Pb(II) with 1,1′-biphenyl-2,2′-dicarboxylate, $Pb_6(dpa)_4(O_2)$ [95] is built from Pb_6O_{18} units each bonded by four different dpa^{2-} anions. The asymmetric unit of the crystal structure contains three crystallographically independent Pb atoms. Within the Pb–O bond length range up to 2.70 Å, all three Pb atoms in the structure of $Pb_6(dpa)_4(O_2)$ have, in accordance with the VSEPR model, the configuration of a ψ-trigonal bipyramid (**II**) with a vacant vertex in the equatorial plane.

4.9. Tricarboxylates and tetracarboxylates

The Pb(II) complex with benzene-1,3,5-tricarboxylic acid (**38**), $Pb_3(btc)_2{\cdot}H_2O$, is a coordination polymer [96]. The structure contains two different btc^{3-} ions and three crystallographically independent Pb atoms. The coordination numbers of Pb(1), Pb(2) and Pb(3) considering distances to the carboxylate oxygen atoms in the range of 2.38–2.58 Å are 4, 4 and 3, respectively. These ligands are arranged in a pyramidal fashion around the central atom. The Pb polyhedra are linked to each other to form a 2D polymeric structure. The analysis of the bond valence sum showed that the Pb–O bond lengths (2.38–2.58 Å) are insufficient to describe the Pb atoms geometry in the structure. After inclusion of the O atoms having weaker bonds with the Pb atom (Pb–O bonds lengths up to 3.07 Å), the values become close to those expected for Pb^{2+}. The coordination geometry of the atoms Pb(1) and Pb(3) can be described as a trigonal bipyramid (**II**) while the Pb(2) atom geometry—as a ψ-pentagonal bipyramid with a vacant vertex in the equatorial plane (**V**) (Table 5).

The structure of $Pb_2(Hbtc)_2(H_2O)_4{\cdot}H_2O$, unlike that of $Pb_3(btc)_2{\cdot}H_2O$ [96], contains two Hbtc^{2-} anions (Table 5) [97,98]. The Pb atom is coordinated by five carboxylate oxygen atoms belonging to five different Hbtc^{2-} anions. According to [97], the Pb coordination geometry in the structure of $Pb_2(Hbtc)_2(H_2O)_4{\cdot}H_2O$ cannot be described by a simple polyhedron, while the VSEPR model predicts the Pb coordination polyhedron to be a ψ-pentagonal bipyramid with a vacant position in the equatorial plane (**V**).

In the complex $Pb_2(bttc)$ (H_4bttc = 1,2,3,4-benzenetetracarboxylic acid, **51**) [99] all four carboxylate groups are deprotonated. The crystal structure of $Pb_2(bttc)$ contains two crystallographically independent Pb atoms with different environments. Both Pb(1) and Pb(2) are coordinated by four carboxylate groups belonging to different carboxylate ligands; however, the coordination modes of the carboxylate groups to Pb(1) and Pb(2) are different. The carboxylate groups surrounding Pb(1) bind to it in four different ways: bidentate, chelating, chelating-monobridging and chelating-dibridging. Two of four carboxylate groups are bonded to the Pb(2) atom in the bidentate–chelate mode while two others are bound as monodentate ligands. The Pb(1) and Pb(2) coordination polyhedra have the geometry of a distorted trigonal bipyramid and an octahedron, respectively. Analysis of interatomic distances and angles in the structure of $Pb_2(bttc)$ has shown that the LPs of Pb(1) and Pb(2) are stereochemically active. According to the VSEPR model, the geometry of Pb(1) coordination polyhedron can be described as a distorted ψ-octahedron (**III**), while the coordination polyhedron of the Pb(2) atom is a distorted ψ-pentagonal bipyramid with the vacant vertex in the equatorial plane (**V**) (Table 5).



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5. Lead(II) oxobenzene complexes

5.1. Nitrophenolates

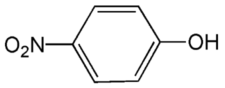
Every Pb atom in the structure of $Pb(nph)_2$ (Hnph = 4-nitrophenol, **52**) is surrounded by four O atoms from four *p*-nitrophenolate anions with formation of a distorted PbO$_4$-polyhedron which is considered by the authors as a square pyramid [100]. The Pb–O bond lengths in the polyhedron are equal to 2.333(8) × 2 and 2.514(8) × 2 Å. Pairs of nph$^-$ anions bridge adjacent Pb ions to form an intersecting double-chain structure. The Pb coordination polyhedron is a ψ-trigonal bipyramid (**II**) (Fig. 11) with apical oxygen atoms O(1B) and O(1D) (Pb–O(1B, 1D) 2.514(8) × 2 Å, angle O(1B)PbO(1D) 162.7(3)°). The equatorial plane is formed by the O(1) and O(1A) atoms (Pb–O(1, 1A) 2.333(8) × 2 Å, angle O(1)PbO(1A) 84.7(3)°) and the stereochemically active lone pair. Four O atoms located at distances 2.984(10)–3.227(12) Å from the Pb atom form secondary Pb–O bonds (Table 6).

Table 6
Stereochemistry of Pb(II) complexes with oxobenzene ligands.

Compound	OverallCN	Shape of the polyhedron	Pb-O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial and equatorial)	Equatorial		
Pb(II) nitrophenolates								
Pb(nph)$_2$	8 (4 + *E*) + 4	ψ-TBP **II**	2.514(8) O(1B) 2.514(8) O(1D)	2.333(8) O(1) 2.333(8) O(1A)	162.7(3)	84.7(3)	2.984(10) O(3G) 2.984(10) O(3E) 3.227(12) O(2E) 3.227(12) O(2G)	[100], FIRPOM
Pb(dnph)$_2$	8 (4 + *E*) + 4	ψ-TBP **II**	2.546(4) O(1B) 2.546(4) O(1C)	2.341(4) O(1) 2.341(4) O(1A)	154.41(17)	85.04(17)	2.800(6) O(2) 2.800(6) O(2A) 3.035(6) O(4D) 3.035(6) O(4E)	[101], AHUBIO
Pb(pic)$_2$·2dmso	8 (5 + *E*) + 3	ψ-OC **III**	2.327(2) O(2)	2.479(2) O(1) 2.488(2) O(21) 2.538(2) O(21^{i}) 2.623(2) O(11)	74.40(7) 79.88(6) 81.16(6) 79.16(6)	68.55(5) 75.90(6) 79.39(6) 125.43(6) Σ = 349.2	2.804(2) O(121) 2.866(2) O(221^{i}) 2.950(2) O(261)	[102], NEDVAU
Pb(styph)(H$_2$O)	9 (6 + *E*) + 3	ψ-PBP$_{eq}$ **V**	2.575(7) O(3) 2.668(5) O(21^{iii})	2.383(5) O(2^{iii}) 2.412(5) O(1^{i}) 2.556(5) O(1^{ii}) 2.704(6) O(11^{i})	110.55	63.18 78.31 87.55 113.14 Σ = 342.18	2.765(6) O(32^{ii}) 3.091(6) O(21) 3.136(6) O(22^{ii})	[103], ZZZGAS02
Pb(II) complexes with other aromatic O-donor ligands								
Pb(bzgly-*O*)$_2$(H$_2$O)$_2$ 2H$_2$O	8 (4 + *E*) + 4	ψ-TBP **II**	2.62(1) O(w1) 2.62(1) O(w1^{i})	2.46(1) O(2) 2.46(1) O(2^{i})	141.3(4)	80.1(3)	2.75(1) O(2^{ii}) 2.75(1) O(2^{iii}) 2.75(1) O(1), 2.75(1) O(1^{i})	[104], TEZMOA
Pb(fuoac)$_2$	8 (4 + *E*) + 4	ψ-TBP **II**	2.529(4) O(2^{ii}) 2.591(4) O(5)	2.360(4) O(6^{i}) 2.444(4) O(1)	146.09(15)	73.24(15)	2.689(4) O(6^{ii}) 2.804(4) O(2) 2.937(4) O(8^{ii}) 3.174(4) O(7^{ii})	[105], OCEQOD
Pb$_2$(vnl)$_2$(H$_2$O)$_2$(ClO$_4$)$_2$	8 (5 + *E*) + 3	ψ-OC **III**	2.305(8) O(1)	2.470(8) O(1A) 2.594(9) O(4) 2.613(10) O(3B) 2.631(9) O(2)	68.6(3) 81.1(3) 81.7(3) 64.2(3)	70.4(3) 77.3(3) 77.6(3) 114.5(3) Σ = 336.2	2.802(14) O(8) 3.045(17) O(5B) 3.090(15) O(6B)	[106], HETJAS
Pb(trop)$_2$	5 (4 + *E*) + 1	ψ-TBP **II**	2.375(12) O(12)	2.298(13) O(11)	124.31(49)	102.04(61)	2.889(11) O(12^{i})	[107], CIFGAA
Pb(trop)(CF$_3$SO$_3$)(H$_2$O)	7 (3 + *E*) + 4	ψ-T **I**	2.293(5) O(2) 2.338(5) O(1) 2.463(6) O(6)		68.37(17) 79.12(19) 85.10(18)		2.763(4) O(1^{ii}) 2.776(5) O(3) 2.784(6) O(4) 2.853(5) O(2^{i})	[107], CIFFIH
Pb$_3$(trop)$_4$(ClO$_4$)$_2$								[107], CIFFON
Pb(1)	8 (4 + *E*) + 4	ψ-TBP **II**	2.460(9) O(1^{i}) 2.460(9) O(1)	2.345(9) O(2^{i}) 2.345(9) O(2)	119.8(3)	95.0(3)	2.845(9) O(11^{i}) 2.845(9) O(11) 3.170(13) O(6^{ii}) 3.170(13) O(6^{iii})	
Pb(2)	7 (4 + *E*) + 3	ψ-TBP **II**	2.351(10) O(12) 2.612(9) O(2)	2.294(10) O(11) 2.433(9) O(1)	133.9(3)	71.1(3)	2.725(10) O(12^{i}) 3.026(37) O(4) 3.111(33) O(3)	

Table 6 (*Continued*)

Compound	OverallCN	Shape of the polyhedron	Pb-O bond distances in the polyhedron (Å)		Bond angles O–Pb–O (°) in the polyhedron between the atoms		Pb–O secondary bonds (Å)	Reference, REFCODE
			Axial	Equatorial	Axial (axial and equatorial)	Equatorial		
$Pb_2(trop)_2(NO_3)_2$ (MeOH)								[107], CIFFUT
Pb(1)	7 $(5+E)+2$	ψ-OC **III**	2.317(9) O(2)	2.346(9) O(1) 2.559(10) O(9) 2.597(8) O(11) 2.672(9) O(3)	67.4(3) 76.9(3) 69.8(3) 75.9(3)	66.5(3) 67.0(3) 89.1(4) 115.4(3) $\Sigma = 338.0$	2.769(8) $O(1^{i})$ 2.821(11) O(5)	
Pb(2)	9 $(3+E)+6$	ψ-T **I**	2.350(9) O(12) 2.361(8) O(11) 2.569(11) O(6)		67.3(3) 73.1(3) 91.8(3		2.758(8) O(2) 2.805(10) O(7) 2.868(10) O(4) 2.980(9) $O(12^{i})$ 3.010(9) O(3) 3.068(10) $O(4^{ii})$	
$Pb(Hnorf)(NO_3)_2$	8 $(4+E)+4$	ψ-TBP **II**	2.427(3) (O3) 2.501(2) $O(2)^{i}$	2.357(3) O(2) 2.537(3) O(4)	132.05(11)	84.23(12)	2.769(4) O(7) 2.840(4) O(5) 2.867(4) O(8) 3.005(3) $O(1)^{i}$	[108], EMUSAG



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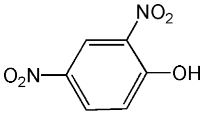
The structure of $Pb(dnph)_2$ (Hdnph = 2,4-dinitrophenol, **53**) is very similar to the structure of $Pb(nph)_2$ [101]. The compound is polymeric with every Pb atom (CN 8) surrounded by four phenoxide atoms and four oxygen atoms from the NO_2-groups. The Pb atoms form, through bridging phenoxide ions, rhombic Pb_2O_2 dimers. The dimers are bonded to each other to form polymeric chains. The coordination geometry is described in [101] as not greatly distorted from cubic and there is clearly no readily identified gap in the coordination sphere. In view of this, the Pb(II) geometry was described by the authors as *holodirected*. According to the VSEPR model, the phenoxide atoms (O(1) atoms) located at one side of the Pb atom on the twofold axis form a ψ-trigonal-bipyramidal coordination polyhedron with the Pb–O bond lengths 2.546(4) × 2 Å (axial) and 2.341(4) × 2 Å (equatorial) indicative of a *hemidirected* geometry. The axial and equatorial angles are equal to 154.41(17)° and 85.04(17)°, respectively (Table 6).



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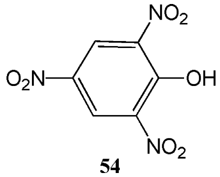
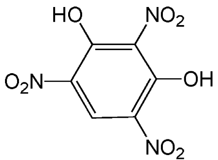
The structure of dmso solvate $Pb(pic)_2 \cdot 2dmso$ (Hpic = picric acid, **54**) is built from centrosymmetrical dimers $[Pb_2(pic)_4(dmso)_4]$ [102]. Both Pb atoms in the dimer are bonded by phenoxide groups of two picrate ligands with formation of a planar, dimeric Pb_2O_2 core. The Pb–O bond lengths in the dimer are asymmetrical: 2.488(2) and 2.538(2) Å. According to the VSEPR model, the geometry of the Pb atom primary coordination sphere in $Pb(pic)_2 \cdot 2dmso$ should be a ψ-octahedron (**III**) (Table 6).



54

The structure of $Pb(styph)(H_2O)$ [103] [H_2styph = 2,4,6-trinitro-1,3-benzenediol (styphnic acid), **55**] shows a substantial similarity with the structure of $Pb(pic)_2 \cdot 2dmso$ [102]. In both structures two Pb atoms form, through phenoxide atoms O(1) from two different anions, dimeric units with asymmetric Pb–O bonds lengths (Pb–O 2.412(5) and 2.556(5) Å, respectively). The coordination polyhedron in $Pb(styph)(H_2O)$ should have a ψ-pentagonal bipyramidal shape with a vacant equatorial vertex (Table 6).



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5.2. Lead(II) complexes with other aromatic O-donor ligands

In the structure of $Pb(bzgly\text{-}O)_2(H_2O)_2 \cdot 2H_2O$ (Hbzgly = *N*-benzoylglycine, **56**) the Pb atom is located on a twofold axis [104].

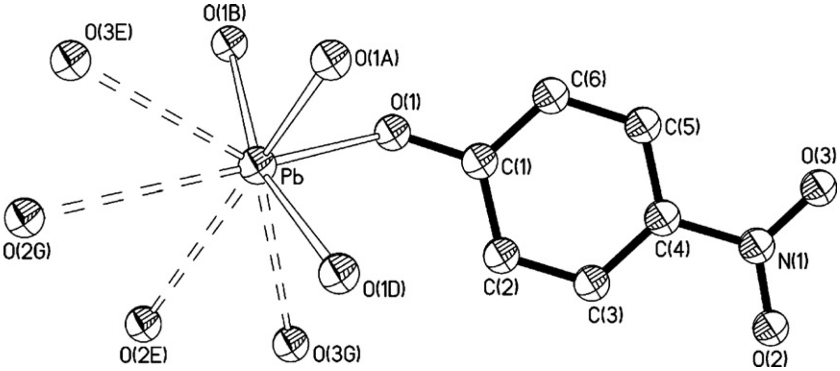
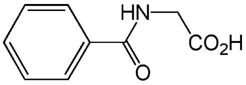


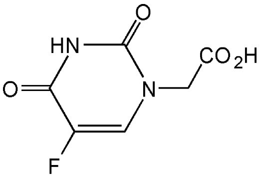
Fig. 11. ORTEP drawing of the coordination environment around the Pb(II) atom in Pb(nph)$_2$. (*) Figures 1–10 and this figure were re-created from the original CIF-files using SHELXTL (Bruker, 2000) [110]. In selected figures the hydrogen atoms were omitted.

The asymmetric unit contains one benzoylglycine ligand that is asymmetrically chelated to one Pb atom through the oxygen atoms of the carboxylate group as well as to a symmetry-related Pb atom through an oxygen atom of the same carboxylate group. Each Pb atom is also coordinated by two H_2O-molecules. The authors of [104] could not unambiguously determine the structure of the Pb coordination polyhedron in this compound or the direction of the stereochemically active LP. The coordination geometry of the Pb atom should be, according to the VSEPR model, a ψ-trigonal bipyramid (**II**) (Table 6).



56

The polymeric structure of Pb(fuoac)$_2$ (Hfuoac = 5-fluorouracil-1-acetic acid, **57**) has two different types of bonds between the ligand and Pb atom [105]. Two oxygen atoms of this carboxylate group asymmetrically chelate one Pb atom (Pb–O(1) 2.444(4) and Pb–O(2) 2.804(4) Å), with O(2) also bound to a symmetry-related Pb. The carboxylate group of the second ligand exhibits only the bridging function. The authors mention that the distribution of the O atoms around the Pb atom suggests a hole in the coordination geometry of the central atom occupied by the assumed stereochemically active LP on Pb^{2+}. Analysis of the interatomic distances Pb–O and the bond angles OPbO enables one to describe the Pb coordination polyhedron as a ψ-trigonal bipyramid (**II**) (Table 6).



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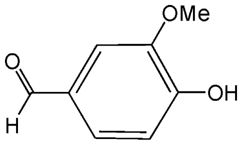
The structure of Pb$_2$(vnl)$_2$(H$_2$O)$_2$(ClO$_4$)$_2$ (Hvnl = 3-methoxyl-4-hydroxyl-phenaldehyde (vanillin), **58**) is formed by complex [Pb$_2$(vnl)$_2$(H$_2$O)$_2$]$^{2+}$ cations and ClO$_4$$^-$ anions [106]. Both Pb atoms in the structure are identically coordinated by five oxygen atoms (Pb–O 2.305(8)–2.631(9) Å) forming a polyhedron of an irregular shape. According to the VSEPR model, the Pb(II) coordination polyhedron should have a ψ-octahedral configuration (Table 6).



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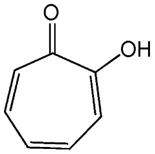
Tropolone (2-hydroxy-2,4,6-cycloheptatriene-1-one, **59**) is a seven-membered non-benzenoid aromatic compound containing two functional groups—carbonyl and hydroxyl. The synthesis and structures of the tropolonate complexes Pb(trop)$_2$, Pb(trop)(CF$_3$SO$_3$)(H$_2$O), Pb$_3$(trop)$_4$(ClO$_4$)$_2$ and Pb$_2$(trop)$_2$(NO$_3$)$_2$(MeOH) have been described [107].



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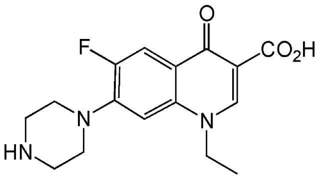
The crystal structure of Pb(trop)$_2$ contains dimeric groups [Pb(trop)$_2$]$_2$, in which the Pb(trop)$_2$ complexes are bonded to each other by comparatively long bridge bonds (Pb–O 2.889(11) Å). One of the tropolonato ligands chelates to the Pb atom, while another one is bidentate–chelate-bridge bonded. The coordination polyhedron of the Pb atom, formed by four chelating O atoms and a stereochemically active LP, is described as a distorted square pyramid with the LP located in the pyramid apical vertex, but this does not comply with the VSEPR model. According to the VSEPR model, the Pb atom geometry in the structure of Pb(trop)$_2$ should correspond to a trigonal pyramid (**II**) with a vacant vertex in the equatorial plane (Table 6).

The unit cell of the crystal structure of Pb(trop)(CF$_3$SO$_3$)(H$_2$O) contains a dimeric group [Pb(trop)(CF$_3$SO$_3$)(H$_2$O)]$_2$ [107]. Unlike the crystal structure of Pb(trop)$_2$, where the dimeric groups are isolated, in Pb(trop)(CF$_3$SO$_3$)(H$_2$O) they are weakly bonded into polymeric chains. The Pb coordination polyhedron is described as a grossly distorted square antiprism with one vertex occupied by the lone electron pair. According to the VSEPR model, the Pb polyhedron should be a ψ-tetrahedron (**I**) formed by three oxygen atoms with short Pb–O bonds (Table 6).

The compound Pb$_3$(trop)$_4$(ClO$_4$)$_2$ has a polymeric chain structure formed by chainlike integration of the fragments {Pb$_3$(trop)$_4$(ClO$_4$)$_2$} with two types of Pb atoms [107]. The Pb(1) and Pb(2) atoms have the same ψ-trigonal-bipyramidal geometry (Table 6).

The structure of $Pb_2(trop)_2(NO_3)_2(MeOH)$ is similar to the polymeric structure of $Pb_3(trop)_4(ClO_4)_2$ and contains two crystallographically independent Pb atoms with CN 7 [107]. According to the VSEPR model, the Pb(1) coordination polyhedron in $Pb_2(trop)_2(NO_3)_2(MeOH)$ comprises a ψ-octahedron (**III**). The Pb(2) coordination polyhedron has a ψ-tetrahedral configuration (Table 6).

A centrosymmetrical molecular structure of $Pb(Hnorf)(NO_3)_2$ [Hnorf = 1-ethyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid (norflaxin), **60**] is formed from dimeric groups $[Pb_2(Hnorf)_2(NO_3)_4]$ united by monodentate bridging oxygen atoms from two norflaxin ligands [108]. The Pb coordination polyhedron is described as a distorted bipyramid. According to the VSEPR model, the coordination polyhedron of the Pb atom in the $Pb(Hnorf)(NO_3)_2$ structure can be described as a ψ-trigonal bipyramid (**II**) (Table 6).



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6. DFT investigations

The DFT calculations of fragments of the crystal structures of a large group of Pb(II) complexes with O-donor ligands and the Pb(II) atom CN from 3 up to 10 was performed. The geometric parameters required for structural calculations were taken from cif-files of respective crystal structures (CCDC, ConQuest version 1.9). The obtained results of calculations of the Pb(II) atom LP composition in the complexes under study with the Pb(II) atom CN equal to $(3+E)+m-(6+E)+m$ are presented in Table 7.

Fig. 12a shows the dependence of the calculated contribution of 6p-orbitals into the Pb(II) atom LP on the CN of the studied compounds with taking into account only primary Pb–O bonds in respective coordination polyhedra. The highest contribution of 6p-orbitals into the Pb(II) atom LP and, therefore, maximum LP stereoactivity were observed for the Pb(II) compounds with the CN equal to $4+E$. With increasing CN of the Pb(II) atom, the 6p-orbital contribution into the LP decreases resulting in a corresponding decrease of stereoactivity of the Pb(II) atom lone electron pair. The elevated values of the 6p-orbital contribution to the Pb(II) atom LP for compounds with the Pb CN equal to $4+E$, as compared to those for compounds with the CN of $3+E$, probably result from the fact that most of the compounds under study contain bidentate

Table 7
DFT studies of Pb(II) atoms in lead(II) complexes with O-donor ligands.

No.	CN	Lone pair NBO on Pb(II)	No.	CN	Lone pair NBO on Pb(II)
CN $(3+E)+m$					
XLVI[a] Pb(1)	3	s(96.17%)p0.04(3.83%)	LXIII	3	s(97.02%)p0.03(2.98%)
	6	s(98.70%)p0.01(1.30%)		8	s(99.01%)p0.01(0.99%)
Pb(2)	3	s(95.83%)p0.04(4.17%)			
	8	s(98.65%)p0.01(1.35%)			
XCVII	3	s(95.79%)p0.04(4.21%)	IV	3	s(95.78%)p0.04(4.22%)
Pb(2)	9	s(98.88%)p0.01(1.12%)		10	s(98.60%)p0.01(1.40%)
XII	3	s(97.03%)p0.03(2.97%)			
	10	s(98.85%)p0.01(1.15%)			
CN $(4+E)+m$					
XXII	4	s(93.42%)p0.07(6.58%)	XXVII	4	s(93.75%)p0.07(6.25%)
				5	s(94.70%)p0.06(5.30%)
XXV	4	s(94.97%)p0.05(5.03%)	XXVI	4	s(95.50%)p0.05(4.50%)
	6	s(98.08%)p0.02(1.92%)		6	s(98.24%)p0.02(1.76%)
XXVIII	4	s(94.13%)p0.06(5.87%)	LX	4	s(95.09%)p0.05(4.91%)
	6	s(96.74%)p0.03(3.26%)		6	s(96.95%)p0.03(3.05%)
LXVIII	4	s(93.89%)p0.07(6.11%)	L	4	s(95.87%)p0.04(4.13%)
	6	s(95.84%)p0.04(4.16%)		7	s(97.31%)p0.03(2.69%)
XXIV	4	s(93.64%)p0.07(6.36%)	LXXXI	4	s(95.95%)p0.04(4.05%)
	7	s(97.32%)p0.03(2.68%)		7	s(96.85%)p0.03(3.15%)
VII	4	s(96.20%)p0.04(3.80%)	XXIX	4	s(96.55%)p0.04(3.45%)
	8	s(97.99%)p0.02(2.01%)		8	s(98.87%)p0.01(1.13%)
XXX	4	s(96.31%)p0.04(3.69%)	LXXXVII	4	s(95.23%)p0.05(4.77%)
	8	s(98.75%)p0.01(1.25%)		8	s(98.60%)p0.01(1.40%)
XXXIV	4	s(96.20%)p0.04(3.80%)	XXI	4	s(96.25%)p0.04(3.75%)
	8	s(99.85%)p0.00(0.15%)		9	s(98.98%)p0.01(1.02%)
CN $(5+E)+m$					
XXXVII	5	s(96.79%)p0.03(3.21%)	XLIX	5	s(95.21%)p0.05(4.79%)
				6	s(97.43%)p0.03(2.57%)
XLVII	5	s(97.37%)p0.03(2.63%)	LXXII	5	s(96.79%)p0.03(3.21%)
	7	s(99.09%)p0.01(0.91%)		7	s(98.42%)p0.02(1.58%)
LXXVI	5	s(95.88%)p0.04(4.12%)	LI	5	s(96.40%)p0.04(3.60%)
	8	s(97.39%)p0.03(2.61%)		8	s(97.48%)p0.02(2.22%)
III	5	s(97.01%)p0.03(2.99%)			
	9	s(98.50%)p0.02(1.50%)			
CN $(6+E)+m$					
VI	6	s(96.83%)p 0.03(3.17%)	LXXIX	6	s(97.75%)p0.02(2.25%)
				8	s(99.07%)p0.01(0.93%)
XLVIII	6	s(98.10%)p0.02(1.90%)	LVI	6	s(96.54%)p0.04(3.46%)
	9	s(99.92%)p0.00(0.08%)		9	s(99.26%)p0.01(0.74%)
LXXXV	6	s(97.13%)p0.03(2.87%)	XC	6	s(96.88%)p0.03(3.12%)
	9	s(99.79%)p0.00(0.21%)		9	s(98.31%)p0.02(1.69%)

[a] Number of the compound from Table 1.

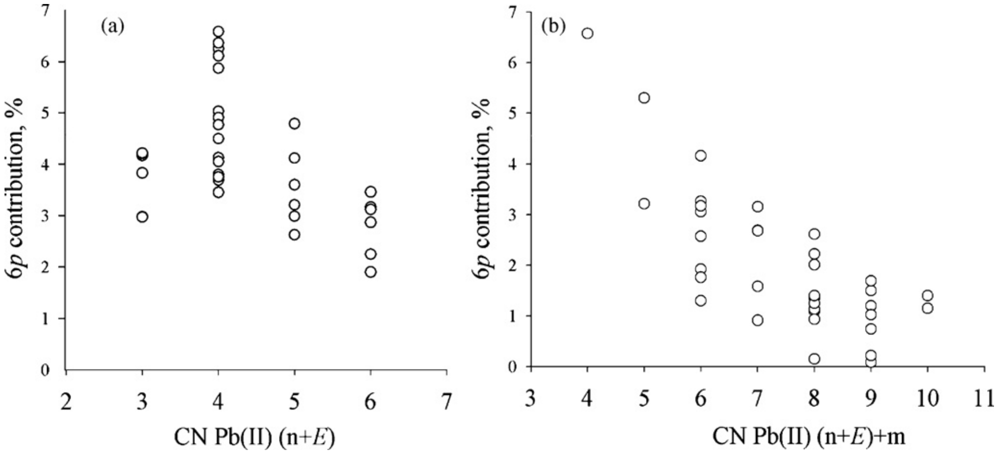

Fig. 12. Dependence of the 6p-orbital contribution into the Pb(II) atom LP on CN: (a) *n*: number of primary Pb–O bonds; (b) *n* + *m*: overall number of Pb–O bonds in polyhedron.

ligands bonded to the Pb(II) atom. This tends to preclude structures with the Pb atom having CN 3 + *E* for this family of O-donor ligands.

Fig. 12b shows the dependences of the calculated contribution of 6p-orbitals to the Pb(II) atom LP including both primary and secondary Pb–O bonds in the polyhedron. As expected, maximum LP stereoactivity is observed in the compound with the Pb atom CN equal to 4 + *E*, in which secondary Pb–O bonds are absent. With an increase of the overall CN, the LP stereoactivity gradually decreases and becomes comparatively low in compounds with larger CN values.

The LP population scattering for the same Pb(II) atom CN observed in the compounds under study is explained by different character of Pb–O chemical bonds in these compounds. The composition of the Pb(II) atom lone electron pair in the compounds is determined mainly by primary Pb–O bonds having a significant covalent character. Secondary bonds formed by the Pb atom with O atoms from adjacent polyhedra, including those located in adjacent chains or layers, are mainly of ionic character and, as a rule, reduce the population of the 6p-polarization contribution into the Pb(II) atom LP. The degree of the LP population reduction depends on properties of ligands forming adjacent polyhedra (ligand residual charge, size and location in the crystal lattice).

The results of the performed quantum chemistry studies of Pb–O complexes with O-donor atom ligands will be presented in a separate paper that is now under preparation for submission [111].

7. Conclusions

There are a large number of Pb(II) complexes with O-donor atoms ligands. The large Pb^{2+} ionic radius (1.19 Å [29]) facilitates the formation of compounds with CNs of the central atom ranging from 2 up to 12 [15]. The common feature of the crystal structures of Pb(II) complexes with O-donor atom ligands and the stereochemically active lone pair of electrons is the presence of two ranges of Pb–O bond lengths in these complexes, the so-called primary and secondary bonds. The primary bonds have a large share of covalent character (donor–acceptor) while the secondary bonds are to a great extent ionic, in most cases they are bridging and serve to unite complexes into chains, layers or three-dimensional networks.

Based on the presence of two Pb–O bond length ranges in the structures of Pb(II) complexes, the CN of the Pb atom in these complexes can be divided into two components: the CN of the Pb atom of the first coordination sphere, taking into account the stereochemically active lone pair of electrons (*n* + *E*) (*n*: the number of Pb–O primary bonds), and the number of secondary bonds (*m*). There are no data on structures of Pb(II) complexes with O-donor ligands and the stereochemically active lone pair containing only two Pb–O primary bonds (CN (2 + *E*) + *m*). Among the 98 crystal structures of Pb(II) complexes with O-donor ligands investigated in this work, only the structures of 10 compounds (12 types of Pb atoms) contain the Pb(II) atom with the CN (3 + *E*) + *m* and the ψ-tetrahedral coordination geometry (Table 8). The lengths of the primary Pb–O bonds in Pb(II) complexes with CN (3 + *E*) + *m* fall into the range 2.25–2.53 Å with the average value of 2.40 Å. The values of the bond angles O–Pb–O vary in the range 68.37–88.88° (Tables 2-6), much less than the value of the bond angle in an ideal tetrahedron (109.5°), confirming a ψ-tetrahedral coordination geometry of the Pb(II) atom in these compounds.

Structures of Pb(II) complexes where the Pb atom has CN (4 + *E*) + *m* should have a ψ-trigonal-bipyramidal coordination geometry according to the VSEPR model. Among the studied crystal structures, complexes with O-donor ligands and CN (4 + *E*) + *m* are highly represented (54 structures) (Table 9). Due to the effect of the stereochemically active lone pair, the axial lengths $Pb–O_{ax}$ in the ψ-trigonal bipyramidal coordination polyhedra of Pb atoms are larger than the equatorial bond lengths while the values of the axial and equatorial angles become less than 180° and 120° as expected for a regular trigonal bipyramid. As seen from Tables 2–6, the structural parameters of the Pb atoms with CN (4 + *E*) + *m* are in full agreement with the VSEPR model for the ψ-trigonal-bipyramidal coordination geometry.

The Pb(II) complexes with the stereochemically active lone pair of electrons and the CN of Pb atom (5 + *E*) + *m* have a ψ-octahedral coordination geometry with the LP in one of the polyhedron's axial positions (Table 10). According to the VSEPR model, the $Pb–O_{ax}$ bond of the ψ-octahedron (**III**) located in the *trans*-position in regard to the LP is shorter as compared to the $Pb–O_{eq}$ bonds in the polyhedron equatorial plane. Due to repulsions between the lone pair and the bonding electron pairs in AX_5E complexes, the bond angles O_{ax}-Pb-O_{eq} in the ψ-octahedron polyhedra have values less than 90°. In the 20 analyzed structures of Pb(II) complexes with the Pb atom having CN (5 + *E*) + *m*, the geometrical parameters of the Pb atoms coordination polyhedra are in full agreement with the ψ-octahedral coordination geometry (Tables 2–6). The lengths of the axial bonds $Pb–O_{ax}$ falling in the range 2.285–2.484 Å are significantly shorter than the equatorial bond lengths $Pb–O_{eq}$ (2.345-2.726 Å) while the angles between the axial and equatorial oxygen atoms $O_{ax}–Pb–O_{eq}$ vary within the range 51.3–89.5°. The sum of bond angles in the equatorial plane around the Pb atom in ψ-octahedral coordination polyhedra is within the range 327.3–357.6° (Tables 2–6).

Table 8
Lead(II) complexes with O-donor ligands and ψ-tetrahedral coordination geometry (CN Pb(II) atoms $(3+E)+m$).

Compound	Overall CN	Reference, REFCODE	Compound	Overall CN	Reference, REFCODE
$Pb(dmso)_3(ClO_4)_2$ Pb(1)[a] Pb(2)	$6\,(3+E)+3$, $8\,(3+E)+5$	[68], LAMJAK	$\{Pb(ino)_2\}_2 \cdot 7H_2O$	$8\,(3+E)+5$	[82], CEZZEN
$Pb_4(odac)_3(NO_3)_2 \cdot H_2O$ Pb(1) Pb(2)	$7\,(3+E)+4$, $7\,(3+E)+4$	[39], LIVKEG	$Pb(O_2CH)_2$	$8\,(3+E)+5$	[30], BIYLAW
$Pb_3(caeph)_2$ Pb(1) Pb(3)	$6\,(3+E)+3$, $8\,(3+E)+5$	[65], DINDUZ	$Pb_2(trop)_2(NO_3)_2(MeOH)$ Pb(2)	$9\,(3+E)+6$	[107], CIFFUT
$Pb_3(caeph)_2$ Pb(1) Pb(3)	$6\,(3+E)+3$, $8\,(3+E)+5$	[66], DINDUZ01	$Pb(ac)_2(18\text{-crown-}6) \cdot 3H_2O$	$10\,(3+E)+7$	[33], LAPPEX
$Pb(trop)(CF_3SO_3)(H_2O)$	$7\,(3+E)+4$	[107], CIFFIH	$Pb(Hval)_2(NO_3)_2(H_2O)_2$	$10\,(3+E)+7$	[41], ESAPET

[a] For Pb(II) complexes with various numbers of central atoms this and subsequent tables contain data on Pb atoms with the same geometry.

Table 9
Lead(II) complexes with O-donor ligands and ψ-trigonal bipyramidal coordination geometry (CN Pb(II) $(4+E)+m$).

Compound	Overall CN	Reference, REFCODE	Compound	Overall CN	Reference, REFCODE
$Pb(tmhd)_2$	$4\,(4+E)$	[49], RIMHAW01	$Pb_6(dpa)_4(O_2)$ Pb(1) Pb(2) Pb(3)	$6\,(4+E)+2$ $6\,(4+E)+2$ $6\,(4+E)+2$	[95], XERSET
$Pb(tmhd)_2$	$4\,(4+E)$	[50], RIMHAW	$Pb(amb)_2$	$6\,(4+E)+2$	[81], ABZORB
$Pb(O_2P^tBu_2)_2$	$4\,(4+E)$	[60], NETCUK	$Pb_2(chdc)_2 \cdot dma$ Pb(2)	$6\,(4+E)+2$	[45], YICRIM
$Pb\{(Ph)_2PO_2\}_2$	$4\,(4+E)$	[59], DPPOPB10	$Pb(pta)_2$	$6\,(4+E)+2$	[52], YODNIO
$Pb(dbm)_2$	$5\,(4+E)+1$	[54], IVEFIY	$Pb(thfbd)_2$	$6\,(4+E)+2$	[53], WAJQON01
$Pb(trop)_2$	$5\,(4+E)+1$	[107], CIFGAA	$Pb(dmfod)_2$	$6\,(4+E)+2$	[49], YAGLAT01
$[Pb\{MeN(CH_2PO_3H)_2\}$ Pb(1) Pb(2)	$5\,(4+E)+1$ $6\,(4+E)+2$	[63], WULYOR	Pb(azel)	$7\,(4+E)+3$	[44], IPAMER
$Pb(hmpyr)_2 \cdot 7H_2O$	$6\,(4+E)+2$	[84], MALFUA	$Pb_2(OH)_2(p\text{-}pht)_2$	$7\,(4+E)+3$	[92], YAPQUC
$Pb(dthb)(dmf)_2$	$7\,(4+E)+3$	[94]	$Pb(hfa)_2(diglyme)$	$8\,(4+E)+4$	[55], ABUTEX
$Pb(Hsal)_2(H_2O)$	$7\,(4+E)+3$	[71], FUFWEI	$Pb(hfa)_2(diglyme)$	$8\,(4+E)+4$	[56], ABUTEX01
$Pb_2(H_2dhb)_4 \cdot 3H_2O$ Pb(1)	$7\,(4+E)+3$	[73], LAJDOP	$Pb(msqu)_2(H_2O)_2 \cdot H_2O$	$8\,(4+E)+4$	[57], NEFVUP
$Pb(Hnsal)_2(H_2O)$	$7\,(4+E)+3$	[75], TEJZUD	$Pb(esqu)_2(H_2O))$	$8\,(4+E)+4$	[57], NEFWAW
$Pb(m\text{-}pht)$ Pb(2)	$7\,(4+E)+3$	[89], WENRIR	$Pb(amsqu)_2(H_2O)_2$	$8\,(4+E)+4$	[58], HERDOX
$Pb(acac)_2$	$7\,(4+E)+3$	[51], WAJQAZ01	Pb(amdph)	$8\,(4+E)+4$	[62], MUHPEK
$Pb_6(dmac)_{12} \cdot 4H_2O$ Pb(1) Pb(3)	$7\,(4+E)+38\,(4+E)+4$	[37], REXBAX	$Pb(sb)(H_2O)_2(4,4\text{-}bpy)$	$8\,(4+E)+4$	[78], NEVLAC
$Pb(glyc)_2$	$8\,(4+E)+4$	[36], PASBAM	$Pb(sb)(H_2O)_2(4,4\text{-}bpy)$	$8\,(4+E)+4$	[79], NEVLAD
$Pb_3(O_2CCCl_3)_6 \cdot 3H_2O$ Pb(1)	$8\,(4+E)+4$	[40], QOZBIQ	$Pb(nb)_2(H_2O)$	$8\,(4+E)+4$	[40], QOZBOW
$Pb(ac)_2 \cdot 2Pb(piv)_2 \cdot 3Hpiv$ Pb(1) Pb(2)	$8\,(4+E)+4$ $8\,(4+E)+4$	[38], TUCPEM	$Pb(ino)_2 \cdot nH_2O$	$8\,(4+E)+4$	[82], CEZZIR
$Pb(ino)(fa)_{0.5}$	$8\,(4+E)+4$	[83], CIBQOU	$Pb(Hnorf)(NO_3)_2$	$8\,(4+E)+4$	[108], EMUSAG
$Pb_2(ino)(btc)(H_2O)$ Pb(1)	$8\,(4+E)+4$	[83], CIBQUA	$Pb_3(btc)_2\ H_2O$ Pb(1) Pb(3)	$8\,(4+E)+4$, $7\,(4+E)+3$	[96], XADLIX
$Pb(o\text{-}pht)(H_2O)$	$8\,(4+E)+4$	[88], YIGZAQ	$Pb_3(trop)_4(ClO_4)_2$ Pb(1) Pb(2)	$8\,(4+E)+4$, $7\,(4+E)+3$	[107], CIFFON
$Pb(p\text{-}pht)(H_2O)$	$8\,(4+E)+4$	[90], INIZAG	$Pb(Hasp)(NO_3)$	$9\,(4+E)+5$	[46], XARQAI
$Pb(p\text{-}pht)(nmp)$ Pb(1)	$8\,(4+E)+4$	[91], XILBAW	$Pb(Hcit) \cdot H_2O$	$9\,(4+E)+5$	[48], MAKZON
$Pb(nph)_2$	$8\,(4+E)+4$	[100], FIRPOM	$Pb_5(caeph)_2(Hcaeph)_2$ Pb(1) Pb(2)	$9\,(4+E)+5$ $7\,(4+E)+3$	[66], EXAHAM
$Pb(dnph)_2$	$8\,(4+E)+4$	[101], AHUBIO	$Pb_4(pbmp)(sip)_2(H_2O)_4 \cdot 2H_2O$ Pb(2)	$9\,(4+E)+5$	[67], CEJXIZ
$Pb(bzgly\text{-}O)_2(H_2O)_2 \cdot 2H_2O$	$8\,(4+E)+4$	[104], TEZMOA	$Pb(pa)_2 \cdot 0.5H_2O$ Pb(1)	$9\,(4+E)+5$	[85], DEBGEW
$Pb(fuoac)_2$	$8\,(4+E)+4$	[105], OCEQOD	$Pb(pa)_2 \cdot 0.5H_2O$ Pb(2)	$9\,(4+E)+5$	[86], ZOWQEH

Among the Pb(II) complexes with the Pb atom having CN $(6+E)+m$ (14 compounds, 22 types of Pb atoms, Table 11), 4 compounds have the structures with the ψ-pentagonal-bipyramidal geometry of the Pb coordination polyhedron with a vacant axial position (ψ-PBP_{ax}). As in the structures with the ψ-octahedral coordination geometry, the lengths of the axial bonds Pb–O_{ax} fall into the same range 2.35–2.45 Å. The Pb–O bonds in the basal planes of the polyhedra are longer and fall into the range 2.40–2.74 Å. The bond angles between the axial and equatorial atoms are also less than 90° while the sum of angles in the equatorial plane around the Pb atom is close to 360° (Tables 2–6).

In 10 crystal structures with Pb atom CN $(6+E)+m$ the coordination polyhedron of the central atom has a ψ-pentagonal-bipyramidal geometry with a vacant equatorial position (ψ-PBP_{eq}). The Pb–O_{ax} lengths in the polyhedra fall in the range 2.349–2.752 Å while the lengths of equatorial bonds Pb–O_{eq} have approximately the same values (2.379–2.760 Å) as in the polyhedra of the Pb atoms with the ψ-PBP_{ax} coordination geometry. The values of the axial

Table 10
Lead(II) complexes with O-donor ligands and ψ-octahedral coordination geometry (CN Pb(II) atoms $(5+E)+m$).

Compound	Overall CN	Reference, REFCODE	Compound	Overall CN	Reference, REFCODE
Pb(pcp)	$5\,(5+E)$	[61], WACKUH	$Pb(4\text{-}HOC_6H_4CO_2)(H_2O) \cdot H_2O$	$8\,(5+E)+3$	[72], AQOHPB
$Pb_2(bttc)$ Pb(1)	$5\,(5+E)$	[99]	$Pb(hca)_2(dmf) \cdot dmf$	$8\,(5+E)+3$	[74], YEXVUT
Pb(sal)	$6\,(5+E)+1$	[70], MENHET	Pb(suc) Pb(1) Pb(2)	$8\,(5+E)+3$ $8\,(5+E)+3$	[40], QOZBAI
$Pb(chdc) \cdot H_2O$	$7\,(5+E)+2$	[45], JEYZUJ	$Pb(nb)_2(H_2O)$	$8\,(5+E)+3$	[40], QOZBUC
$Pb(H_2aedp) \cdot H_2O$	$7\,(5+E)+2$	[64], KICYUR	$Pb_4(OH)_4(ino)_4 \cdot nH_2O$	$8\,(5+E)+3$	[82], CEZZOX
Pb(phca)	$7\,(5+E)+2$	[62], MUHPAG	$Pb(p\text{-}pht)(dma)$	$8\,(5+E)+3$	[45], YICREI
$Pb(dmso)_5(ClO_4)$	$7\,(5+E)+2$	[68], LAMHUC	$Pb(pic)_2 \cdot 2dmso$	$8\,(5+E)+3$	[102], NEDVAU
$Pb(H_2ssa)_2(H_2O)$	$7\,(5+E)+2$	[80], PIKCAO	$Pb_2(vnl)_2(H_2O)_2(ClO_4)_2$	$8\,(5+E)+3$	[106], HETJAS
$Pb(mcpa)_2 \cdot H_2O$	$7\,(5+E)+2$	[87], MURZOO	$Pb(ac)_2 \cdot 3H_2O$	$9\,(5+E)+4$	[31], PBACTH10
Pb(malo)	$8\,(5+E)+3$	[42], BOPZOV10	$Pb(ac)_2 \cdot 3H_2O$	$9\,(5+E)+4$	[32], PBACTH02

Table 11
Lead(II) complexes with O-donor ligands and ψ-pentagonal bipyramidal coordination geometry (CN Pb(II) atoms $(6+E)+m$).

Compound	Overall CN	Reference, REFCODE	Compound	Overall CN	Reference, REFCODE
ψ-Pentagonal bipyramidal with a vacant axial site					
$Pb(crot)_2$	6 $(6+E)$	[35], DUPKAA	$Pb(squ)(H_2O)_2{\cdot}2H_2O$	8 $(6+E)+2$	[57], NEFWEA
$Pb_2(Hglyglu)_2(ClO_4)_2{\cdot}H_2O$	8 $(6+E)+2$	[47], OHETEA	$Pb(sb)(H_2O)_2$	9 $(6+E)+3$	[77], PECZUT
ψ-Pentagonal bipyramidal with a vacant equatorial site					
$Pb(htno)_2$	7 $(6+E)+1$	[34], QILWEN	$Pb(hmsul)_2(H_2O)$	9 $(6+E)+3$	[69], PEFDAF
Pb(male)	8 $(6+E)+2$	[43], VATYUL	$Pb_2(Hbtc)_2(H_2O)_4{\cdot}H_2O$	9 $(6+\mathrm{E})+3$	[97], CERPOF
$Pb(pda)_2{\cdot}H_2O$	8 $(6+E)+2$	[86], ZOWQIL	$Pb_2(Hbtc)_2(H_2O)_4{\cdot}H_2O$	9 $(6+E)+3$	[98]
Pb(napdc)(dmf)	8 $(6+E)+2$	[93], LEKGOY	$Pb(styph)(H_2O)$	9 $(6+E)+3$	[103], ZZZGAS02
Pb(ndc)(dma)	8 $(6+E)+2$	[45], YICRAE	$Pb(dnsal)(H_2O){\cdot}0.25H_2O$	10 $(6+E)+4$	[76], JEGTIZ

bond angles O_{ax}–Pb–O_{ax} are usually in the range 140–160° and, in just two structures, have significantly lower values (110.6° and 118.7°).

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