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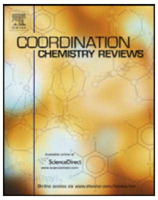

Review

Lead(II) carboxylate supramolecular compounds: Coordination modes, structures and nano-structures aspects

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Contents

Abbreviations: CSD, Cambridge Structural Database; MOFs, metal–organic frameworks; SBUs, secondary building units; BPDC, 4,4′-biphenyldicarboxylate; NDC, naphthalenedicarboxylate; bdc, benzenedicarboxylate; DHBDC, 2,5-dihydroxybenzenedicarboxylate; H_5Dtpa, diethylenetriamine-pentaacetic acid; HL, 2-chlorobenzoic acid; phen, 1,10-phenanthroline; H_2pipz, piperazinediium; pydc, pyridine dicarboxylate; OAc^-, acetate; L^2, 1,4,7-triazacyclononane; bpy, 2,2′-bipyridine; L^3, o-fluorobenzoic acid; H_2Edta^{2-}, dihydrogenethylenediaminetetraacetato; tu, thiourea; tata, melamine, 2,4,6-triamino-1,3,5-triazine; L^4, 5-nitroisophthalate; L^5, 2-bromobenzoato; $qina^-$, quinaldic acid; DMSO, dimethyl sulfoxide; H_3tpaa, α, α, α″-nitrilotri(6-methyl-2-pyridinecarboxylic acid); HINO, isonicotinic acid N-oxide; pro, prolin; H_2dpaea, N,N-bis[(6-carboxypyridin-2-yl)-methyl]ethylamine]; 3-HPYD, 3-(3-pyridyl)acrylic acid; rctt-tpcb, rctt-tetrakis(2-pyridyl)cyclobutane; L^6, H_3saltren; sdac, semicarbazidediacetic acid; DABT, N,N′-bidentatediaminobithiazole; ox, oxalate; Hpala, N-(2-pyridylmethyl)-L-alanine; H_4L^7, isopropylimino-bis(methylenephosphonic acid); $B(Im)_4$, (imidazolyl)borate; 4-carboxy-TEMPO, carboxy-2,2,6,6-tetramethylpiperidinyloxy; phe, phenylalanine; 4-Hpyc, 4-pyridinecarboxylic acid; H_2fum, fumaric acid; dpdp, dipyrido[3,2-a:2′,3′-c] phenazine; H_2dnty, 3,5-dinitrotyrosine; H_2Mal, maleic acid; H_4L^8, isopropylimino-bis-(methylenephosphonic acid); SIP, 5-sulfoisophalate; 4,4′-bipy, 4,4′-bipyridine; sb, sulfobenzoate; tpy, 2,2′:6′,2″-terpyridine; L^9, quinolin-8-olate; dmphen, dimethyl-1,10-phenanthroline; hyba, hydroxybenzoate; ends, endonorbornene-cis-5,6-dicarboxylate; L^{10}, pimelic acid; H_2adip, adipic acid; H_2oba, 4,4′-oxybis(benzoic acid); $Hssal_2{}^-$, 5-sulfosalicylate; bpe, trans-1,2-bis(4-pyridyl)ethylene; H_2glu, glutaric acid; H_2suc, succinic acid; H_2dpdc, 2,2′-diphenyldicarboxylic acid; DMF, N,N-dimethylformamide; en, ethane-1,2-diamine; 3,3′-ADB, 3,3-azodibenzoic acid; GTSC, alkylglyoxylate thiosemicarbazones; L^{11}, L-phenylalanine; DTB, 2,2′-dithiodibenzenecarboxylate; H_3BTC, 1,3,5-benzenetricarboxylic acid; H_4L^{12}, N-cyclohexylimino-bis(methylenephosphonic acid); 3-carboxy-PROXYL, carboxy-2,2,5,5-tetramethylpyrrolidinyloxy; 8-Quin, 8-hydroxychinolate; a4-ptz^-, 5-[N-acetato(4-pyridyl)] tetrazole; Bs-glu, N-benzesulfonyl-L-glutamic acid; Na_2Pra_2biim, 1,10-di(propionic acid)-2,2′-biimidazole; H_2biim, 2,2′-biimidazole; DHB, 2,6-dihydroxybenzoate; Hbpacb, 3,5-bis[(4-pyridylamino)carbonyl]benzoic acid]; tsgly-N,O, N-tosylglycinato-N,O; SEM, scanning electron microscopy; H-Norf, norfloxacin; DCP, 3,6-dicarboxylatopyridazine; leu, L-leucinato; H_3L^{13}, N-(phosphonomethyl)-N-methyl glycine; HL^{14}, 5-methyl-pyrazine-2-carboxylic acid; H_2sa, salicylic acid; L^{15}, N,N′-diacetate imidazolium; tart, tartrate; L^{16}, oxydiacetate; sbc, 2-sulfonatobenzoate; pyterpy, 4′-(4-pyridyl)-2,2′:6′,2″ terpyridine; $trenMe_6$, $N(CH_2CH_2NMe_2)_3$; L^{17}, 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane; PAA^-, phenylacetate; HMPOAc, monophenyl acetic acid; Hdpmta, [(4,6-dimethyl-2-pyrimidinyl)thio] acetic acid; ba, benzoate; H_4Hmdta, hexamethylene-1,6-diaminetetraacetic acid; bzgly-O, N-benzoylglycinato-O; $atza^-$, 5-aminotetrazole-1-acetato; Val, valine; HNic, 4-nicotinic acid; ebp, 4,4′-[(1E)-ethane-1,2-diyl]bis[pyridine]; CHDC, cyclohexanedicarboxylate; L^{18}, calix[4]diquinone bis(acid); sac, saccharinate; trz, 1,2,4-triazole; L^{19}, aminoguanidinium^{1+}; hca, trans-4-hydroxycinnamic; $[emim]_2[O_2CMe]$, 1-ethyl-3-methylimidazolium ethanoate; IAH, Indole-3-acetic acid; FCA, furancarboxylate; bpdc, 1,1′-biphenyl-2,2′-dicarboxylate; fba, fluorobenzoate; L^{20}, 2,5-dimethylbenzene-1,4-diol; L^{21}, bis[4-(1H-1,3,7,8-tetraazacyclopenta[l]phenanthren-2-yl)phenol]; endc, endonorbornene-cis-5,6-dicarboxylate; HNNO, nicotinic acid N-oxide; dpp, 4,7-diphenyl-1,10 phenanthroline; dppz, dipyrido[3,2-a:2′,3′-c]phenazine; tcpn, 2-(1H-1,3,7,8-tetraazacyclopenta[l]phen-anthren-2-yl)naphthol; L^{22}, 3,5-diaminobenzoate; L^{23}, isobutylimino-bis(methylenephosphonic acid); 3,4-TDTA, 3,4-toluenediamine-N,N,N′,N′-tetraacetate; H_3IDC, imidazole-4,5-dicarboxylic acid); Hlie, isoleucine; L^{24}, proline-N-methyl-phosphonic acid; $dnob^{3-}$, 4,6-dinitro-5-oxido-1,3-benzenedicarboxylate; tcpp, 4-(1H-1,3,7,8-tetraazacyclopenta[l]phenanthren-2-yl)phenol; H_2chdc, 1,4-cyclohexanedicarboxylic acid; 5-FUOAc, 5-fluorouracil-1-acetate; NTP, nitroterephthalate; CHZ, carbohydrazide; HPHT, benzenecarboxylate; NaH_2BTS, 5-sulfoisophthalic acid monosodium salt; H_3L^{25}, N-(phosphonomethyl)-N-methylglycine; H_4L^{26}, aminodiphosphonic acid; H_6L^{27}, aminotriphosphonic acid; H_4PMIDA, $H_2O_3PCH_2N(CH_2CO_2H)_2$; Adi, adipic acid; pdc, pyrazole-dicarboxylic acid; H_2L^{28}, 3-Pyridyl-CH_2(Me)$N(CH_2PO_3H_2)$; H_3Nta, nitrilotriacetic acid; $C_9H_{14}O_4$, azelate; GEH_2, glycylglutamic acid; L^{29}, glycolate; $[Hbet][Tf_2N]$, betainium bis(trifluoromethylsulfonyl)imide; H_2L^{30}, phenylarsonic acid; H_2ip, isophthalic acid; dma, N,N-dimethyl-Gacetamide; Fc, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$; NTA^{3+}, nitrilotriacetate; Hsal, $O_2CC_6H_4$-2-OH; salen, bis(3-methoxy)-salicylideneimine); BzO^-, $C_6H_5COO^-$; L^{31}, 2-((methylamino)methyl)-6-(iminomethyl)-4-bromophenolate; (HTSCs), acetylferrocene thiosemicarbazones.

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We dedicate this paper to Hossein Aghabozorg, the top Iranian scientist, researcher and distinguished professor of Inorganic chemistry at Tarbiat Moallem University, who died at the age of 62 due to cancer disease. God bless his soul.

Keywords:
Lead(II)
Supramolecular
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Nano-structure
Coordination polymer
Lone-pair stereoactivity

ABSTRACT

In recent years, the chemistry of metal-coordination polymers has been advanced due to their diverse topologies and potential applications in smart optoelectronic, magnetic, microporous and biomimetic materials with specific structures, properties, and reactivities. Metal carboxylates have emerged as a large family of open framework materials. Recently, metal carboxylate chemistry has enhanced because of the increasing importance of hybrid inorganic–organic compounds with potential applications in separation, catalysis, and gas storage. So far, research on coordination polymers has considerably been concentrated on incorporation of s-, d-, and even f-block metal ions as coordination centers. As a heavy p-block metal ion, lead(II), with its large radius, flexible coordination environment, and variable stereochemical activity, is suitable for formation of unusual network topologies with interesting properties. This review provides an overview of all lead(II) carboxylate supramolecular compounds reported since 1990 and an investigation of their coordination modes, properties and structures. The variety of coordination modes of carboxylate groups increase the strength and stability of the resulting architectures. These modes include (η^1), (μ^2-η^1:η^1), (η^2), (μ_2-η^2), (μ_3-η^1:η^2), (μ_3-η^1:η^2), (μ_2-η^2:η^1), (μ_3-η^1:η^2:η^1) and (μ_4-η^2:η^2) that have created multiplicity polymeric structures with different dimensions. In this study it was found that carboxylate groups in many of lead(II) coordination polymers form more than a single type of coordination mode and among all of these modes maximum number belonged to chelating (η^2) mode.

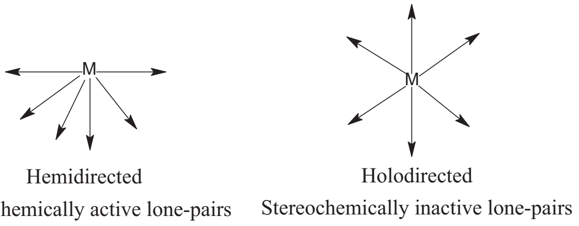
1. Introduction

The development of coordination polymer research has been enforced by the growth of crystal engineering and supramolecular chemistry [1,2]. A coordination polymer contains metal ions linked by coordinated ligands into an infinite array. Coordination polymers constitute one of the most important classes of organic–inorganic hybrid materials [3,4] that have been the subject of intensive research in recent years [5]. The rational design via self-assembly depends on a variety of parameters, basically including the suitable pre-designed organic ligands and metal centers with versatile coordination geometries [6]. Design and synthesis of novel discrete and polymeric metal–organic complexes are attracting more attention, not only for their interesting molecular topologies, but also for their potential applications as functional materials [7], ions exchange [3], catalysis, molecular recognition, nonlinear optics [8,9], molecular magnetic materials, electrical conductivity [10,11], separation and gas storage [12,13]. The structure and properties of coordination polymers depend on the coordination habits and geometries of both metal ions and connecting ligands, as well as on the influence of secondary interactions such as hydrogen bonding, π–π stacking interactions and so on [14]. Several factors, including the coordination bonds and secondary interactions, the metal-to-ligand molar ratio, the coordinative function of the ligands, the type of metal ions, the presence of solvent molecules, counterions and organic guest molecules should be taken into account in the process of the design and synthesis of metal-coordination polymers [15,16].

Divalent lead, with its electronic configuration [Xe] $4f^{14}$ $5d^{10}$ $6s^2$, is a heavy toxic metal [17], easy to extract, dense, highly malleable and stable to corrosion [18]. Problem of environmental contamination is widespread owing to several industrial activities, mainly battery making and recycling, oil refining, paint manufacturing [19], metal alloys, glasses, ceramic and radiation shielding materials [20]. Lead(II) contains the $6s^2$ lone pair, which can cause distortion in coordination sphere [21–26] and frequently discussed in considering the "stereo-chemical activity" of valence shell electron lone pairs [27–33]. In 1998, Shimoni-Livny discussed the possible stereo-chemical activity of the lone pair of lead(II) compounds based on a thorough review of crystal data available in the CSD. They classify lead coordination as holodirected which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of encompassing sphere, while hemidirected refers to those cases where the bonds to ligand atoms are directed only to a part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand (Scheme 1) [34–39].

Lone pair activity may depend on the following factors: (1) low versus high coordination number, (2) hard versus soft ligands, (3) attractive versus repulsive interactions among ligands, (4) whether the lone pair has p character, (5) fewer or more electron donation from ligands to metal [40]. Lead(II) complexes are interesting and frequently discussed in considering the coordination and forms stable complexes with both soft and hard donor atom ligands [41–47].

The effects of ligands on the construction of the coordination polymers are studied and play a role in determining the network structure of a coordination polymer. Carboxylates are a large family of O-donor ligands and are very abundant due to both the strong bonds that they form and the wide range of such possible ligands [1]. Because of the rich coordination modes of the carboxylate groups that can afford neutral metal–organic frameworks, carboxylate ligands are suitable candidate for the preparation of multi-dimensional coordination networks [48]. Increasing the number of donor atoms of the ligands and the number of chelating rings usually results in higher stability of the complexes [49]. They exhibit diverse coordination modes, such as mono-dentate terminal and bridging, chelating, and chelating, bridging (Scheme 2). The ability of the carboxylate groups to form both chelating and bridging coordination modes, indicates that they do not operate as linear linking groups and this makes the coordination networks more complicated [3,50].



Scheme 1. Lone pair stereo-chemical properties.

Recently, the rapid development in the synthesis and characterization of MOFs has received considerable attention [51,52]. Most of porous structures were constructed from discrete metal–carboxylate clusters and produce rigid entities of simple geometry, referred to as SBUs [53]. Up to now, several MOFs based on carboxylates (BPDC, 2,6-NDC, 1,4-bdc, DHBDC, etc.) have been reported [53,54].

In the last two our reviews structures and properties of mercury(II) and thallium(I) coordination polymers were reported [55,56]. In the present review we describe structures and properties of the lead(II) coordination polymers, contain only carboxylate ligand, and their mixed–ligand complexes. In addition we consider their coordination modes and topological types of 1D, 2D and 3D coordination polymers. In each compound, position and the way of linking of carboxylate ligand to central ion and stereo-activity of lone pair in divalent lead(II) compounds are discussed. Two review papers of lead(II) complexes with oxygen donor ligands [20] and sulfur and selenium donor ligands [41] have been published by Davidovich and Whitmire. The present report is a detailed review of lead(II) carboxylate coordination polymers that mentions more than 250 compounds containing carboxylate ligands.

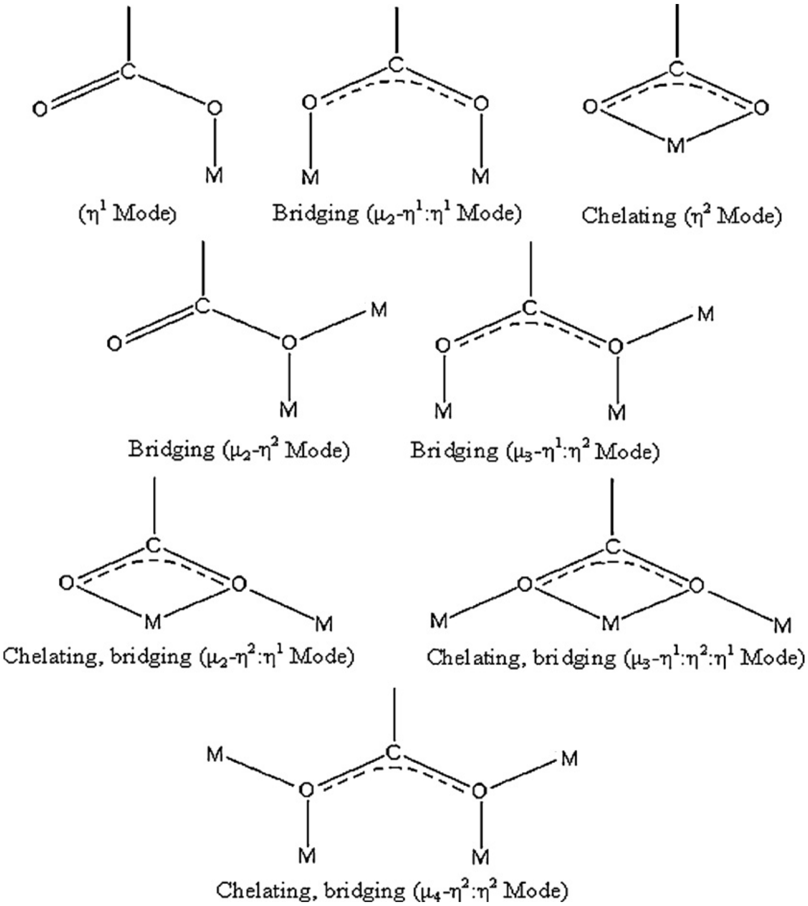
2. Mono-donor coordination mode (η^1)

2.1. Discrete complexes

$[Pb(H_3Dtpa)]\cdot 2H_2O$ (**1**) [57] forms discrete coordination polymer only with carboxylate group of the related ligand. $[Pb(phen)_2(L)_2]\cdot 2.5H_2O$ (**2**) [58], (pipz)[Pb(2-6-pydc)$_2$]$\cdot 2H_2O$ (**3**) [59], $[Pb(OAc)L^2BPh_4]_2$ (**4**) [19], $[Pb(L^3)_2(bpy)]$ (**5**) [60], $[Pb(H_2Edta)(tu)]$ (**6**), $Pb(H_2Edta)\cdot 2tu\cdot H_2O$ (**7**) [61], $(tataH_2)_2[Pb(pydc)_2]_2\cdot 2tata\cdot 4H_2O$ (**8**) [62], $[Pb(L^4)_2(phen)]\cdot H_2O$ (**9**) [63], $[Pb(L^5)_2(phen)_2]\cdot 2.5H_2O$ (**10**) [64] and $[Pb(qina)_2(DMSO)]\cdot H_2O$ (**11**) [65], form novel mixed–ligand lead(II) complexes that one of them has possessed carboxylate groups. Compounds **6** and **11** contain two-dimensional supramolecular compound formed through hydrogen bonding and π–π stacking interactions. Compound **6** is linked in twin polymeric chains (ribbons) through strong hydrogen bonding. In complex **11** the coordination number of Pb(II) ion is four and two qina$^-$ ligands coordinate to the Pb(II) ions with two nitrogen atoms and two mono-donor carboxylate oxygen atoms (Fig. 1).

In compound **9**, the coordination geometry of the Pb(II) atom is best described as highly distorted tetrahedral, made up of two nitrogen atoms of a phenanthroline ligand and two oxygen atoms from two mono-donor carboxylate groups from two 5-nitroisophthalate anions (Fig. 2).

In compound **5** each Pb(II) atom is coordinated by two nitrogen and two oxygen atoms, to complete a significantly distorted PbN_2O_2 polyhedron. The molecules form 1D chains along the *a*-axis via weak Pb···O and Pb···Pb interactions. The chains are connected



Scheme 2. The coordination modes of carboxylate ligands.

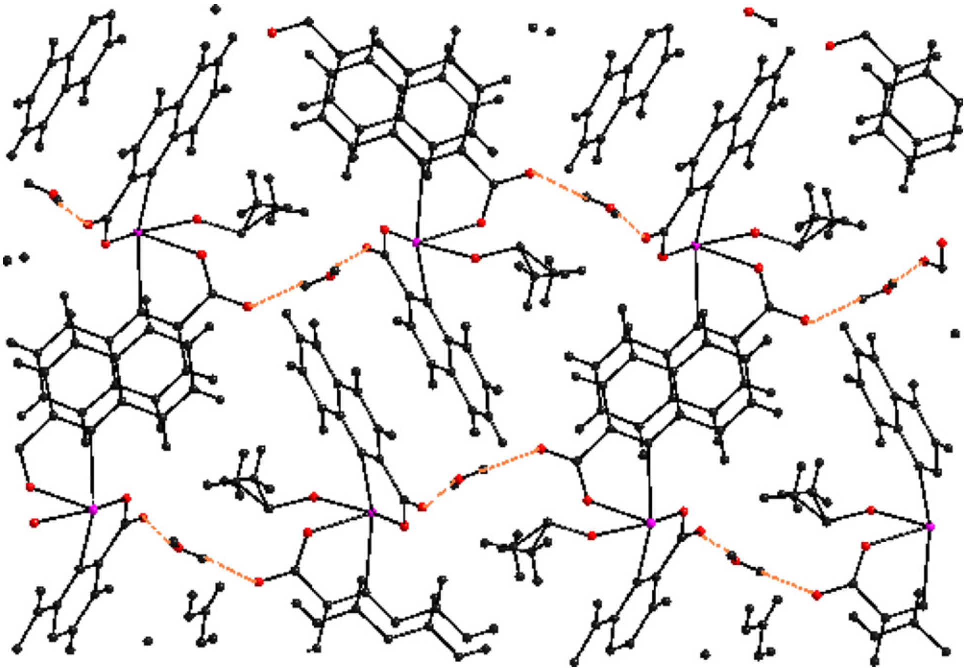


Fig. 1. Two-dimensional net structure in compound **11** [65].

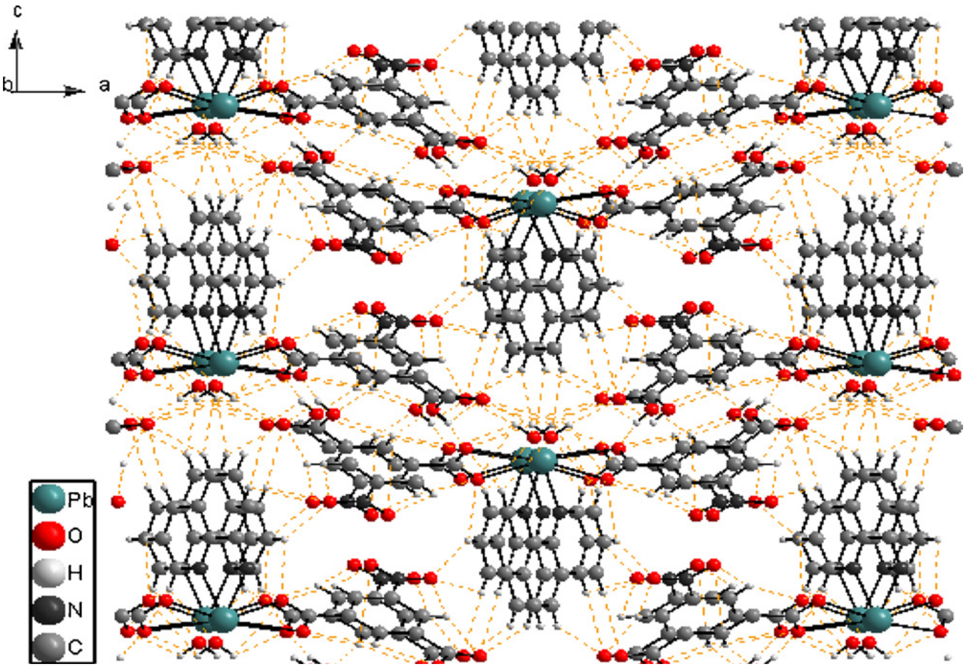


Fig. 2. Three-dimensional network formed by hydrogen bonding and $\pi\cdots\pi$ stacking interactions in compound **9** [63].

to each other via weak intermolecular hydrogen bonding. These interactions form the 3D network.

2.2. One-dimensional coordination polymers

Compounds [Pb(H_2Edta)]·1.5H_2O (**12**) [66], [Pb-(Htpaa)]$_2$ (**13**) [67], [Pb($INO)_2$]·3H_2O (**14**) [68] and [Pb(pro)(H_2O)]$_n$ (**15**) [69] form 1D coordination polymers only with carboxylate group of the related ligand. Compounds [Pb(H_2tpaa)Cl] (**16**) and [Pb(Hdpaea)Cl] (**17**) [67] form mixed–ligand lead(II) complexes. In compound **14** each Pb(II) center has a tetrahedral environment coordinated by four oxygen atoms. The oxygen atoms are located on one side of the Pb(II) ion which adopts a hemidirected structural geometry and shows the presence of a stereo-chemically active lone electron pair. All INO ligands adopting a bidentate-bridged coordination mode, through mono-donor carboxylate moieties and pyridyl N-oxide groups link to a pair of lead(II) centers to form [$Pb_2(INO)_2$] units. These units are expanded into a 1D infinite chain through corner-sharing lead(II) polyhedrons. The 1D chains are further extended into a 3D supramolecular framework through Pb···O interactions [70] and multipoint hydrogen bonding between water molecules and carboxylate oxygen atoms. Interestingly, when viewed along the *b*-axis the 3D network contains 1D rectangle channels (Fig. 3) which are filled by three uncoordinated water molecules.

Compound **15** is a 1D chain polymer as a result of water bridging. Coordination number of Pb(II) is six with a ‘stereo-chemically active’ lone electron pair, and the coordination sphere is hemidirected.

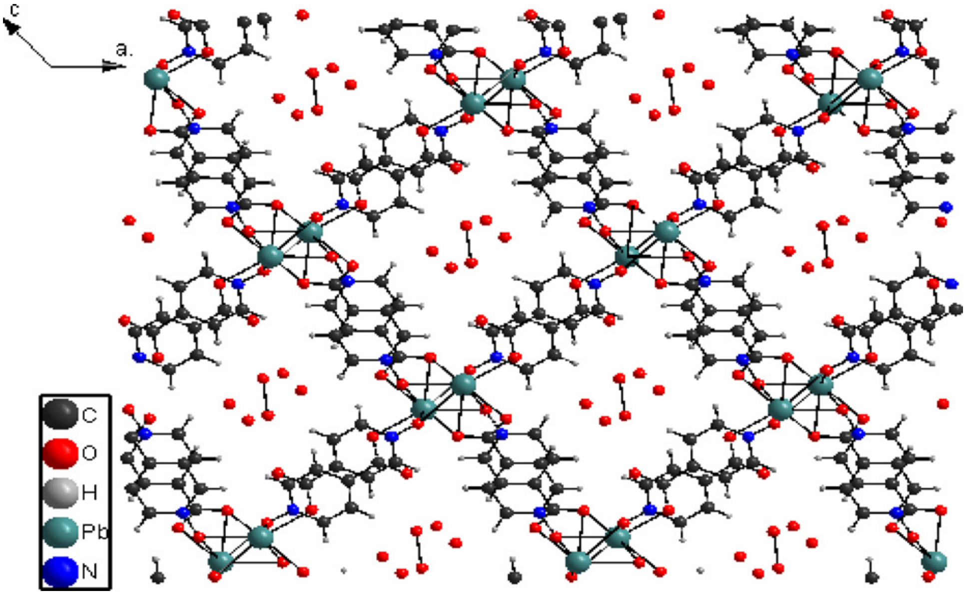


Fig. 3. Perspective view of the 3D supramolecular network in compound **14**, highlighting the rectangular nano-channels along the *b*-axis [68].

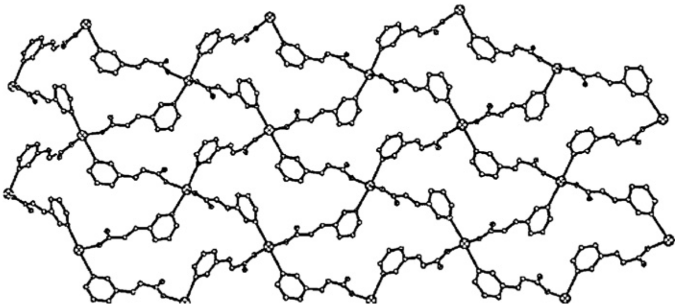


Fig. 4. Two-dimensional wave-like layer in compound **18** [48].

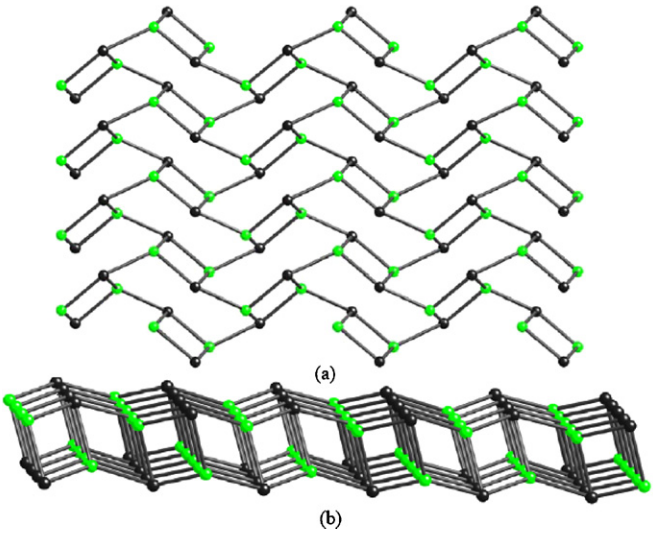


Fig. 5. Simplified schematic diagram showing the structure of compound **19** (a) in (1 0 1) plane and (b) viewed from *b*-axis. [71].

2.3. Two-dimensional coordination polymers

In $[Pb(3\text{-}PYD)_2]_n$ (**18**) [48], ligand 3-PYD bridges Pb(II) atoms through its pyridyl nitrogen atom and mono-donor carboxylate group, generating a head-to-tail aggregated $\{Pb(3\text{-}PYD)\}_4$ ring. The $\{Pb(3\text{-}PYD)\}_4$ rings are further extended into a 2D wave-like layer by sharing Pb(II) joints and ligand 3-PYD edges (Fig. 4).

Compound $[Pb(rctt\text{-}tpcb)(O_2CCF_3)_2]$ (**19**) [71] has formed from upright squares zigzag structure. The bottom edges of the squares are bonded to the adjacent rows alternately to form this 2D coordination polymeric sheet with the layer thickness of 8.7 Å. This connectivity generates larger ring linked by the edges of four squares and empty spaces are occupied by the free non-bonded pyridyl rings of the rctt-tpcb ligands (Fig. 5).

2.4. Three-dimensional coordination polymers

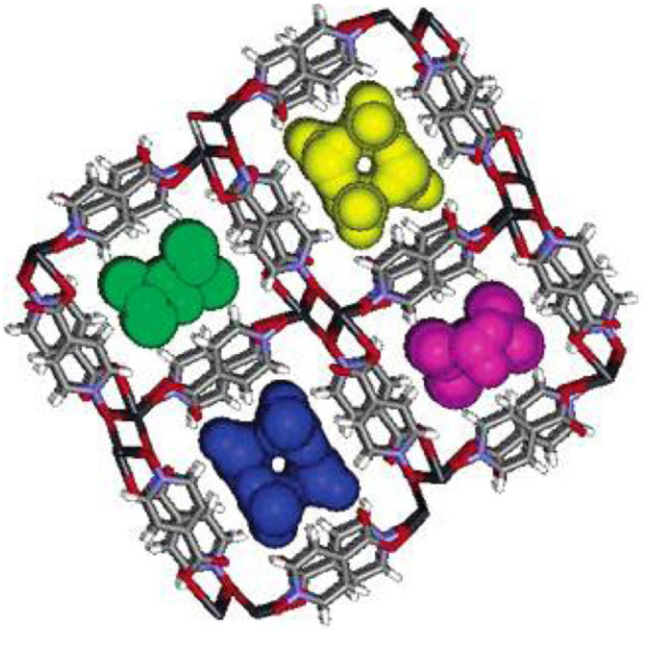


Fig. 6. The framework of compound **20** viewed along the *c*-axis, showing four array types of water molecules in two distinct nano-channels arranged alternately [72].

Compound $[Pb(INO)_2]_2{\cdot}7H_2O$ (**20**) [72] contains two alternate 1D nano-channels (A and B) with different sizes and shapes. Such biporous materials [51] with two (or more) distinct channels may be used as the simultaneous isolation or transportation of two different guests possible. Channel A is approximately a square, whereas channel B is roughly a rectangle (Fig. 6). In complex **20**, notably, (1) two distinct 1D channels were observed in a 3D coordination network; (2) the lattice water molecules fill in two distinct channels in different manners, and (3) leading to an array of 1D water tube with a double-stranded chain and an ordered 1D water chain involving a cyclic $(H_2O)_4$ unit.

3. Bi-donor coordination polymers

3.1. Bridging (μ_2-η^1:η^1) mode

3.1.1. Discrete complexes

Two equivalent $[Pb(H_2L^6)]^+$ units in $[Pb_2(H_2L^6)_2(\mu_2\text{-}OAc)]^+$ (**21**) [73] are connected by a bridging acetate group to form a dimmer lead(II) complex, $[Pb_2(H_2L^6)_2(\mu_2\text{-}OAc)]^+$. The uncoordinated acetate counter-ion is involved in intermolecular hydrogen bonding with the oxygen atom of consecutive cations (Fig. 7). In compound **21** both lead(II) centers have an irregular geometry, bound by five atoms with the sixth coordination site comprising the remaining $6s^2$ lone pair.

3.1.2. One-dimensional coordination polymers

Compounds $[Pb(sdac){\cdot}H_2O]$ (**22**) [74] and $[Pb(DABT)]_n$ (**23**) [75] are 1D coordination polymers in which hydrogen bonding help to stabilize the structure and form two-dimensional supramolecule. $\{[Pb(phen)_2(ox)]{\cdot}5H_2O\}_n$ (**24**) [76], $[Pb(phen)(OAc)_2]$ (**25**) [77],

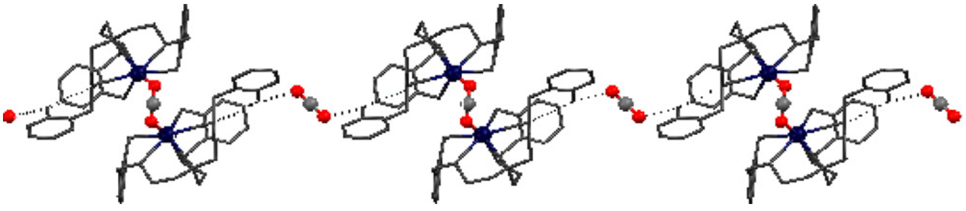


Fig. 7. The arrangement of 1D chain containing $[Pb(H_2L^6)]^+$ units in compound **21** [73].

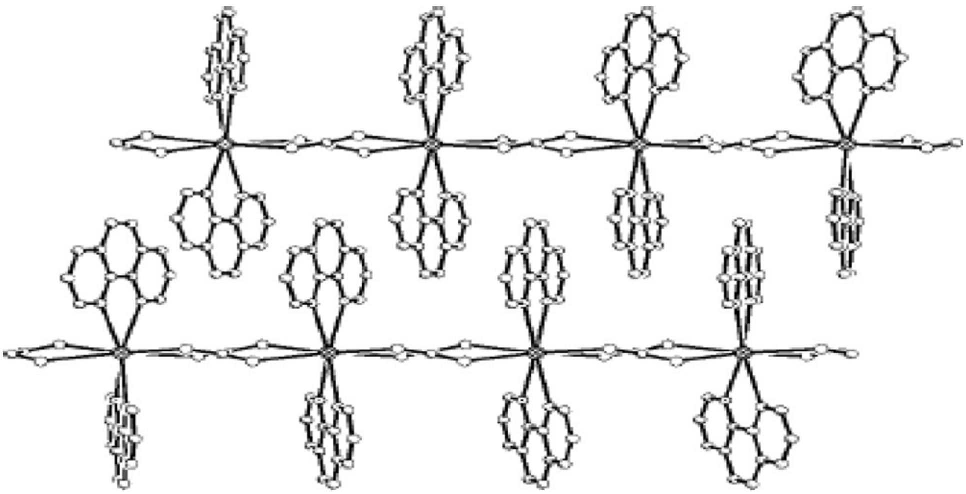


Fig. 8. Perspective view of the two-dimensional network formed by the π–π stacking interactions between one-dimensional ribbons in compound **24** viewed along the *c*-axis [76].

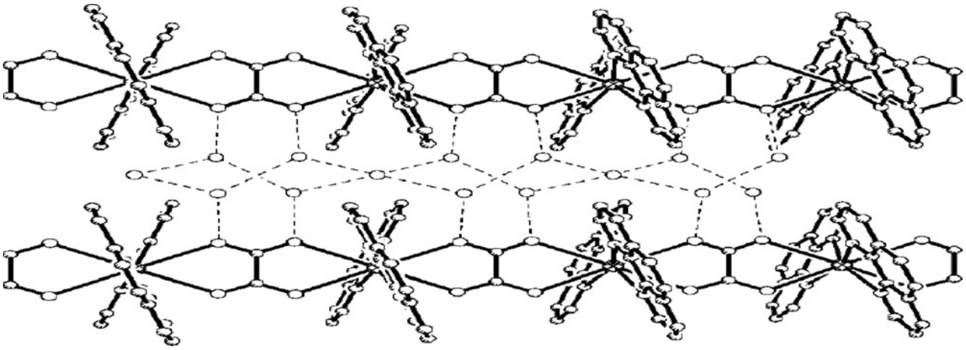


Fig. 9. The hydrogen bonding interaction between the coordination layers and the lattice water chain along the *a*-axis in compound **24** [76].

[Pb(CF_3-COO)$_2$(15-crown-5)] (**26**) [78] and [Pb(pala)(ClO_4)]$_n$ (**27**) [79] form 1D mixed–ligand lead(II) complexes. In compound **24** each Pb(II) atom is eight-coordinated and generates a N_4O_4 environment with a square-antiprismatic geometry (D_4d symmetry). Each ox group acts as a bischelate coordination mode, further bridges to Pb(II) atom, generating a one-dimensional chain (Fig. 8). Phen ligands are alternately attached to both sides of the chain and adjacent polymeric chains are packed through inter-calation of the lateral phen ligands in a zipper-like fashion into a two-dimensional layer (Fig. 8) exhibiting very strong inter-chain π–π

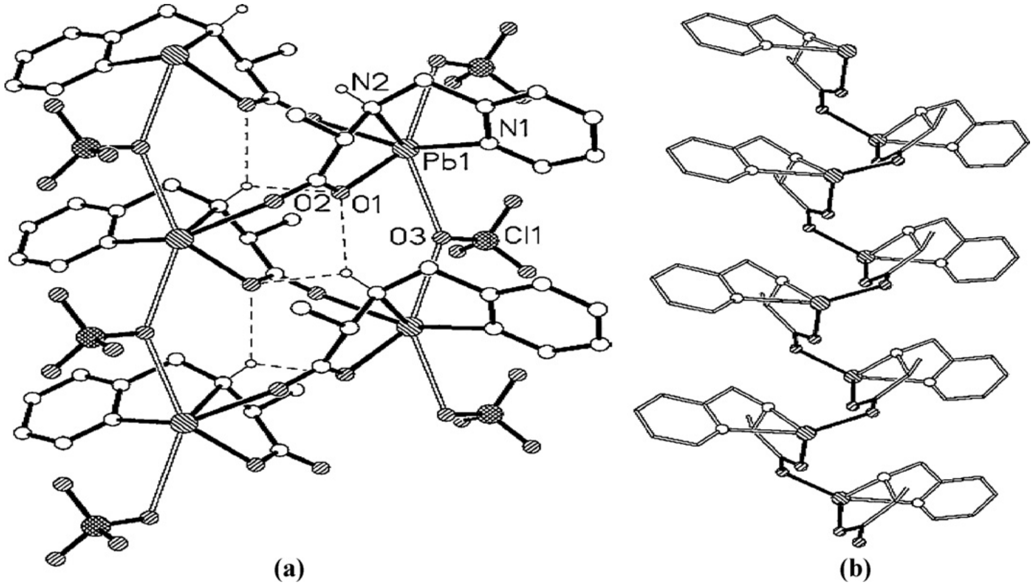


Fig. 10. (a) Interactions of ClO_4^- ion and N–H···O bond in the helical structure of compound **27** with scaffoldings and (b) a perspective view of the helical coordination polymeric chain structure in compound **27** [79].

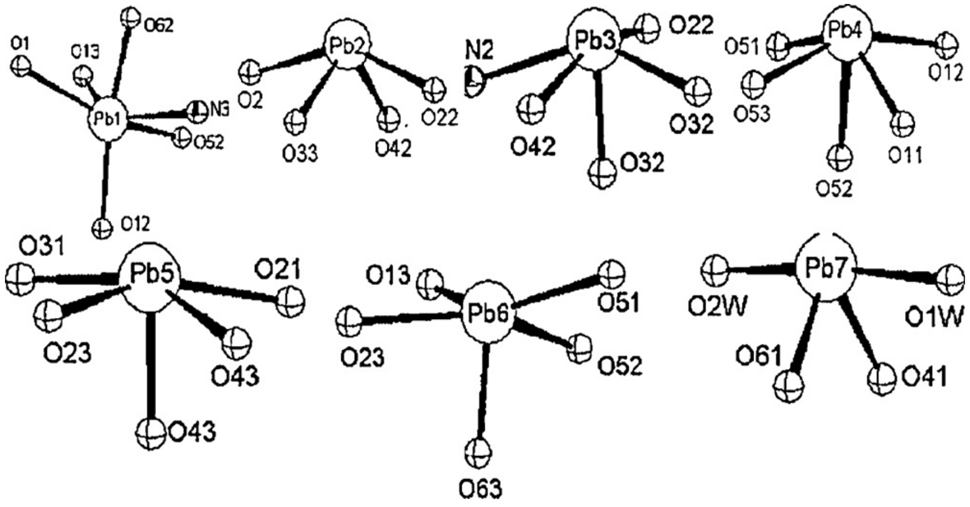


Fig. 11. The coordination geometries around the lead(II) ions in complex **28** [80].

stacking interactions with the face-to-face distance of 3.25 Å. There are two crystallographic positions for the five water molecules in the $[Pb(phen)_2(ox)]\cdot 5H_2O$ unit, to generate one-dimensional ribbons running along the *b*-axis as (Fig. 9). The water molecules intercalates into the two adjacent layers and further connects via hydrogen bonding with the ox oxygen atoms within the π–π stacked layers, hence forming a three-dimensional network in the lattice (Fig. 9). In compound **27** the perchlorate anion acts as a coordinating ligand as inferred from the medium-strong interactions present between an oxygen atom of the ClO_4^- anion and Pb(II). The bonding between Pb(II) and the neighboring carbonyl oxygen atom generates a 1D helical polymer (Fig. 10a). The helical polymers are further stabilized by bridging perchlorate anions and very weak N–H···O hydrogen bond. In this complex the carboxylate anions act as bi-donor ligand with each oxygen atom bonded to two different Pb atoms and have zigzag 1D polymeric structure (Fig. 10b).

3.1.3. Two-dimensional coordination polymers

Compounds $[Pb_7(3\text{-}O_3S\text{-}C_6H_4\text{-}CO_2)(L^7)_3(H_2O)_2]\cdot 2H_2O$ (**28**) [80], Pb[B(Im)$_4$](4-carboxy-TEMPO) (**29**) [81], $[Pb(INO)(N_3)(H_2O)]_n$ (**30**) [82], $[Pb(phe)_2]_n$ (**31**) [83], $[Pb(fum)(dpdp)]\cdot H_2O$ (**32**)

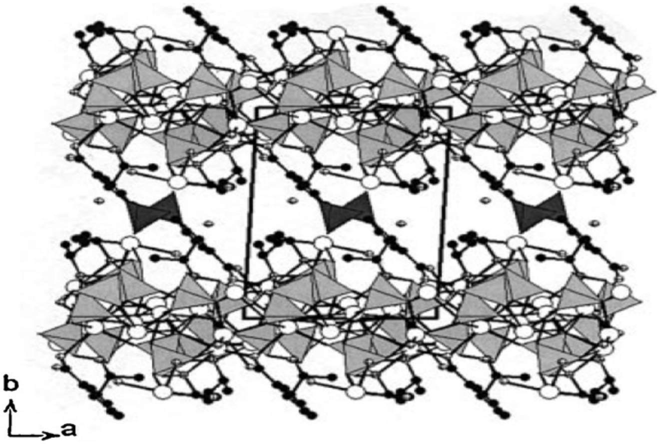
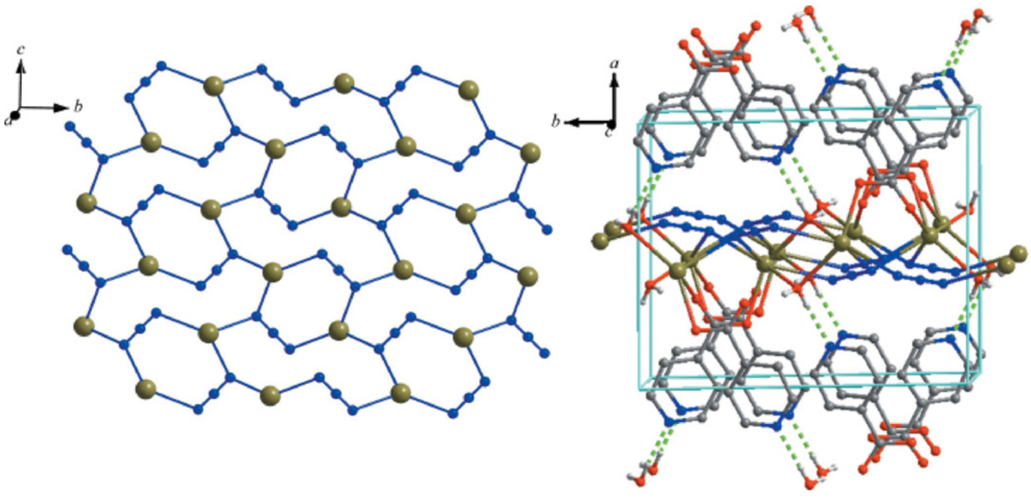


Fig. 12. View of the structure of complex **28** down the *c*-axis. The C–PO_3 and C–SO_3 tetrahedra are shaded in light and dark grey, respectively. Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively [80].



(a) (b)

Fig. 13. (a) Two-dimensional coordination polymer formed by Pb(II) ions and azide ligands and (b) a packing diagram of compound **30**, showing the water–isonicotinate O–H···N hydrogen-bond network in the adjacent two-dimensional layers (dashed lines) [82].

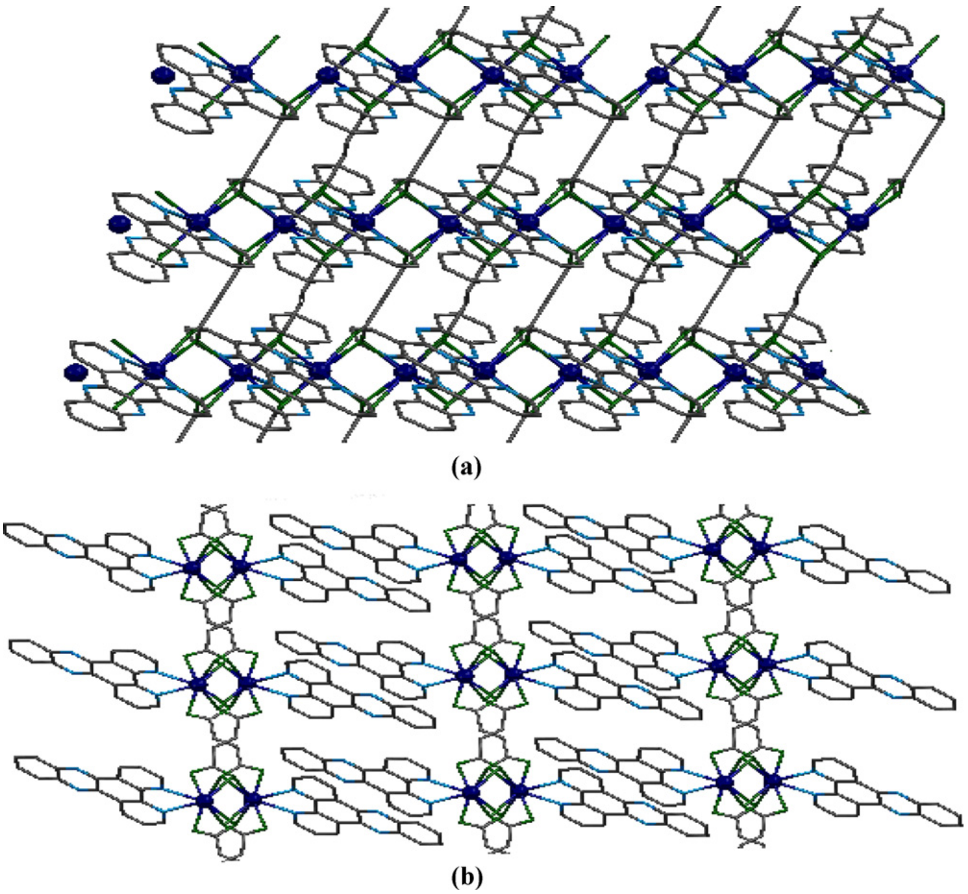


Fig. 14. (a) The layer structure of compound **32** and (b) the 3D supramolecular structure of compound **32** formed through interlayer π–π interactions [15].

[15], [Pb(μ-4-pyc)(μ-NCS)-(μ-H_2O)]$_n$ (**33**), [Pb(μ-4-pyc)(μ-N3)(μ-H_2O)]$_n$ (**34**) [84], [Pb(2,5-pdcaH)$_2$]·$2H_2O$ (**35**) and [Pb(2,4-pydc)]·H_2O (**36**) [85] form two-dimensional lead(II) coordination polymers. Compounds **28** and **31** have been formed from only carboxylate group of the related ligand whereas compounds **29**, **30**, **31**, **32**, **33**, **34**, **35** and **36** form mixed–ligand complexes. Compound **28** is composed of seven lead(II) ions with different coordination spheres (Fig. 11). The sulfonate group acts as a pendant group, hanging between two layers (Fig. 12).

In compound **30** each azide ligand bridges three Pb(II) ions to form a two-dimensional three-connected 6^3 topology network. The carboxylate group of the isonicotinate unit and the aqua ligand act as coligands to bridge Pb(II) ions (Fig. 13a). Adjacent two-dimensional layers are connected by hydrogen-bonding interactions between the isonicotinate nitrogen atom and the water molecule, resulting in an extended three-dimensional network (Fig. 13b).

In the structure of **32**, each fum ligand bridges four Pb(II) centers in a tetradentate mode, generating a novel layer structure (Fig. 14a). Additionally, the interplanar distance between two neighboring dpdp ligands of adjacent layers are ca. 3.54 and 3.50 Å, indicating the presence of face-to-face π–π interactions that extend the layers to a unique 3D supramolecular structure (Fig. 14b). The carboxylate moiety of the 4-pyc$^-$ ligand in compounds **33** and **34** act as a bridging group in a bridging (μ_2-η^1:η^1) coordination mode. The X–Pb–Y angles suggest that there is a vacant site in the coordination sphere of the lead(II) ion due to lone pair-bond pair repulsion (Figs. 15a and 16a). Nano-sized particles of compounds **33** and **34** have been prepared by sonochemical method in aqueous solution. The average size of the particles is around 88 and 96 nm for compounds **33** and **34**, respectively (Figs. 15b and 16b).

3.1.4. Three-dimensional coordination polymers

Compounds [$Pb_5(O_3PCH_2CH_2CO_2)_2(O_3PCH_2CH_2COOH)_2$] (**37**) [86], [Pb(dnty)(0.5H_2O)] (**38**) [87] and {[Pb_4O_3]$C_2H_2(CO_2)_2$·1/2H_2O.TRIMAL} (**39**) [88] form 3D coordination polymers and in these compounds the carboxylate group of the related ligands acts as bridging (μ_2-η^1:η^1) mode. In compound **39** the lone

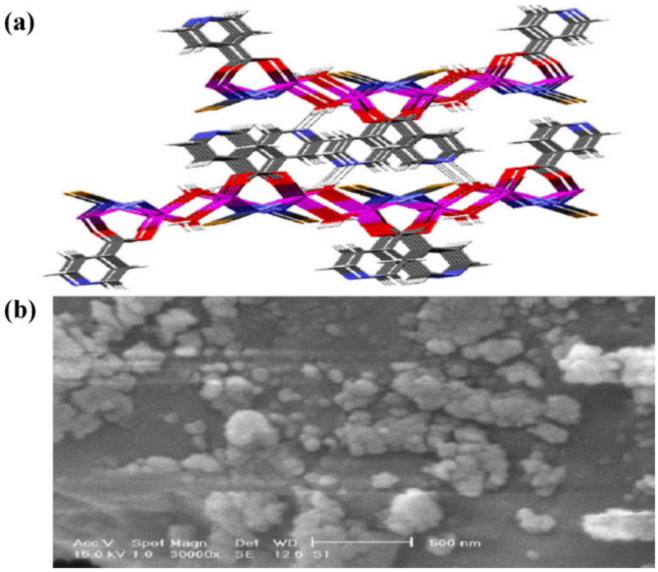


Fig. 15. (a) A fragment of the 2D polymer and showing hydrogen bonding in compound **33** and (b) SEM photograph of compound **33** nano-particles prepared by sonochemical method [84].

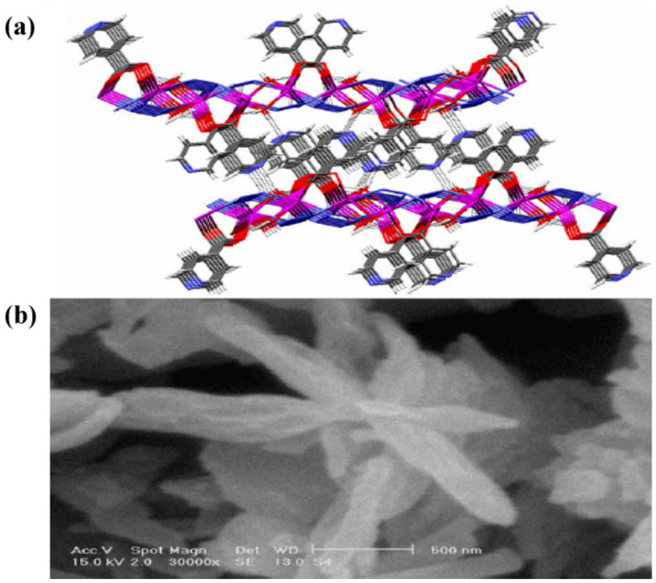


Fig. 16. (a) A fragment of the 2D polymer and showing hydrogen bonding in compound **34** and (b) SEM photograph of compound **34** nano-rods prepared by sonochemical method [84].

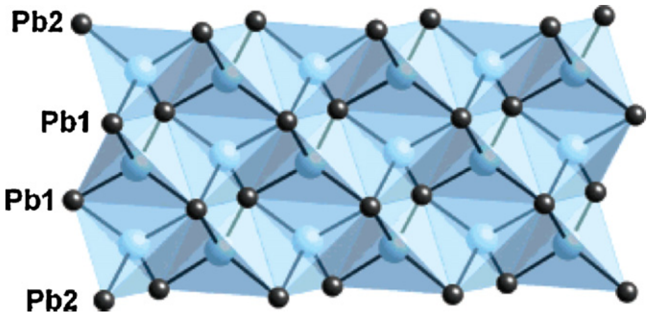


Fig. 17. Infinite [Pb_4O_3] slab in compound **39**, built up by (OPb_4) tetrahedra, viewed approximately along the *a*-axis [88].

pair of electrons on the two independent Pb(II) atoms causes their coordination geometry to be distorted and hemidirected. The structure of compound **39** consists of infinite OPb_4 tetrahedra (Fig. 17) running along the *c*-axis and linked together into a three-dimensional network by tetradentate maleate anionic ligands (Fig. 18).

Compounds [$Pb_4(H_2L^8)(SIP)_2(H_2O)_4{\cdot}2H_2O$] (**40**) [89], [$Pb_4(OH)_4(INO)_4$]$\cdot nH_2O$ (**41**) [72,90] and {[Pb(4-sb)(4,4′-bipy)$_{1/2}$]$\cdot$(4,4′-bipy)$_{1/2}$}$_n$ (**42**) [91] form mixed–ligand three-dimensional coordination polymers. In complex **41** each hepta-coordinated Pb(II) center is bound to three hydroxyl oxygen atoms through μ_3-OH atoms, and each μ_3-OH bridges to three Pb(II); thus, it forms a usual M_4O_4 core. The Pb_4O_4 core is bonded to four carboxylate groups from four different INO ligands to expand to four different orientations. The INO ligand acts as a tetra-donor ligand and bridges four lead(II) ions through two carboxylate O atoms and one N-oxide oxygen atom. The resulting 3D network contains 1D square nano-channels (Fig. 19).

Compound **42** displays a 3D network, in which each Pb(II) center is eight-coordinated in a dicapped trigonal prism with a $PbNO_7$ chromophore. The carboxylate group in this complex acts as bridging (μ_2-η^1:η^1) mode. There are π–π interactions not only between coordinated 4,4′-bipyridine and free 4,4′-bipyridine ligands but also between coordinated 4,4′-bipyridine and 4-sb, as well as between free 4,4′-bipyridine ligand and 4-sb ligand (Fig. 20).

3.2. *Chelating (η^2) mode*

3.2.1. *Discrete complexes*

The coordination number in [Pb(tpy)$(OAc)_2$] (**43**) [92] is seven and weak interaction of lead(II) with the oxygen atoms of an adjacent molecule produces an one-dimensional chain. There are π–π stacking interactions between the parallel aromatic rings separated by a distance of about 3.5 Å. In [$Pb(phen)_2(OAc)$](ClO_4) (**44**) [93], the Pb(II) atom of the monomeric complex is coordinated by four nitrogen atoms of two phen ligands and two oxygen atoms of the acetate ligand. The arrangement of Pb(II) atoms coordinated by oxygen and nitrogen atoms of phen and acetate ligand shows that the lone pair electrons are active and result in a hemidirected lead(II) geometry. Both independent Pb(II) atoms in [$Pb_2(L^9)_2(OAc)_2$] (**45**) [94] are chelated by acetate and substituted by quinolin-8-olate anions. In [Pb(2,9-dmphen)(3-hyba)$_2$]$\cdot$dmphen$_2{\cdot}3H_2O$ (**46**) [95] the Pb(II) ion is coordinated by two N atoms from one dmphen ligand

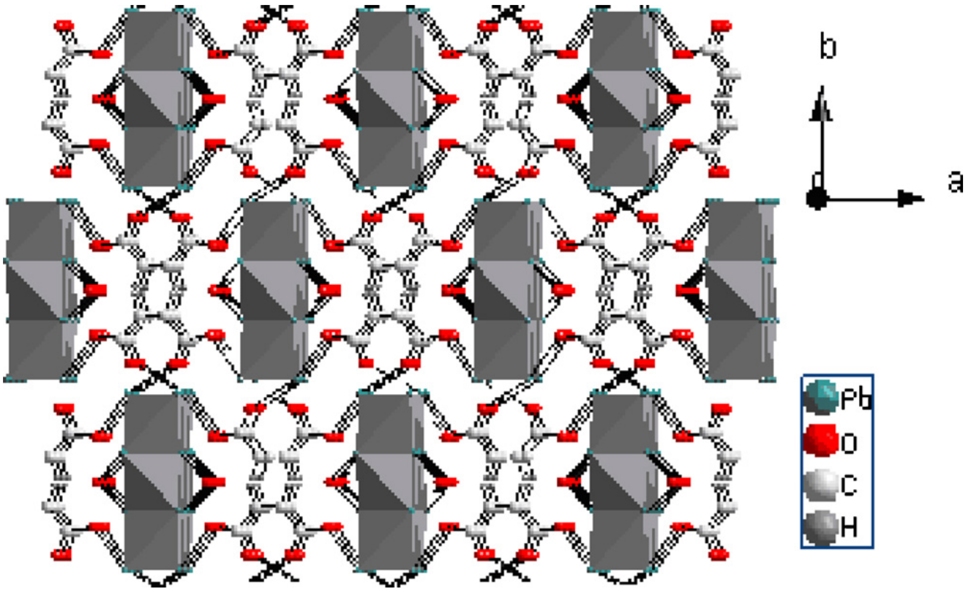


Fig. 18. View of compound **39**, approximately along the *c*-axis (grey OPb_4 tetrahedra) [88].

Fig. 19. Perspective view of the 3D network in compound **41**, highlighting the square nano-channels along the *c*-axis [90].

and four O atoms from two 3-hydroxybenzoate anions. Compound $[Pb(endc)(phen)\cdot 3H_2O]_2$ (**47**) [27], is a hepta-coordinated dimmer and the Pb(II) atoms have hemidirected coordination geometry. Also compounds $[Pb_2(phen)_2(L^{10})_2]$ (**48**) [96], $[Pb_2(PF_6)_2(OAC)_2\{C_{36}H_{46}N_6\text{-}Se_2\}]$ (**49**) [97], $[Pb(adip)(dpdp)]_2$ (**50**), $[Pb_2(oba)(dpdp)_2]\cdot 2(dpdp)\cdot 2(NO_3)\cdot 2H_2O$ (**51**) [15], $[ArPb(OAc)_3]$ (**52**), $[Ar_2Pb(OAc)_2]$ (**53**), $[(o\text{-Tolyl})_2Pb(OAc)_2]$ (**54**) [98] and $[Pb_2(Hssal)_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})(H_2O)_2]$ (**55**) [16] form discrete complexes. In compound **48** the Pb(II) atoms are coordinated by two nitrogen atoms of one phen ligand and four oxygen atoms of two chelating carboxylate groups. The mean interplanar distance of 3.44 Å suggests that the intermolecular π–π stacking interactions are responsible for supramolecular assembly of the dinuclear molecules into layers. The formed layers are further assembled by intermolecular C–H···O hydrogen bonding to generate 3D framework with the hydrogen bonded H_2O molecules located in 1D tunnels (Fig. 21).

The structure of the compound **49** consists of $[Pb_2(OAc)_2\{C_{36}H_{46}N_6Se_2\}]^{+2}$ cation and PF_6^- anions. The geometry around each Pb(II) is a distorted octahedron due to a stereo-chemically active lone pair on lead(II) atoms. The two metal atoms and the bridging oxygen atoms form a central four-membered Pb_2O_2 ring. Each acetate ion in the molecular unit acts as chelating ligand toward one lead(II) atom and is bridging

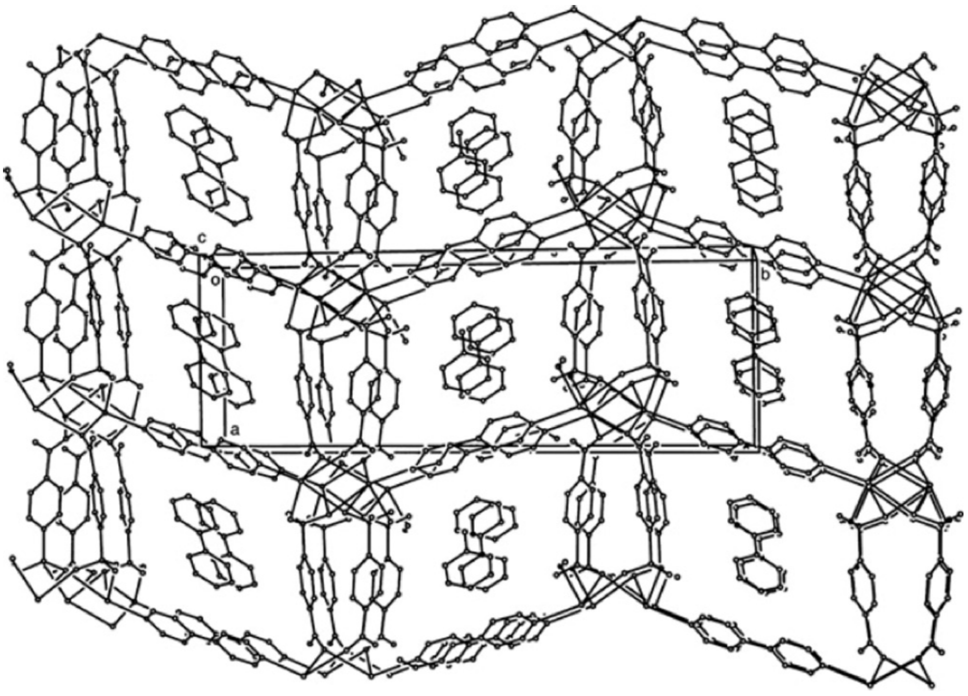


Fig. 20. A view of 3D network of complex **42**. Uncoordinated 4,4′-bipyridine molecules occupy the nano-channels [91].

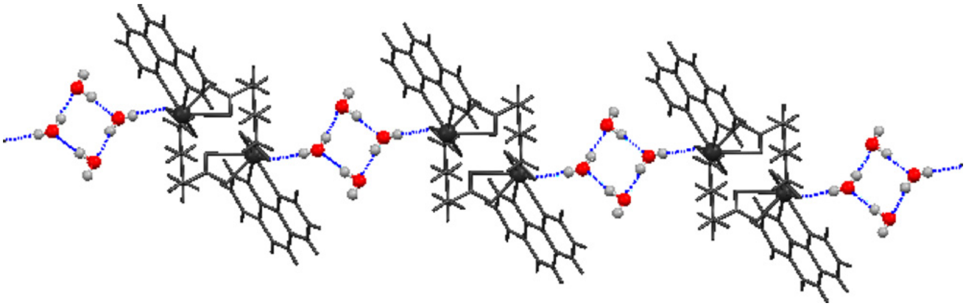


Fig. 21. H_2O molecules located in 1D tunnels extending along the [100] direction in compound **48** [96].

between the two lead(II) through one of its oxygen atoms. This is an interesting example of a binuclear lead(II) complex of a monocycle where the two lead(II) atoms as well as the chelating acetate anions are wrapped by the macrocycle cavity. Each Pb(II) atom in the two molecules is coordinated with three nitrogen atoms.

Complexes **50** and **51** have dinuclear structures, which are further stacked via strong π–π interactions to form 2D layers. The $[Pb(adip)(dpdp)]_2$ dimer comprises two adip, two dpdp ligands, and two Pb(II) atoms. Indeed, the dpdp ligands from adjacent dimers are paired to furnish strong π–π interactions resulting in an interesting 2D supramolecular layer (Fig. 22).

3.2.2. *One-dimensional coordination polymers*

The Pb(II) atom in $[Pb(fum)(4,7\text{-dmphen})]_n$ (**56**) [99] is coordinated by four carboxylate O atoms and two N atoms resulting in PbN_2O_6 polyhedron. The centrosymmetric fum ligands bridge neighboring Pb(II) atoms to generate a chain structure. Aromatic π–π stacking between dmphen ligands in adjacent chains leads to a two-dimensional supramolecular array.

Compounds $[Pb(glu)(dpdp)]_n$ (**57**), $[Pb(suc)(dpdp)]_n$ (**58**), $\{[Pb_2(1,4\text{-bdc})_2(dpdp)_2]\cdot H_2O\}_n$ (**59**), $[Pb(dpdc)(dpdp)]_n$ (**60**) and $\{[Pb(1,3\text{-bdc})(dpdp)]\cdot H_2O\}_n$ (**61**) [15], extend by types of π–π interactions. In **58**, the Pb(II) center is located in a distorted pentagonal bipyramidal coordination sphere formed by four oxygen atoms from two distinct glu ligands, two nitrogen atoms from one chelating dpdp ligand, and a lone electron pair. The carboxylate oxygen atoms from the glu ligands and two nitrogen atoms from the same dpdp ligand make up the basal plane, whereas the axial positions are occupied by one oxygen atom and the lone electrons pair. A notable feature for **57** is the presence of a helical chain (Fig. 23a). The glu ligands bridge each pair of adjacent Pb(II) atoms into a single-stranded helical chain with a long pitch of 7.851 Å. The approximately parallel orientation of the dpdp ligands allows pairing of neighboring related single-stranded helical chains to generate a supramolecular layer under the direction of aromatic π–π stacking interactions among the dpdp pairs (Fig. 23b). Two adjacent helical chains of the same supramolecular layer show opposite chiralities. In compound **60**, the Pb(II) atom is located in the center of a distorted pentagonal bipyramidal coordination geometry, which is defined by four oxygen atoms of two dpdc ligands, two nitrogen atoms from one chelating dpdp ligand, and the lone pair of electrons. The dpdp ligands are extended in a parallel fashion at both sides of a single-stranded helical chain (Fig. 24a). Interestingly, the aromatic stacking of dpdp ligands forms a 1D supramolecular dpdp array through two types of π–π interactions (Fig. 24b). The neighboring helical chains interact through these π–π stackings to form 2D supramolecular layers. Furthermore, another type of π–π interaction between the dpdp ligands in neighboring layers extend the 2D supramolecular arrays into an interesting 3D supramolecular structure, which is the striking features of complex **60** (Fig. 24c).

Compound $[Pb(2\text{-hyba})_2(dmphen)]_n$ (**62**) [100] forms a zigzag polymeric chain along the *c*-axis through bridging hydroxy groups of two 2-hydroxybenzoate ligands (Fig. 25). Also compounds $[Pb(Hssal)(2,2'\text{-bipy})(DMF)]_n$ (**63**) [101] and $[Pb(Hssal)(phen)(4,4'\text{-bipy})_{0.5}]_n$ (**64**) [16] are one-dimensional ladder-like chains. In compound **63** the lead(II) ion is holodirected and ladder-like chain is formed in DMF/H_2O (Fig. 26). Ladder-like chain in compound **64** is formed with mono-donor 4,4′-bipyridine.

Compounds $[Pb(3\text{-sb})(phen)(H_2O)]_n$ (**65**) [102], $[Pb(3\text{-sb})(bpy)(H_2O)]_n$ (**66**) [103], $[Pb(Hssal)(phen)(DMF)]_n$ (**67**) [101], $[Pb(en)(NO_3)(OAc)]$ (**68**) [104], $[Pb(bpy)(NCS)(OAc)]_n$ (**69**) [105], $\{Pb[C_6H_4(COO)_2][phen]\}_n$ (**70**) [106], $[Pb(3,3'\text{-ADB})(phen)]_n$ (**71**) [107], $[PbPh_2(OAc)(MeGTSC)]_n$ (**72**),

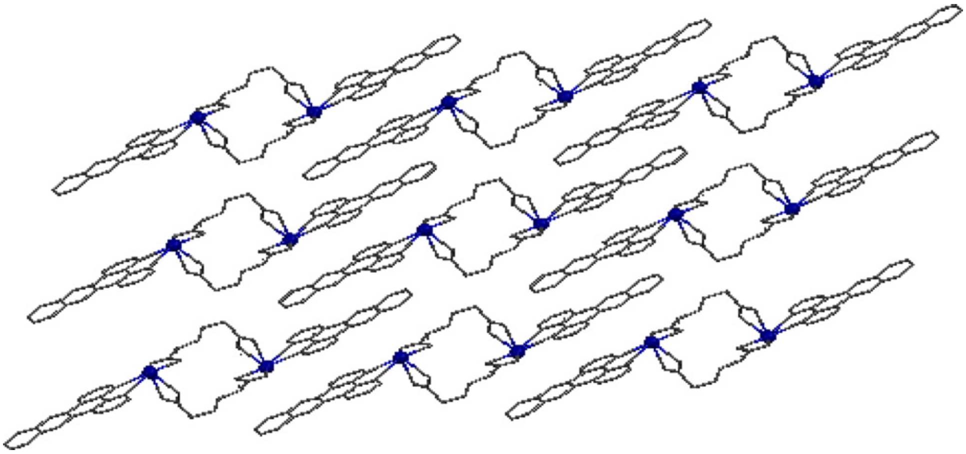


Fig. 22. The 2D supramolecular structure of compound **50** formed through π–π interactions [15].

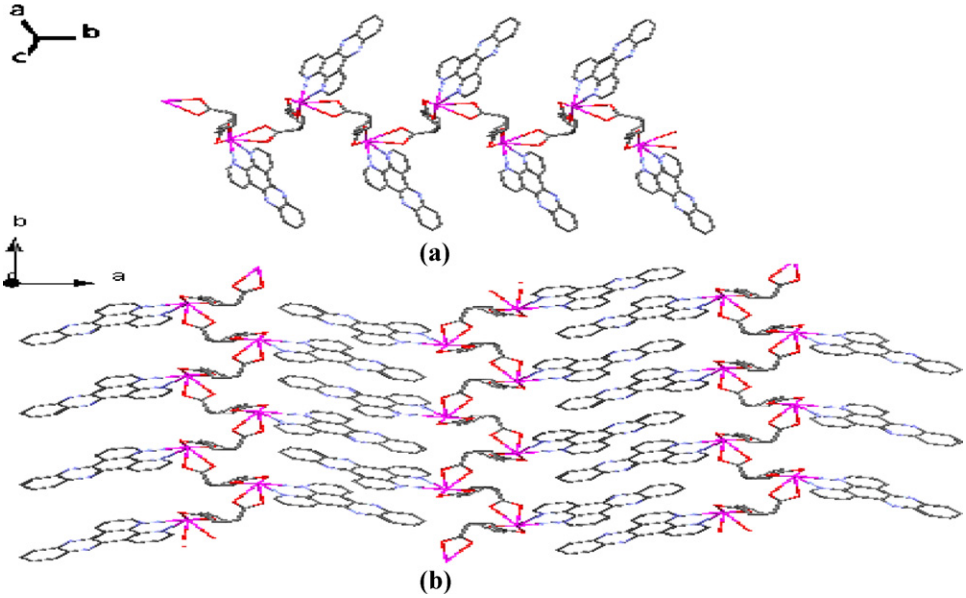


Fig. 23. (a) The 1D helical chain structure of compound **57** and (b) the layer structure of compound **57** formed through π–π stacking interactions [15].

[PbPh$_2$(OAc)(EtGTSC)] (**73**), [PbPh$_2$(OAc)(BuGTSC)] (**74**) [108], {Pb[(DMF)]$_2$[(DTB)$_2$]}$_n$ (**75**) [109] and [Pb(L^{11})$_2$(NO$_3$)(H$_2$O)$_2$](NO$_3$) (**76**) [110] form one-dimensional coordination polymers through chelating mode.

3.2.3. Two-dimensional coordination polymers

Compounds [Pb(Hssal)(2,2′-bipy)(bpe)$_{0.5}$]$_n$ (**77**) [16], {Pb$_3$(HL^{12})(H$_2$L^{12})(H$_2$BTC)-(H$_2$O)·H$_3$BTC·H$_2$O}$_n$ (**78**) [111], [Pb(4-sb)(2,2′-bipy)]$_n$ (**79**) [91], {Pb[B(Im)$_4$](3-carboxy-PROXYL)

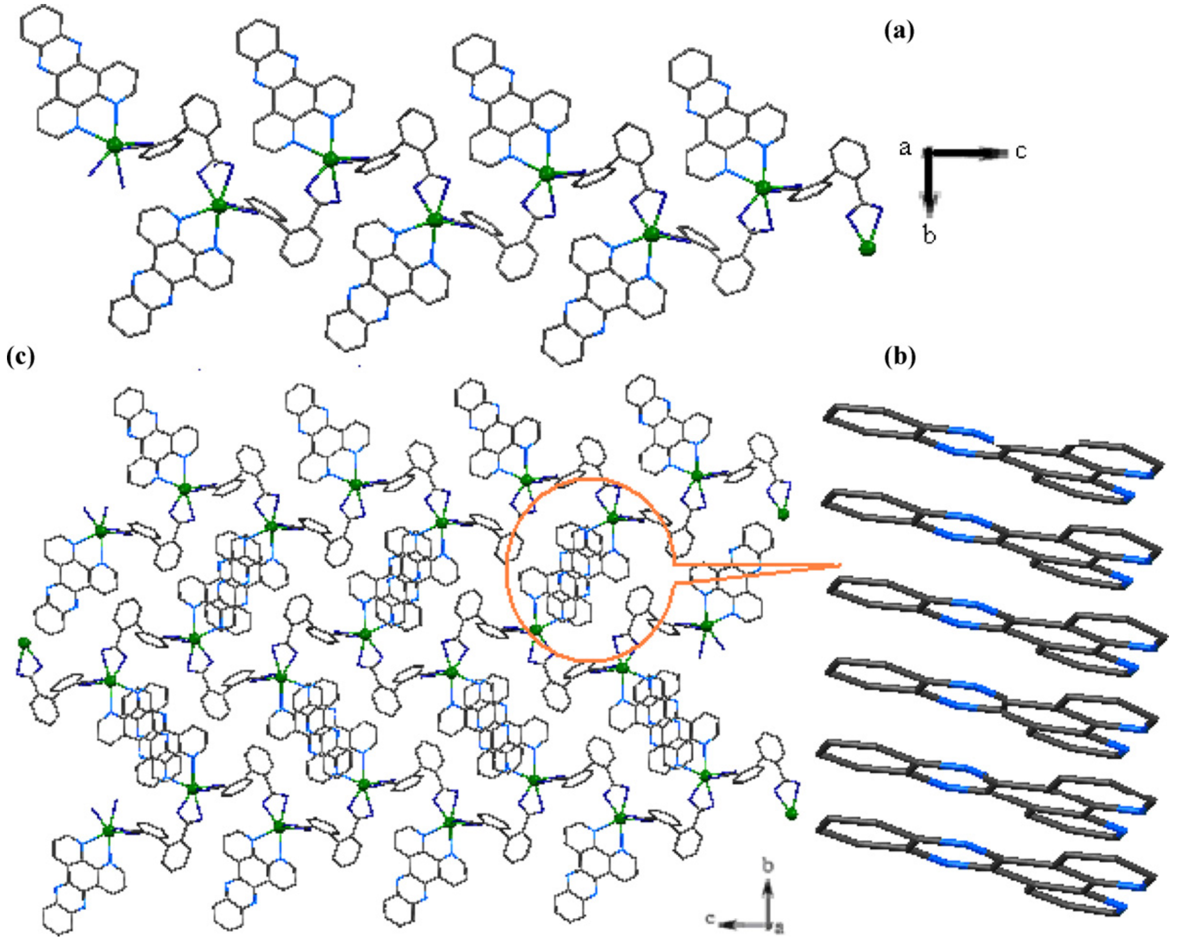


Fig. 24. (a) The helical chain structure of compound **60**, (b) the unusual 1D supramolecular dpdp arrays through two types of π–π interactions and (c) the 3D supramolecular structure of compound **60** formed through the 1D supramolecular dpdp arrays [15].

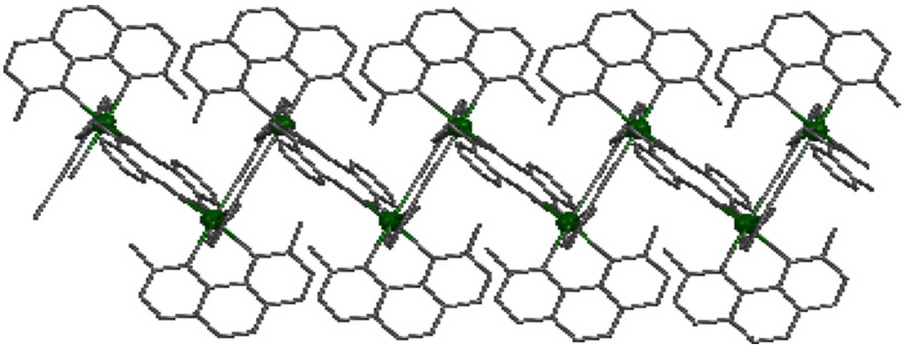


Fig. 25. A zigzag polymeric chain of compound **62** along the *c*-axis [100].

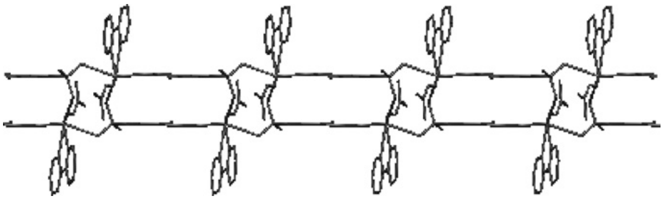


Fig. 26. A ladder-like chain of compound **63** [101].

$(H_2O)\}_n$ (**80**) [90], $\{Pb[B(Im)_4](C_6H_5COO)(0.5H_2O)\}_n$ (**81**) [112], $[Pb(8\text{-Quin})(4\text{-pyc})]_n$ (**82**) [113], $[PbCl(a4\text{-ptz})]_n$ (**83**) [114], $[Pb(Hssal)(2,2'\text{-bipy})(H_2O)]_n$ (**84**) [101] and $[Pb_2(Bs\text{-glu})_2(phen)_2]_n$ (**85**) [115] form 2D mixed–ligand complexes with chelating (η^2) mode. Compound **78** is composed of three lead(II) ions, Pb1 is four-coordinate and its coordination geometry is described as a ψ-PbO_4 with the fifth coordination site occupied by the lone pair of electrons. Pb2 and Pb3 are five-coordinate and their coordination geometry is described as a ψ-PbO_5 octahedron with the sixth site occupied by the lone pair of electrons (Fig. 27).

In compound **80** the carboxylate is bi-donor with both oxygens coordinating to the lead(II) atom in an asymmetric fashion. The lead(II) borate units form two-dimensional layers in compound **80**, with the lead(II) metal sites facing the layer interface. PROXYL anion binds to the Pb sites in solid state and occupies the interlayer spacing.

3.2.4. Three-dimensional coordination polymers

Complexes $[Pb(Pra_2biim)(H_2O)]_n{\cdot}nH_2O$ (**86**) [116], $[Pb(2,6\text{-DHB})_2]$ (**87**) [117], $\{[Pb(bpacb)(OAc)]{\cdot}DMF\}_n$ (**88**) [118], $[Pb(tsgly\text{-}N,O){\cdot}H_2O]$ (**89**) [119] and $[Pb(3\text{-pyc})_2]_n$ (**90**) [120] form 3D coordination polymers. In compound **86** ligand H_2biim forms helical coordination polymer in either cis or trans coordinating mode. Pra_2biim^- uses all six coordinating atoms available including four chelating carboxylate O and two N atoms. The most striking feature of **86** is the microporous structure featuring hexagonal channels constructed from left and right-handed helical chains (Figs. 28 and 29). The centered space group yields the two types (R and L) of helical tubes alternately arranged around the hexagonal channels. As it can be seen from Fig. 29c and d, the two carboxyl arms of Pra_2biim^- chelate the two metal centers to inter-connect the helical tubes into a unique open framework (Fig. 28).

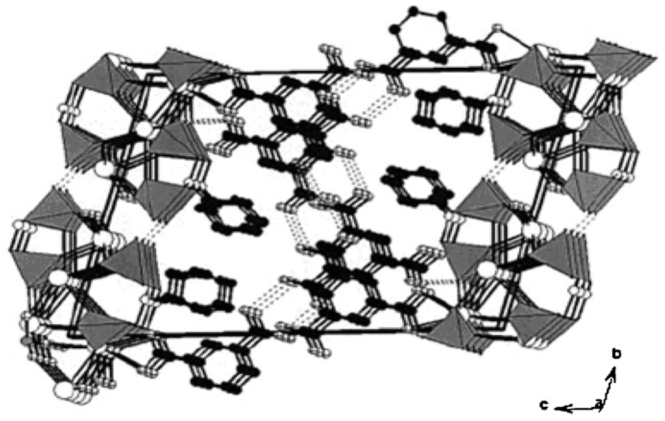


Fig. 27. View of the structure of complex **78** down the *a*-axis; the C–PO_3 tetrahedra are shaded in grey, and Pb, N, O and C atoms are represented by open, octanded, crossed and black circles, respectively; hydrogen bonding is drawn as dotted lines [111].

In compound **87**, the lead(II) atoms are coordinated to eight oxygen atoms with a distorted dodecahedral environment (PbO_8). Each carboxylate group of the DHB binds with a single Pb(II) atom in a chelating coordination mode. Each PbO_8 polyhedron is connected to six DHBs and each DHB coordinates to three Pb(II) atoms forming a 3,6-connected three-dimensional net. The three-dimensional structure consists of infinite one-dimensional channels along two directions. The three-dimensional net structure has π–π interactions involving the aromatic rings. In compound **88** the Pb(II) atoms are in the hemidirected geometry. One of oxygen atoms from $bpacb^-$ ligand is a bridging (η^2) and connects lead(II) atoms to each other. The polymeric structure has large pores that consist of DMF as guest molecules and the hydrogen bonding is the important interaction for DMF stability in pores. Oxygen atoms of DMF molecule and acetate anion connect to amidic nitrogen of terminal pyridine rings of ligand $bpacb^-$ by hydrogen bonding (O···N–H) (Fig. 30a). The nano-sized compound **88** is prepared by ultrasonic irradiation and characterized by powder XRD and SEM. The average size of the particles is 60 nm (Fig. 30b). Also nanobelts of a lead(II) coordination polymer, are synthesized by a sonochemical method with average size of about 90 nm (Fig. 31b). The carboxylate moiety of the 3-pyc^- ligand acts in chelating (η^2) mode, where two oxygen atoms of the carboxylate group bidentately coordinate to a lead(II) ion, creating a four-membered chelate rings (Fig. 31a).

3.3. Bridging (μ_2-η^2) mode

3.3.1. Discrete complexes

Complex $[Pb(H\text{-}Norf)(ONO_2)_2]_2$ (**91**) [121] forms an antibacterial drug norfloxacin as a ligand and the heavy-metal lead(II). Compound **91** is a dimer in which the two lead(II) ions are bridged by two oxygen atoms derived from two carboxylate groups (mono-donor bridging). Each lead(II) is coordinated in a distorted trigonal–bipyramidal coordination environment by the carboxylate oxygen atoms, quinolone carbonyl and oxygen atoms derived from two mono-donor nitrate anions. The nitrogen atom of the piperazine ring is protonated and thereby loses its coordination ability. The Pb···Pb separation within compound **91** is 4.0852(4) Å,

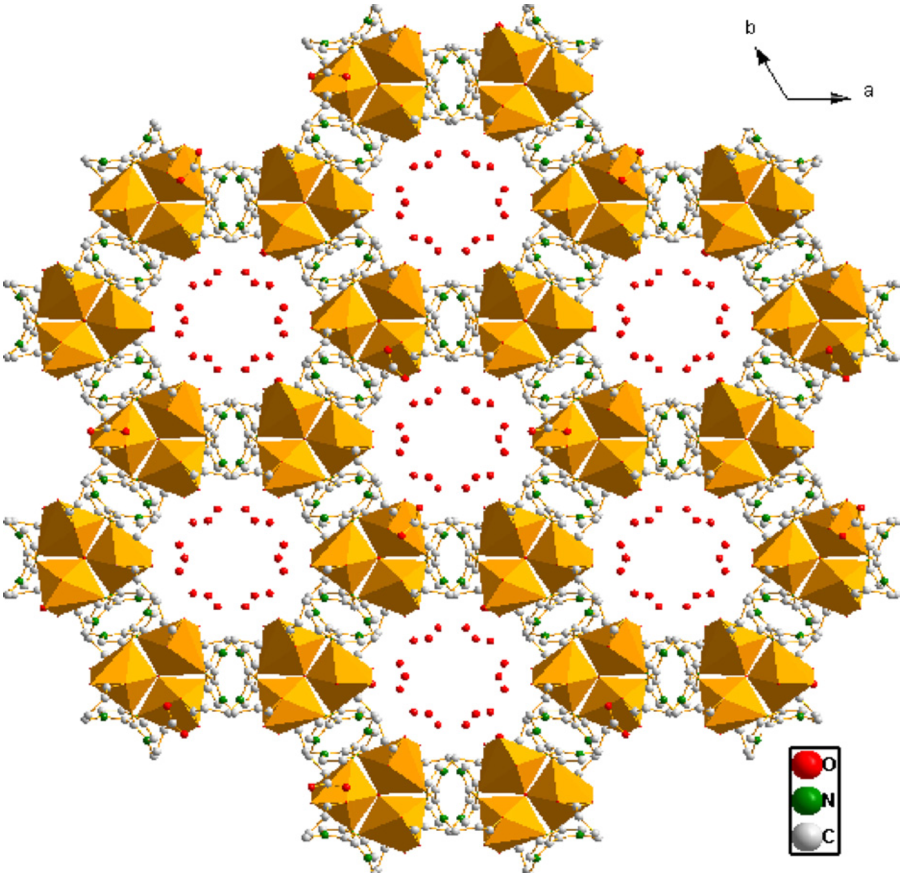


Fig. 28. Polyhedral representation of the microporous open framework in compound **86** [116].

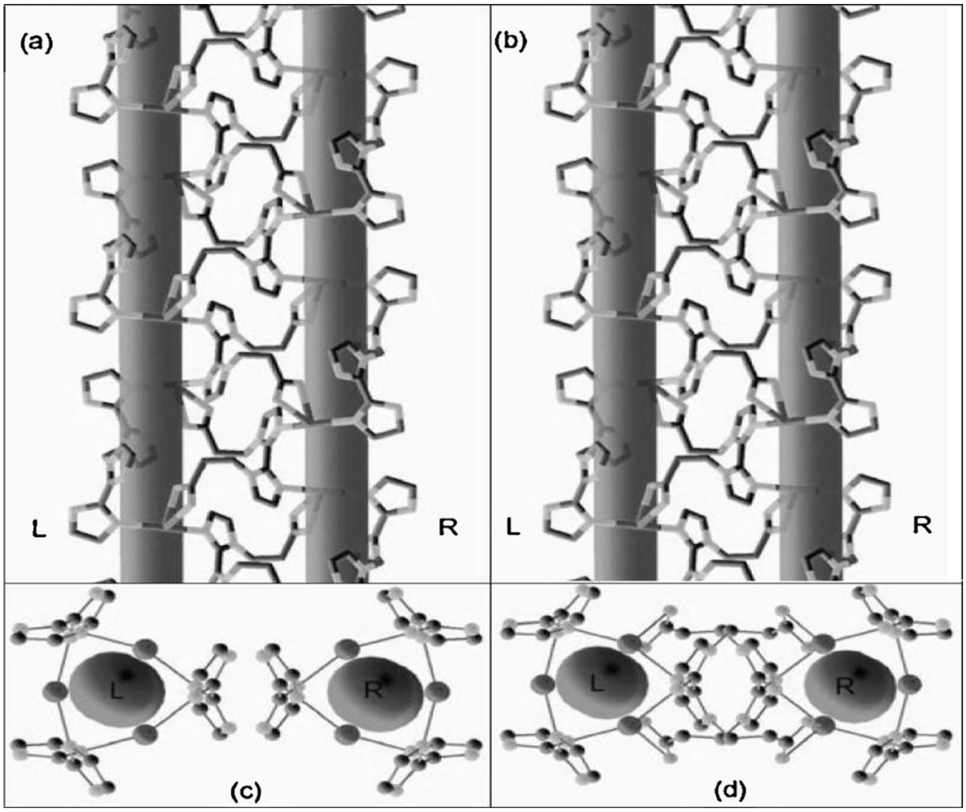


Fig. 29. (a) View of the helical chains along *b*-axis and (b) view along the *c*-axis. (c and d) Neighboring helical chains are interconnected by the carboxyl arms of Pra_2biim [116].

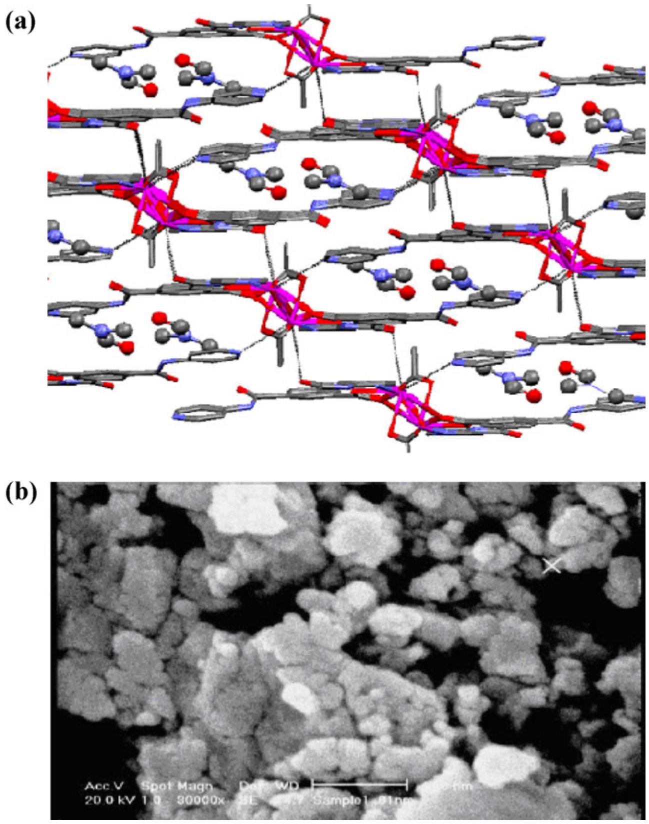


Fig. 30. (a) A perspective view of the packing down the *b*-axis in compound **88**, showing the free DMF molecules lying in the pores and (b) SEM image of nano-sized compound **88** [118].

which is somewhat longer than that of the lead(II) citrate aqueous complex. Interaction between oxygen and nitrogen atoms extends to a 1D structure (Fig. 32).

3.3.2. One-dimensional coordination polymers

Compounds $[Pb(\mu\text{-}NO_2)(\mu\text{-pyc})(H_2O)]_n$ (**92**) [122], $[Pb(H_2O)_2DCP]_n$ (**93**) [123] and $[Pb(leu)(NO_3)]$ (**94**) [124] form one-dimensional coordination polymers. In compound **92** the lead(II) ion is coordinated by water molecules, 2-pyridinecarboxilate and nitrite ligands, resulting in seven-coordinate complex. The structure consists of $Pb(H_2O)$ units bridged by $NO_2{}^-$ and 2-pyc$^-$ ligands, thus forming two-dimensional infinite layers. The asymmetric unit in compound **94** contains two independent $Pb(leu)(NO_3)$ moieties. The metal center is coordinated to a non-zwitterionic leucinato ligand, through the amine N and one O carboxylate atom and to a nitrate anion. Both ligands bridge two symmetry related Pb(II) ions, forming a zigzag 1D polymeric framework (Fig. 33). In the case of compound **94**, two polymeric 1D chains run along the short axis [0 1 0]. The coordination sphere is PbO_6N with the hemidirected geometry and the lone pair is located trans to the leu ligand.

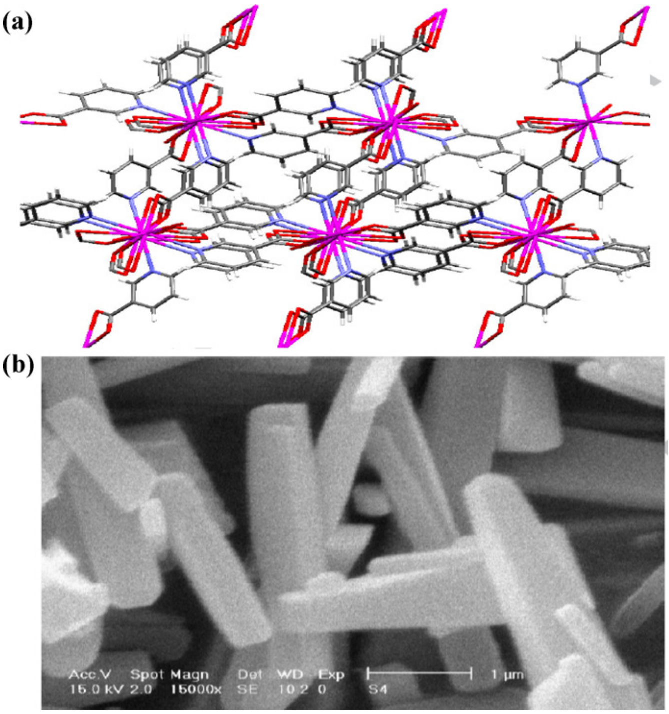


Fig. 31. (a) Depiction of three-dimensional network in compound **90** and (b) SEM photograph of compound **90** nanobelts [120].

3.3.3. Two-dimensional coordination polymers

In $[Pb(2\text{-pyc})(N_3)(H_2O)]_n$ (**95**) [125] the lead(II) ion is coordinated by 2-pyc$^-$, water and $N_3{}^-$ ligand and coordination number in this complex is six. The building blocks of $[Pb_2(\mu\text{-}H_2O)_2]$ are bridged by the $N_3{}^-$ and 2-pyc$^-$ anions and each lead(II) atom is coordinated by three oxygen atoms of 2-pyc$^-$ ligands, two water molecules and three nitrogen atoms of azide anions. The carboxylate moiety of the 2-pyc$^-$ ligand acts as a bridging group where two oxygen atoms of the carboxylate group bidentately coordinate to a lead(II) ion, creating a four-membered chelate ring (Fig. 34a). One of them also bridges two adjacent lead(II) ions. There is not any vacant site on lead(II) environment and the X–Pb–X angle shows that the coordination sphere of the lead(II) is holodirected. Nanostructure of compound **95** is prepared by sonochemical method and the SEM shows that it is composed of rods with size of about 80 nm, with all rods arranged so that they form a strawberry network (Fig. 34b). The asymmetric unit in the compound $[Pb_3L_2{}^{13}\text{-}H_2O]_n$ (**96**) [126] contains three unique Pb(II) ions, two carboxylate-phosphonate ligands and a lattice water molecule. Both Pb(1) and Pb(2) are five coordinated by a tri-donor chelating ligand and two phosphonate oxygen atoms from two neighboring ligands. Pb(3) is five-coordinated by two carboxylate and three phosphonate oxygen atoms from five ligands and all carboxylate groups are unidentate. The inter-connection of the lead(II) ions via bridging phosphonate ligands forms a 2D lead(II) carboxylate phosphonate layer. The lattice water molecules are located at the

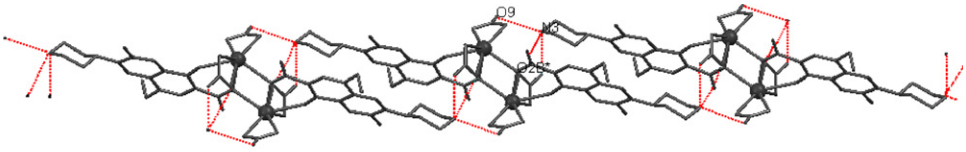


Fig. 32. A fragment of the one-dimensional polymer in compound **91** formed through O···N interactions [121].

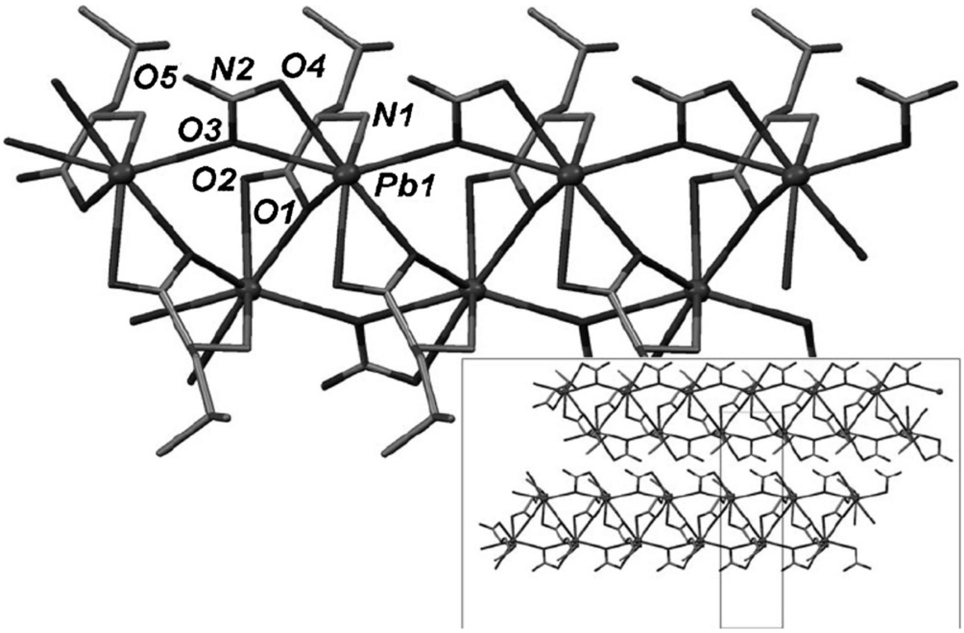


Fig. 33. A part of the polymeric structure of compound **94**. Labeled atoms belong to the asymmetric unit [124].

interlayer space and form hydrogen bonding with non-coordinated carboxylate oxygen atoms.

4. Tri-donor coordination mode

4.1. Bridging (μ_3-η^1:η^2) mode

4.1.1. Two-dimensional coordination polymer

In the complexes $[Pb_3L_2{}^{13}(H_2O)]$ (**97**) [126], $[Pb(L^{14})(\mu_2\text{-}Cl)(H_2O)]_n$ (**98**) [127], $\{[Pb(3\text{-sb})(H_2O)_2]\cdot 4,4'\text{bpy}\}_n$ (**99**) [128], $[(OPb_2)_2(ox)(NO_3)_2]_n$ (**100**) [129], $[Pb(sa)]_n$ (**101**) [130] and $[Pb(2\text{-pyc})(NCS)]_n$ (**102**) [131] the carboxylate groups act as tri-donor coordination mode. The asymmetric unit of $[Pb_3L_2{}^{13}(H_2O)]$ (**97**) contains three unique Pb(II) ions, Pb(1) and Pb(2) each is six-coordinated by one tridentate chelating carboxylate-phosphonate ligand and three phosphonate oxygen atoms. The inter-connection of lead(II) ions through bridging carboxylate and phosphonate groups results in the formation of a double layer. In the metal carboxylate chain, each pair of lead(II) ions is bridged by a pair of carboxylate groups, and the lattice water molecules are located in the middle of the inter-layer space. Compound **97** has the same empirical formula as **96** that is synthesized by hydrothermal method. However, different coordination modes of ligand L^{13} in compounds **96** and **97** produce different layer structures. In compound **98** the deprotonated L^{14} ligand adopts tetra-donor bridging mode. One carboxylate group is coordinated to one Pb(II) ion, then one of the coordinated oxygen atoms of carboxylate via tri-donor bridging mode and one pyrazine nitrogen atom are further linked to the neighboring Pb(II) atom. The lead(II) is coordinated by three carboxylate oxygen atoms and one nitrogen atom from L^{14} ligand, one water molecule (O3) and two bridged chloride atoms. Pb(II) ions are extended via bridging carboxylate groups and bridging chloride atoms into a 2D layer structure. It is interesting that infinite Pb–O–Pb and Pb–Cl–Pb helical chains can be observed with a helical pitch. In one layer right-handed Pb–O–Pb and left-handed Pb–Cl–Pb are inter-connected via Pb(II) ions as hingers while in the other, the neighboring one the opposite chiral Pb–O–Pb and Pb–Cl–Pb helical chains are inter-linked (Fig. 35).

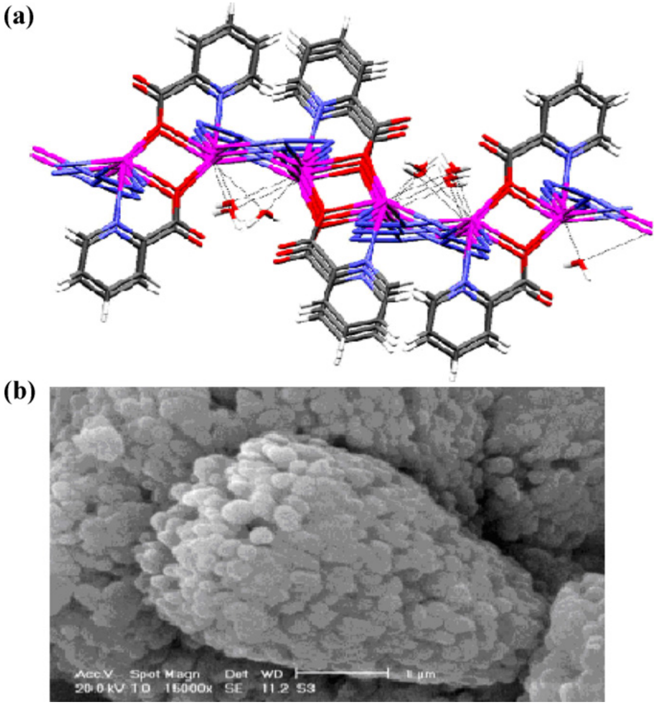


Fig. 34. (a) Fragment of the two-dimensional polymer in **95** and (b) SEM photograph of compound **95** nano-strawberry [125].

In compound **99**, the Pb(II) atoms are linked by 3-sulfonatobenzoate anions as μ_4-bridging coordination mode to give double layers. The carboxylate groups are coordinated to two Pb(II) atoms through a tri-donor bridging mode, and form a two-dimensional coordination polymer. Ligand 4,4′-bipyridine is uncoordinated and is linked to coordinated water molecules via O–H···N hydrogen bonding. As a result of hydrogen bondings between uncoordinated 4,4′-bipyridine and coordinated water molecules the double layer structure is extended to give a 3D supramolecular network (Fig. 36). In compound **102** the lead(II) ions are coordinated by both NCS^- and pyc^- anions, resulting in a two-dimensional framework (Fig. 37a). The carboxylate moiety of

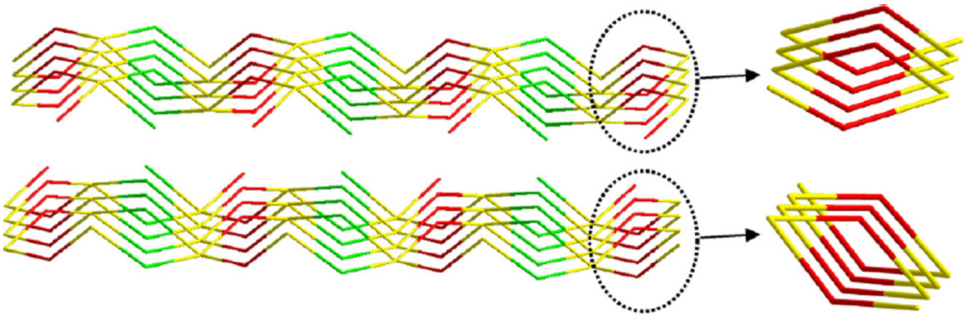


Fig. 35. Side view of the 2D layers indicating neighboring layers contain the opposite chiral Pb–O–Pb helical chains (yellow: lead(II) ions; red: oxygen; green: chloride atoms, the other atoms are omitted for clarity) [127].

the pyc⁻ ligand acts as tri-donor bridging (μ_3-η^1:η^2) coordination mode. Nano-particles of compound **102** have been prepared by sonochemical method and the average size of the particles is around 55 nm (Fig. 37b).

4.1.2. Three-dimensional coordination polymers

Compounds $[PbCl(L^{15})]_n$ (**103**) [132], $Pb_2(OH)_2[p\text{-}O_2C\text{–}C_6H_4\text{–}CO_2]_n$ (**104**) [133], $[Pb(tart)]_n$ (**105**) [134], $Pb(L^{16})(H_2O)]_n$ (**106**) [135], $[Pb_2(4\text{-pyc})_2I_2(H_2O)]_n$ (**107**) and $[Pb(3\text{-pyc})I]_n$ (**108**) [136] are three-dimensional coordination polymers and the carboxylate groups in these coordination polymers act as tri-donor bridging (μ_3-η^1:η^2) coordination mode. In compound **103** each of the zwitterionic N,N′-diacetate imidazolium anions acts as bridging ligand and links four lead(II) atoms. The Pb(II) atoms are eight-coordinated with a significantly distorted monocapped pentagonal bipyramidal geometry by two μ_2-Cl and six oxygen atoms from four carboxylate groups. Along *c*-axis, the monocapped pentagonal bipyramidally coordinated Pb(II) atoms are connected by the N,N′-diacetate imidazolium anions into one-dimensional right-handed helical chains (Fig. 38a). Each helical unit includes five Pb(II) atoms and four zwitterionic ligands, and the right-handed helix is generated from the crystallographic 4_1 axis. The infinitely right-handed helical chains are held together to form a 3D homochiral porous metal–organic framework. A space-filling model shows the open rectangular channels in the individual framework (Fig. 38b).

Compounds **107** and **108** are three-dimensional neutral metallopolymers bridged by 4-pyc⁻ and 3-pyc⁻, water and iodide ligands, thus forming infinite frameworks (Figs. 39a and 40a). The carboxylate moiety of the pyc⁻ ligands in these compounds acts as both a bi-donor and a bridging group (totally tri-donor) in μ_3-η^1:η^2 coordination mode, where two oxygen atoms of the carboxylate group bidentately coordinate to a lead(II) ion, creating a four-membered chelate ring. Nano-particles of compounds **107** and **108** were prepared by sonochemical method. The SEM photograph shows that the compounds **107** and **108** are nano-fiber and nano-particles, respectively (Figs. 39b and 40b).

4.2. Chelating, bridging (μ_2-η^2:η^1) mode

4.2.1. Discrete complexes

Compounds $[Pb_2(sbc)_2(phen)_2]\cdot 2H_2O$ (**109**) [137], $[Pb(phen)(OAc)(NCS)]_2$ (**110**) [138], $[Pb(pyterpy)(l\text{-}OAc)]_2(ClO_4)_2$ (**111**) [139], $[(trenMe_6)Pb(OAc)]_2(BPh_4)_2$ (**112**) [140] and $[\{PbL^{17}(OAc)\}_2][BPh_4]_2\cdot 2EtOH$ (**113**) [141] form discrete structure. In complex **109**, each Pb(II) atom coordinates to three O atoms from two carboxylate groups of sbc anions, and to two N atoms from phen ligand. In addition, each sbc anion acts as a tetra-

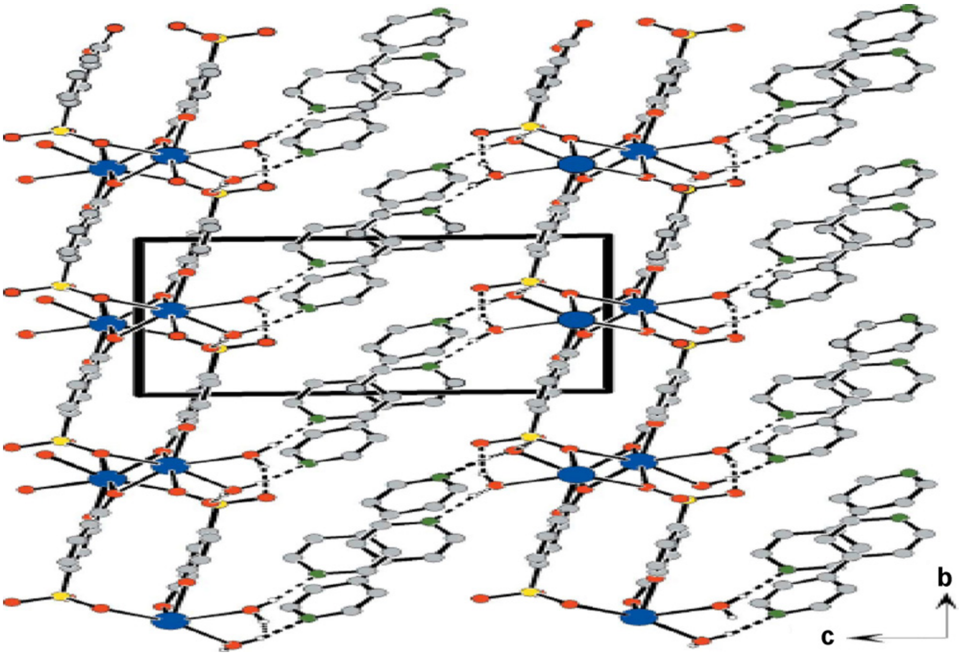


Fig. 36. Packing diagram of compound **99**. H atoms, except those of water molecules, have been omitted [128].

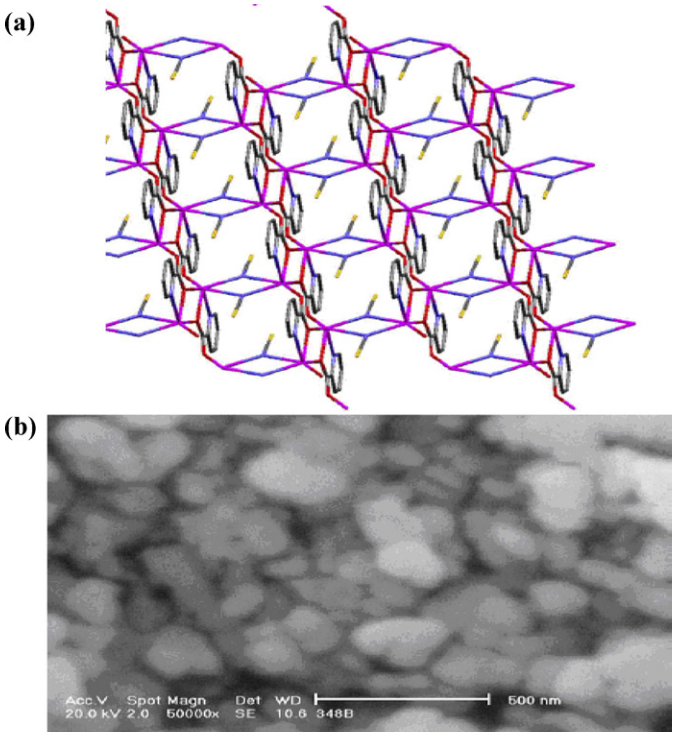


Fig. 37. (a) Fragment of the two-dimensional polymer in compound **102** and (b) SEM photograph of compound **102** nano-particles [131].

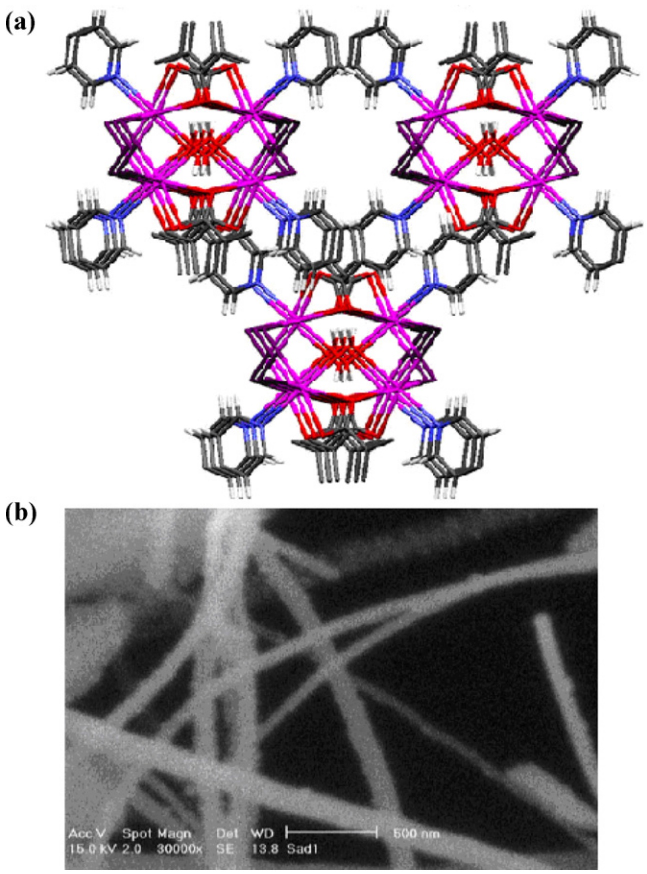


Fig. 39. (a) Fragment of the 3D polymer in compound **107** and (b) SEM photograph of compound **107** nano-fibers prepared by sonochemical method [136].

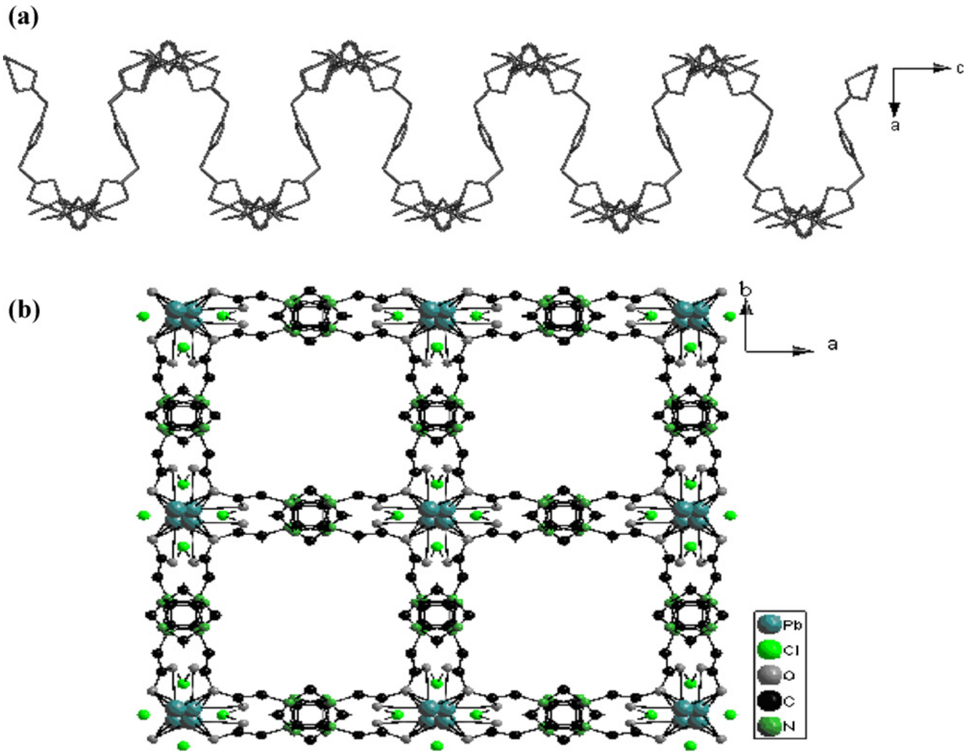


Fig. 38. (a) View of the right-handed helical chain in **103** and (b) a space-filling model showing the open rectangular nano-channels in the individual framework of compound **103** [132].

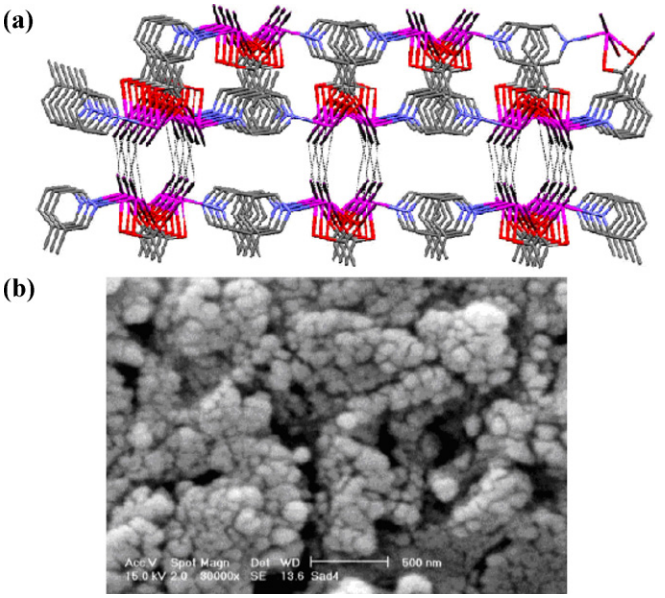


Fig. 40. (a) Fragment of the 3D coordination polymer and (b) SEM photograph of compound **108** nano-particles prepared by sonochemical method [136].

donor ligand, connecting two Pb(II) atoms through its bridging and chelating carboxylate group and its monodentate sulfonate group. Each pair of Pb(II) atoms are therefore connected by two different kinds of bridge, namely a carboxylate short bridge and a carboxylate–sulfonate long bridge. There is also a special position of $\bar{1}$ site symmetry at the center of the two Pb(II) atoms (Fig. 41). Complex **110** consists of dimeric units of $[Pb(phen)(OAc)(NCS)]_2$. Each lead(II) atom is coordinated by the nitrogen atoms of phen and thiocyanate ligands as well as oxygen atoms of an acetate ligand with Pb–O distances of 2.322 and 2.674 Å. The weak interaction of lead(II) with oxygen atoms of an adjacent molecule produces dimer units in the solid state. In fact, each Pb(II) atom in this structure with five normal bonds forms two 'weak' Pb···O bonds with the exact distances of Pb1···O2 = 3.190 Å. The presence of a lone pair of electrons on the lead(II) atom is apparently the reason that the bridging interactions are so long. Hydrogen-bonding and π–π interactions grow the dimeric structure to one-dimensional chains. In compound **111** the dimer units are also aligned parallel to each other and inter-connected by weak $N_{pyterpy}$–$HC(CH_3-)$ hydrogen bonding and grow the dimeric structures into one-dimensional chains.

4.2.2. One-dimensional coordination polymers

In the one-dimensional coordination polymers of $\{[Pb(PAA)_2]_n$ (**114**) [142], $[Pb(MPAcO)_2]_n$ (**115**) [143], $[Pb(\mu_2\text{-dpmta})_2(H_2O)_2]_n$ (**116**) [144], $[Pb_2(NO_3)(ba)_3(phen)_2]$ (**117**) [145] and $[PbPh_2(GTSC)]\cdot H_2O$ (**118**) [146] the carboxylate groups act as tri-donor ligand with both chelating and bridging mode. In compound **114** the lead(II) atoms are six-coordinate and each PAA^- anion acts as a three-connecting ligand. The carboxylate groups of the PAA^- ligand act as both bi-donor chelating, and bridging group where two oxygen atoms of the carboxylate group coordinate to a lead(II) ion, also one of these oxygen atoms bridges to other lead(II) atom. The lone pair of lead(II) is 'active' and the arrangement of O-atoms suggests a gap or a hole in coordination geometry around the Pb(II) atoms. An observed gap possibly occupied by a 'stereo-active' electron lone pair. This lead(II) coordination polymer shows some Pb···C interactions and involve an η^4 interaction with the phenyl groups of neighboring molecules. Hence, the Pb(II) coordi-

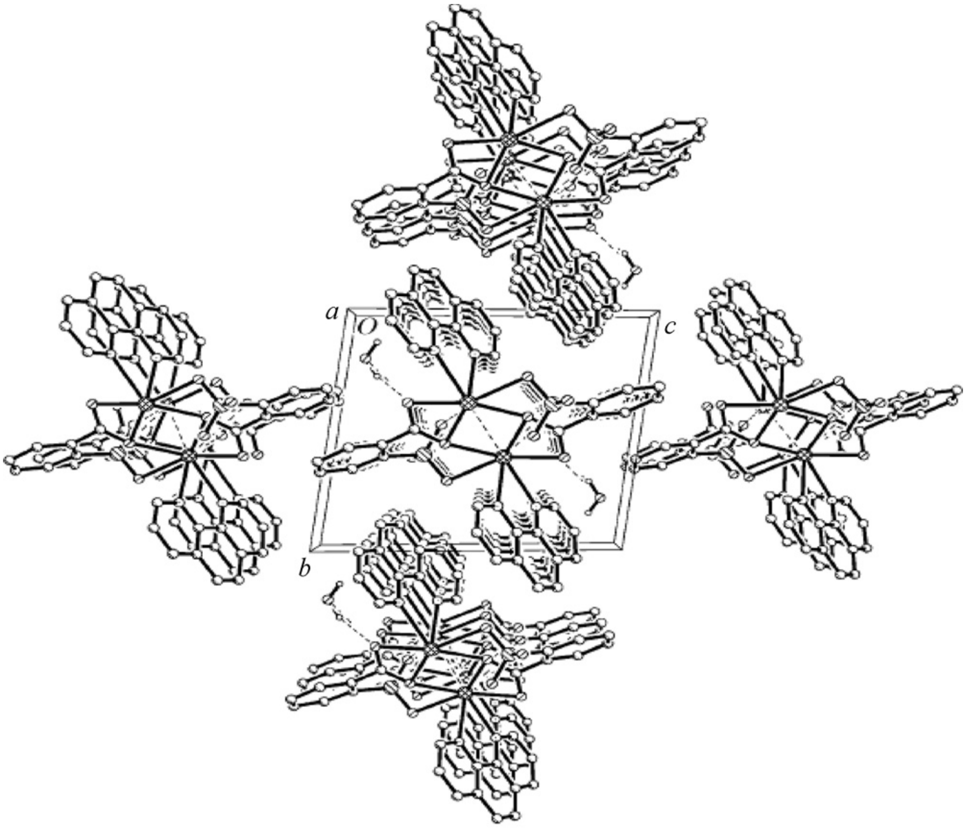


Fig. 41. A perspective view of the molecular packing of **109** along the *a*-axis, illustrating the hydrogen bonding and π–π interactions [137].

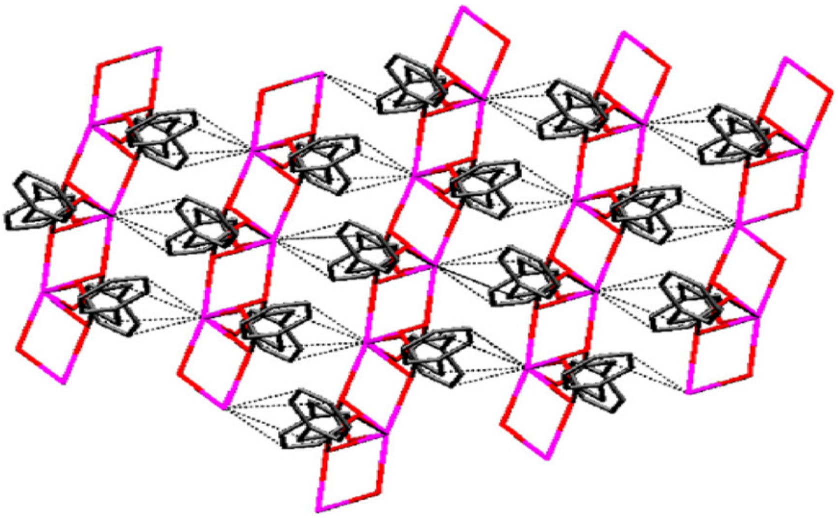


Fig. 42. 2D packing of **114** and Pb···C interactions [142].

nation sphere is completed and rather than a PbO_6 coordination sphere, the complex contains a tetrahapto (C_4O_6Pb) center with an irregular ten coordination number (Fig. 42).

Compound **115** has an one-dimensional structure and the lead(II) atoms are six-coordinate. The carboxylate group of the $MPAcO^-$ ligand acts as both bi-donor chelating and bridging group where two oxygen atoms of the carboxylate group coordinate to a lead(II) ion, also one of these oxygen atoms bridge to other lead(II) atom (Fig. 43a). Nano-structure of this compound has been synthesized by a sonochemical method and the average size of the particles is around 85 nm (Fig. 43b). Compound **116** has also 1D chain structure consisting of two kinds of rhomboidal Pb_2O_2 rings, in which a large amount of H-bonding is involved. By π–π interactions parallel chains are further assembled to a 2D supramolecular network.

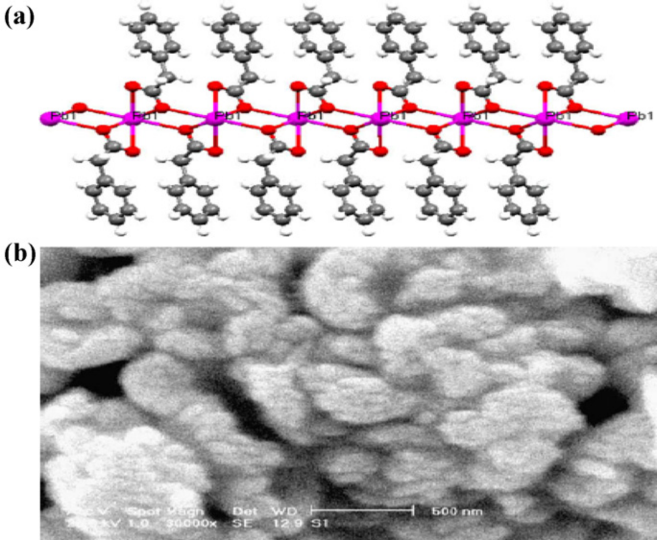


Fig. 43. (a) A one-dimensional chain of compound **115** and (b) SEM photograph of compound **115** nano-particles [143].

4.2.3. Two-dimensional coordination polymers

Compound $[Pb_3(ssal)_2(phen)_3]_n$ (**119**) [101] is a 2D structure and in this complex there are three types of Pb(II) ions with coordination numbers 6, 7 and 8. Each carboxylate group of $ssal^{3-}$ ligand acts as chelating and bridging modes (totally tri-donor) where the two O atoms coordinate to a Pb(II) ion and one of them is bridged to an adjacent Pb(II) ion (Fig. 44).

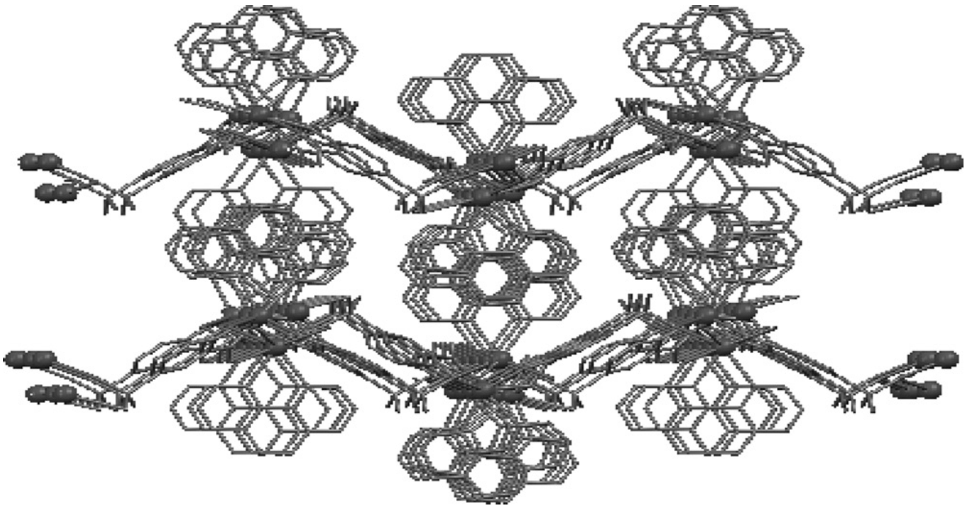


Fig. 44. Fragment of the two-dimensional coordination polymer in compound **119** [101].

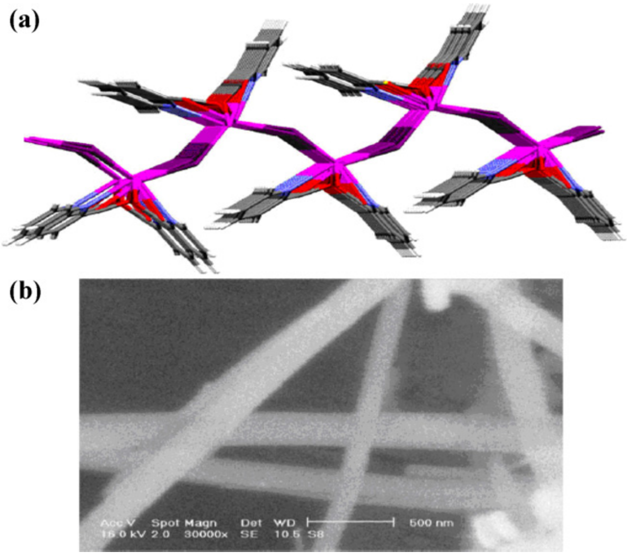


Fig. 45. (a) A two-dimensional packing of compound **120** and (b) SEM photograph of compound **120** nano-wires [147].

Two isostructure lead(II) complexes, $[Pb_2(2\text{-pyc})_2(I)_2]_n$ (**120**) and $[Pb_2(2\text{-pyc})_2(Br)_2]_n$ (**121**) [147], are synthesized by a sonochemical method and produce the nano-sized coordination polymers. The average size of the particles is around 98 and 95 nm for compounds **120**–**121**, respectively. The carboxylate moiety of the pyc⁻ ligand in these compounds acts as both a bi-donor and a bridging group (totally tri-donor) in a μ_2-η^2:η^1 mode (Figs. 45 and 46).

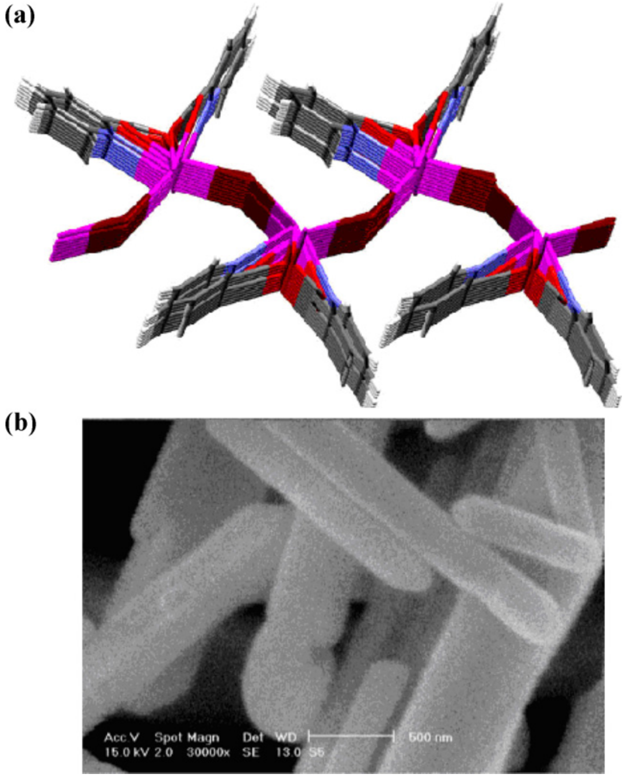


Fig. 46. (a) A two-dimensional packing of compound **121** and (b) SEM photograph of compound **121** nano-rods [147].

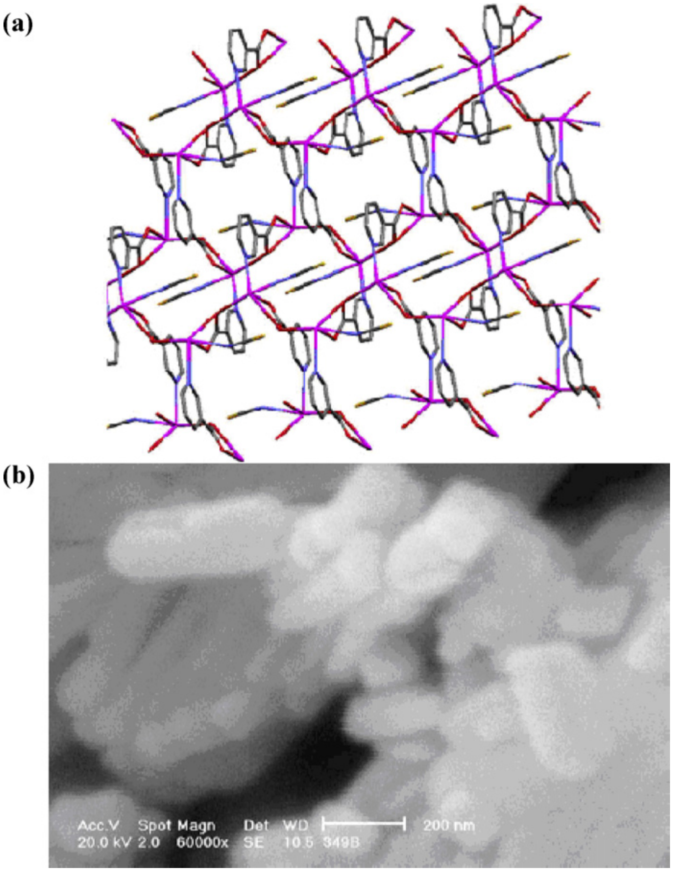


Fig. 47. (a) A two-dimensional packing of compound **122** and (b) SEM photograph of compound **122** nano-rods [131].

The carboxylate moiety of the pyc⁻ ligand in $[Pb(3\text{-pyc})(NCS)]_n$ (**122**) [131] acts as both a bi-donor and a bridging group (totally tri-donor) in a μ_2-η^2:η^1 mode, where two oxygen atoms of the carboxylate group bidentately coordinate to a lead(II) ion, creating a four-membered chelate ring. One of them also bridges two adjacent lead(II) ions, yielding a two-dimensional coordination polymer. The X–Pb–Y angles in this compound suggest that there is a vacant site in the coordination sphere of the lead(II) atom due to lone pair-bond pair repulsion. Hence, the geometry of the nearest coordination environment of every lead(II) atom is likely caused by an interplay of several factors: the geometrical constraints of the coordinated NCS⁻ and pyc⁻ anions and the influence of a stereo-chemically active lone pair of electrons. Nano-particles of compound **122** are prepared by sonochemical method and the size of the particles is around 55 nm (Fig. 47).

In $\{[Pb(phen)(sb)]\cdot nH_2O\}_n$ (**123**) [148] both the sulfonyl and carboxy groups of the sb ligand bridge the neighboring Pb(II) atoms to form a two-dimensional sheet structure. Three kinds of metal-containing rings, [Pb···O···Pb···O], $[Pb\cdots sb\cdots Pb\cdots SO_3]$ and [Pb···sb···Pb···sb], are observed in the sheet network. Compounds $[Pb(bpy)(OAc)(ClO_4)]_n$ (**124**) [149], $\{Pb_2(H_2Hmdta)(NO_3)_2\cdot 6H_2O\}_n$ (**125**) [57], $\{[Pb(bzgly\text{-}O)_2]\cdot 4H_2O\}_n$ (**126**) [119] and $[PbCl(atza)]_n$ (**127**) [114] form two-dimensional coordination polymers. In this compounds the carboxylate groups are coordinated to lead(II) atoms as both a bi-donor chelating and a bridging group in a μ_2-η^2:η^1 mode.

4.2.4. Three-dimensional coordination polymers

Compounds $[Pb(\mu_3\text{-Nic})_2]_n$ (**128**) [150] and $\{[Pb(1,4\text{-bdc})(C_2H_5OH)]\cdot(C_2H_5OH)\}_n$: MOF-70 (**129**) [53] form nonporous and porous three-dimensional coordination polymers, respectively. The porous three-dimensional coordination polymers

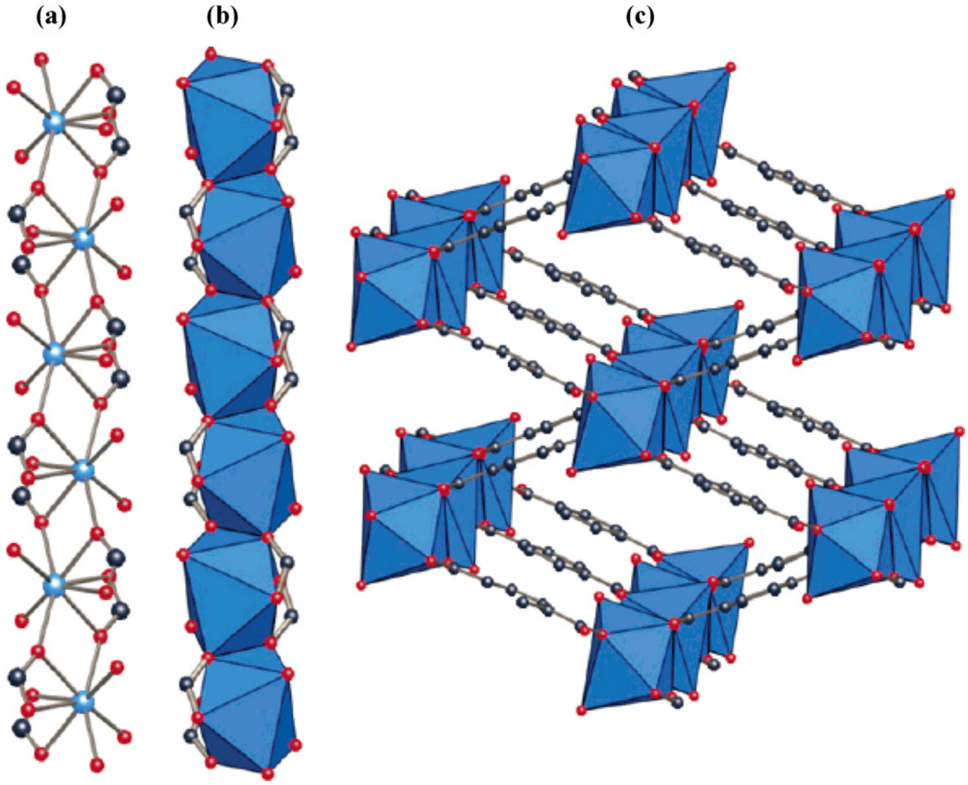


Fig. 48. $\{[Pb(1,4\text{-}bdc)(C_2H_5OH)]\cdot(C_2H_5OH)\}_n$; MOF-70: ball-and-stick representation of SBU (a) SBU with Pb shown as polyhedra (b) and view of crystalline nano-porous framework with inorganic SBUs linked together via the benzene ring of 1,4-benzenedicarboxylate (c) (EtOH guest molecules have been omitted for clarity) [53].

from heavy metals such as lead(II) have rarely been reported. However the compound **129** is first lead(II) metal–organic framework (MOF 70) and the Pb–O–C rods in this compound are constructed from 8-coordinated Pb(II) centers, where each is bonded to carboxylate groups of four 1,4-bdc linkers (Fig. 48). This connectivity pattern is repeated infinitely to create Pb–O–C rods along the *a*-direction and to give edge shared PbO_8. The rods are linked by the benzene rings of 1,4-bdc, which connect each rod to four neighboring rods in the *c* and *b* directions, generating 13.1×5.4 Å^2 one-dimensional rhombic nano-channels in the *a* direction.

5. Tetra-donor coordination polymers

5.1. Chelating, bridging (μ_3-η^1:η^2:η^1) mode

5.1.1. One-dimensional coordination polymers

The acetate anions in the compounds $[Pb(phen)(OAc)(O_2NO)]$ (**130**) [151] and $[Pb(phen)(OAc)(O_2ClO_2)]$ (**131**) [152] act as a tetra-donor ligands with both chelating and bridging (μ_3-η^1:η^2:η^1) mode. In compound **130** the Pb(II) atom has an asymmetrical eight coordination and the arrangement of ligands suggests a hemidirected geometry (Fig. 49).

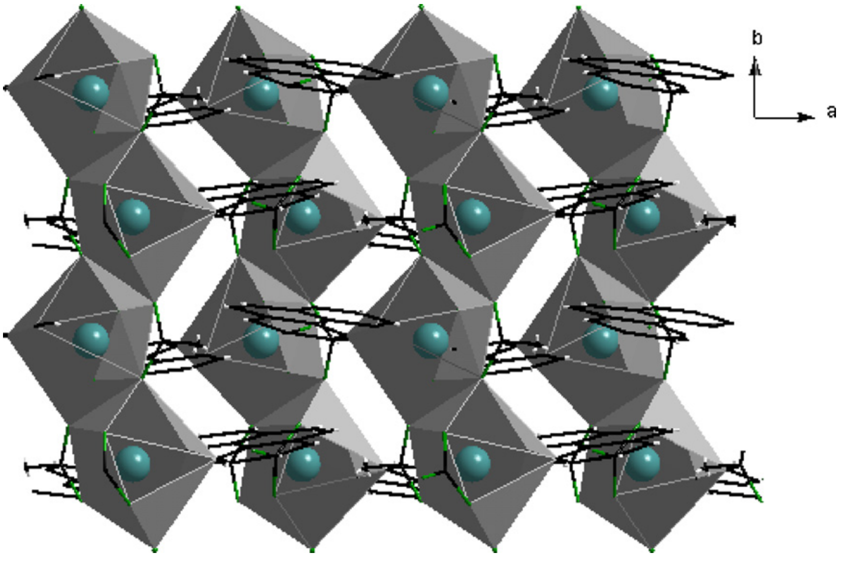


Fig. 49. A fragment of the one-dimensional chain in compound **130** [151].

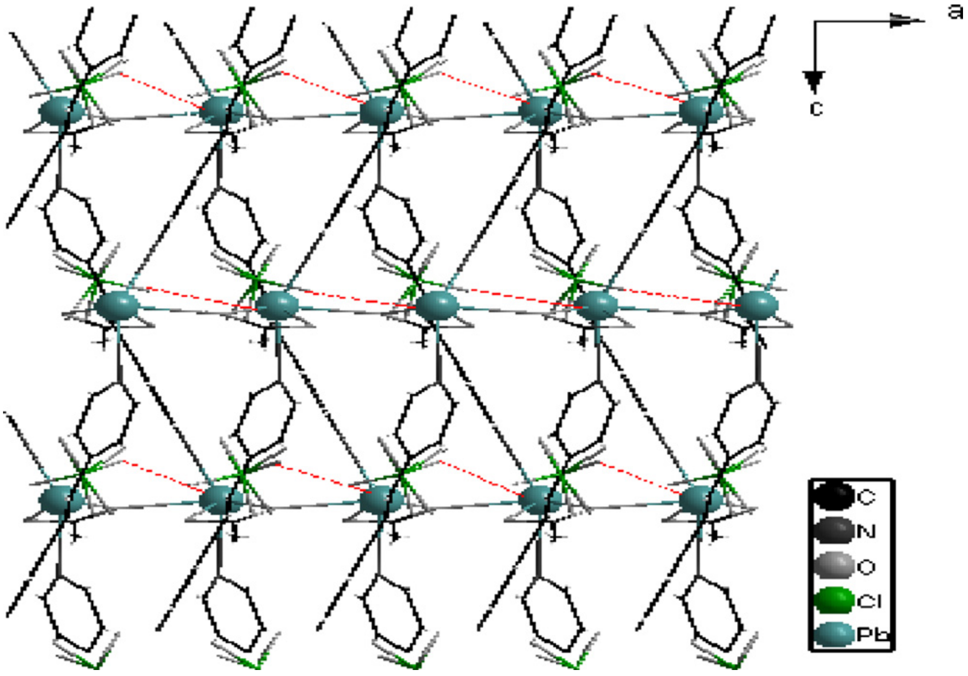


Fig. 50. Fragment of the two-dimensional layer in **132** viewed along the *b*-axis [153].

5.1.2. Two-dimensional coordination polymers

The structure of $\{[Pb(\mu\text{-OAc})(\mu\text{-ebp})](ClO_4)\}_n$ (**132**) [153] consists of $[Pb(\mu\text{-OAc})(\mu\text{-ebp})]^+$ cations and ClO_4^- anions. The cationic complex is a two-dimensional framework, in which Pb(II) atoms are bridged by both OAc^- and ebp ligands as illustrated in Fig. 50. The carboxylate moiety of the OAc^- ligand acts as both bidentate and bridging group (totally tetra-donor) where the two oxygen atoms of the carboxylate group bidentately coordinate to Pb(II) atoms, creating a four-membered chelate ring, and one of them also bridges two adjacent Pb(II) atoms, yielding an one-dimensional chain. These one-dimensional chains are further linked by the ebp ligands and thus creating a two-dimensional coordination polymer (Fig. 50). Although ClO_4^- anions act as a counter-ion, it also makes weak interactions with the Pb(II) center. The arrangement of the ligands exhibits hemidirected geometry, and the coordination gap around the Pb(II) ion is possibly occupied by an active lone pair of electrons. The compound [Pb(1,2-CHDC)] (**133**) [154] is a layered coordination polymer and the eight oxygen atoms of the CHDC anions are coordinated to two crystallographically distinct lead(II) atoms. Each PbO_8 polyhedron is connected to three polyhedra, by sharing an edge and two faces, thus forming an infinite two-dimensional Pb–O–Pb (3,6-net) honeycomb layer.

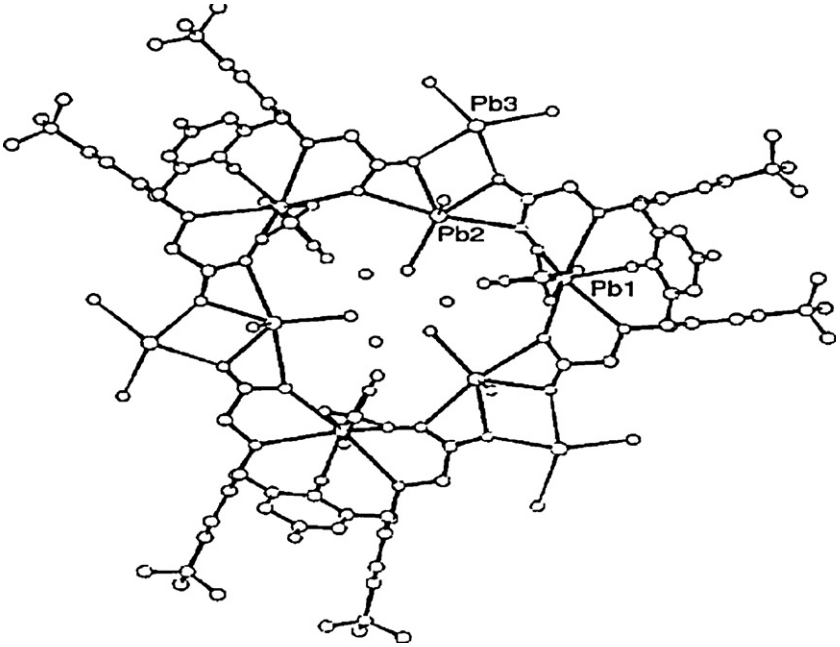


Fig. 51. The trimeric structure of compound **134** [155].

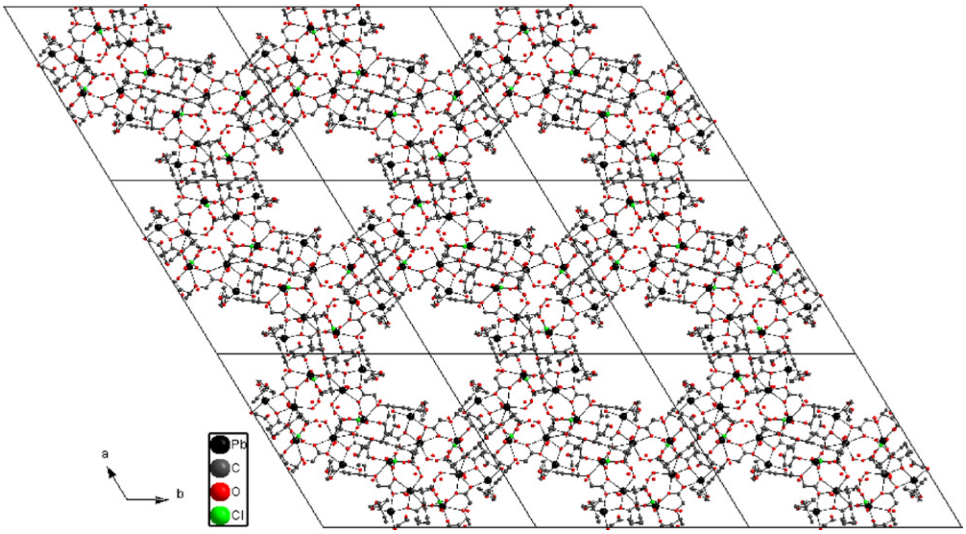


Fig. 52. Crystal packing of **134** in the *z* projection showing the presence of small channels within the trimer and large nano-channels between trimers [155].

5.1.3. Three-dimensional coordination polymers

Compounds $[Pb_9(L^{18}\text{-}2H)_3(ClO_4)_6(OH)_6]$ (**134**) [155], $[Pb(H_2O)(\mu\text{-}OAc)(\mu\text{-}sac)]_n$ (**135**) [156] and $[Pb_2(trz)_2(OAc)(NO_2)]_n$ (**136**) [17] form three-dimensional coordination polymers. Compound **134** consists of trimeric $[Pb_9(L^{17}\text{-}H)_3\text{-}(ClO_4)_6(OH)_6]$ units (Fig. 51) and there are three independent lead(II) atoms in the its structure. The lead(II) atom is ten or eleven coordinate and the $[Pb_9(L^{18}\text{-}2H)_3(ClO_4)_6(OH)_6]$ trimer contains a small channel around the 3-fold axis filled with disordered solvent molecules. In addition there is a much larger channel that is relatively free from significant electron density though the presence of highly mobile and thus disordered solvent molecules cannot be ruled out (Fig. 52).

5.2. Chelating, bridging (μ_4-η^2:η^2) mode

Compound $\{[Pb_2(NO_3)_2(ox)]\cdot 2H_2O\}$ (**137**) [157] shows a two-dimensional coordination polymer built up from the stacking of double sheets with a thickness of 4.6 Å that is greater than the interlayer spacing (1.4 Å). The two layers are held together by hydrogen bonding (dashed lines in Fig. 53). An oxygen atom of water molecule forms one of the edges (3.292 Å) of the PbO_{10} polyhedron. The Pb(II) atom is ten-fold coordinated and bonded to four oxygen atoms of nitrate, four oxygen atoms of oxalate and two oxygen atoms of water ligands. The oxalate anion is connected both as mono-donor and as bi-donor (μ_4-η^2:η^2) modes leading to a O–O edge of normal length.

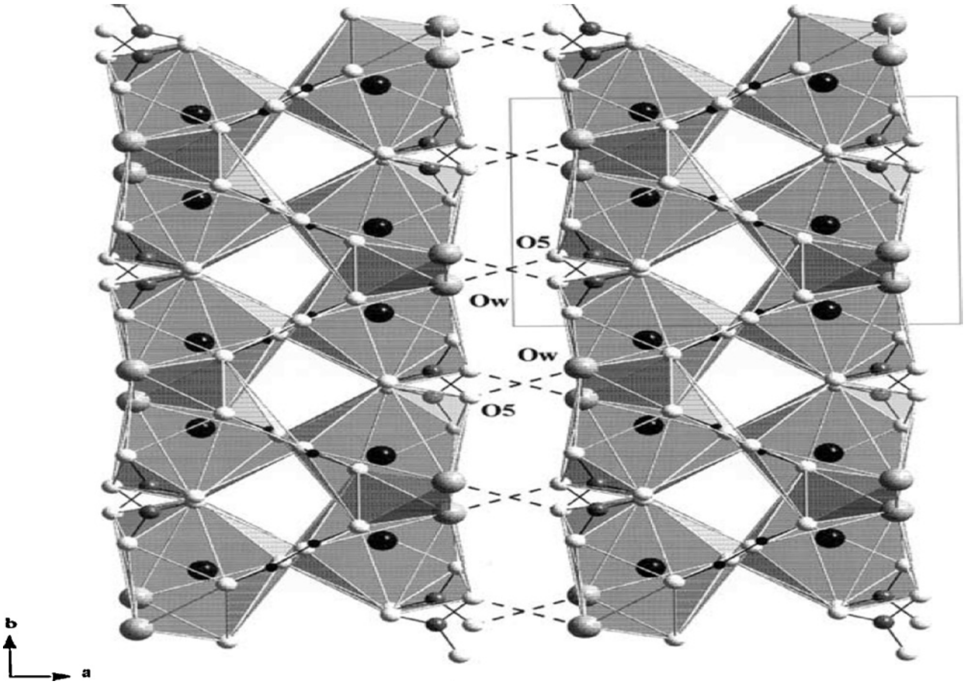


Fig. 53. Polyhedral representation of the structure of compound **137** projected along the *c*-axis. The hydrogen bonding is shown in dashed lines. Black circle: Pb; large grey circle: H_2O; small grey circle: O from $C_2O_2{}^{4-}$ and $NO_3{}^-$ anions; small dark–grey circle: N; small black circle: C [157].

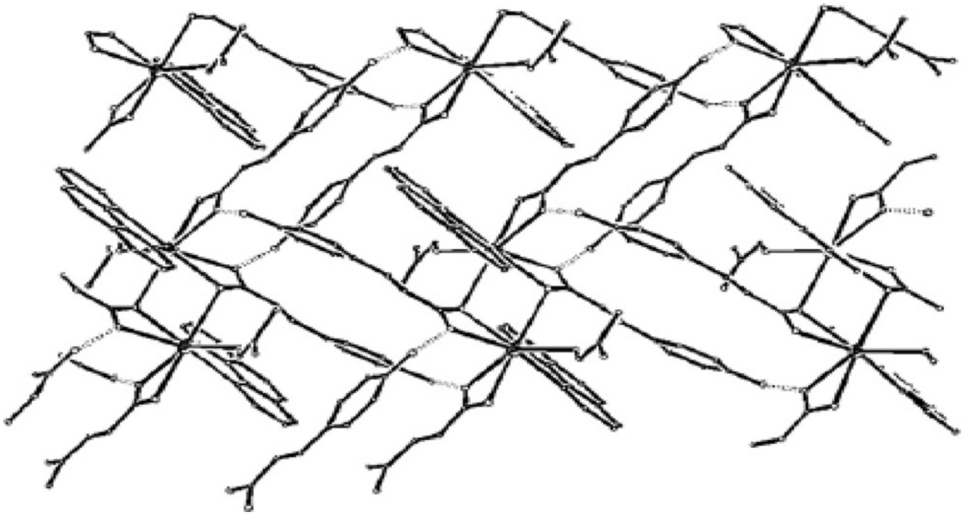


Fig. 54. View of a 2D network of complex **139** constructed by hydrogen bonding (hydrogen atoms were omitted; only oxygen atoms of the DMF molecule were preserved for clarity) [159].

6. Multiple-type coordination modes

6.1. Discrete complexes

Compounds $[(L^{19})_2Pb(Edta)]\cdot3.5H_2O$ (**138**) [158], $[Pb(hca)_2(phen)\cdot DMF]_2$ (**139**) [159], [Pb(8-Quin)AOc] (**140**) [113], $[emim]_2[Pb(OAc)_4]$ (**141**) [160], $[Pb(Val)_2(H_2O)_2(NO_3)_2]$ (**142**) [161], $[Pb(phen)(IA)_2]$ (**143**) [162], $[Pb(1)(dpaea)(H_2O)]_2\cdot[Pb(2)(dpaea)]\cdot6H_2O$ (**144**) [67] and $Pb_4(2\text{-}FCA)_8(H_2O_2)$ (**145**) [163] show discrete structures and in these complexes the carboxylate groups of related ligands show more than one type coordination modes. The carboxylate groups act in the compounds **138**, **141**, **142** and **143** as both bi-donor (η^2) and mono-donor (η^1) coordination modes, in the compound **139** and **140** as both bi-donor (η^2) and tri-donor (μ_2-η^2:η^1) coordination modes, in compound **144** as both bi-donor (μ_2-η^2) and mono-donor (η^1) coordination modes, and in compound **145** as not only tri-donor chelating, bridging (μ_2-η^2:η^1) but also bridging (μ_3-η^1:η^2) coordination modes. The asymmetric unit in compound **138** consists of one $[Pb(O_2CMe)_4]^{2-}$ unit and two $[emim]^+$ cations. Four ethanoate anions are involved in two different bonding modes: three of them are bonded via one oxygen atom, and the other one is chelating. Three non-coordinated oxygen atoms are involved in C–H···O hydrogen bonding with the cations, and extend toward the void associated with the lead(II) center. The large void in the coordination sphere around the lead(II) center is indicative of a stereo-chemically active lone pair. Compound **139** shows a dimeric structure and each lead(II) atom is eight-coordinated with N_2O_6 donor atom array: two N atoms from a phen molecule, four O atoms from two chelating hca ligands, one μ_3-O atom from the adjacent $[Pb(hca)_2(phen)(DMF)]$ unit, and one O atom from the DMF molecule. The uncoordinated phenolic group has a strong interaction with one of the oxygen atoms from the coordinated carboxylate group via hydrogen bonding. The dimers of $[Pb(hca)_2(phen)(DMF)]_2$ are thus connected to form a 2D hydrogen-bond network (Fig. 54).

6.2. One-dimensional coordination polymers

The structure of compounds $[Pb(bpe)(OAc)(O_2CCF_3)]_n$ (**146**) [164], $[Pb(1,3\text{-}bdc)(phen)]_n$ (**147**) [165], $[Pb_2(Bs\text{-}glu)_2(bpy)_2]_n$ (**148**) [115], $\{[Pb_6(O_2CCH(CH_3)_2)_{12}]\cdot4H_2O\}_n$ (**149**) [166], $[PbEn(OAc)_2]_n$ (**150**) [167], $[Pb_2(2\text{-}fba)_4(H_2O)_2]_n$ (**151**) [168], $[Pb_2(OAc)_4(L^{20})]_n$ (**152**) [169], $\{[Pb_2(HVal)_5](ClO_4)_4\cdot2(H_2O)\}_n$ (**153**) [124], $\{[Pb_2(H_2O)_2(HBTC)_2]\cdot3H_2O\}_n$ (**154**) [170], $[Pb_2(3\text{-}hyba)_4(phen)_2(H_2O)_2]\cdot H_2O$ (**155**) [171], $\{[Pb(phen)(L^{21})_2]\cdot2H_2O\}_n$ (**156**) [172], $[Pb(endc)_2(phen)]_n$ (**157**) [27], $Pb_4(2\text{-}FCA)_8(H_2O_2)$ (**158**) [163], $[Pb(2,6\text{-}pydc)]_n$ (**159**) [173], $[Pb_6(bpdc)_4O_2]_n$ (**160**) [174], $[Pb(NNO)(fum)_{0.5}]_n$ (**161**) [3], $[Pb(NDC)(dpp)]_n$ (**162**) and $[Pb(NDC)(dppz)]_n$ (**163**) [175] consists of 1D chains and the carboxylate groups in their structures have more than one type coordination modes. In the compounds **156**, **157**, **161** and **162** the carboxylate groups act not only as bi-donor (η^2) but also as mono-donor (η^1) coordination modes and in the compounds **148**, **149** and **155** act as both bi-donor (η^2) and tri-donor (μ_2-η^2:η^1) coordination modes. In compounds **152** and **158** the carboxylate groups act as both tri-donor (μ_2-η^2:η^1) and tetra-donor (μ_3-η^1:η^2:η^1) coordination modes. In compounds **155** and **163** carboxylate groups have three different coordination modes {mono-donor (η^1), bi-donor (η^2) as well as tetra-donor (μ_3-η^1:η^2:η^1) coordination modes in compound **154** and mono-donor (η^1), bi-donor (η^2) as well as (μ_2-η^1:η^1) coordination modes in compound **163**}. Complex **146** contains spiral 1D coordination polymer entangled in a “warp and weft” interwoven structure. The highly distorted Pb(II) metal center is strongly coordinated to the N atoms of two bpe ligands and chelated by an acetate anion and an oxygen atom of the $CF_3CO_2^-$ ligand. The crystallographic inversion center and glide plane present at the centers of the carbon–carbon double bonds of the bpe ligand generate spiral 1D coordination polymers. The spiral chains are running approximately in parallel but crossing over the C=C bond in perpendicular directions (Fig. 55). In compound **146** each $[Pb(bpe)]_n^{2n+}$ strand crosses over the next in almost parallel ABAB sequence. The carboxylate group in $CF_3CO_2^-$ and OAc^- acts as mono-donor (η^1) and bi-donor chelating (η^2) coordination modes, respectively. The comparison of the coordination mode in reported compounds indicates that carboxylate group in some of lead(II) complexes containing acetate anions acts as bi-donor chelating (η^2) coordination mode. Also in some of the mixed–ligand compounds that one of them has possessed acetate anions, carboxylate group of acetate ligand acts as variety types of coordination mode in another carboxylate ligand. For example, in complexes **88** and **254** there are two types of carboxylate ligands that one of them is acetate anion. Acetate anions act as bi-donor chelating (η^2) coordination mode and second ligands too act as bi-donor chelating (η^2) and tri-donor chelating, bridging (μ_2-η^2:η^1) in compound **88** and **254**, respectively. Compounds **43**, **44**, **45**, **52**, **54**, **68**, **69**, **72**, **74**, **110**, **111**, **112**, **141**, **146**, **248**, **249**, **251**, **252** and **253** contain acetate anions as the only carboxylate ligand

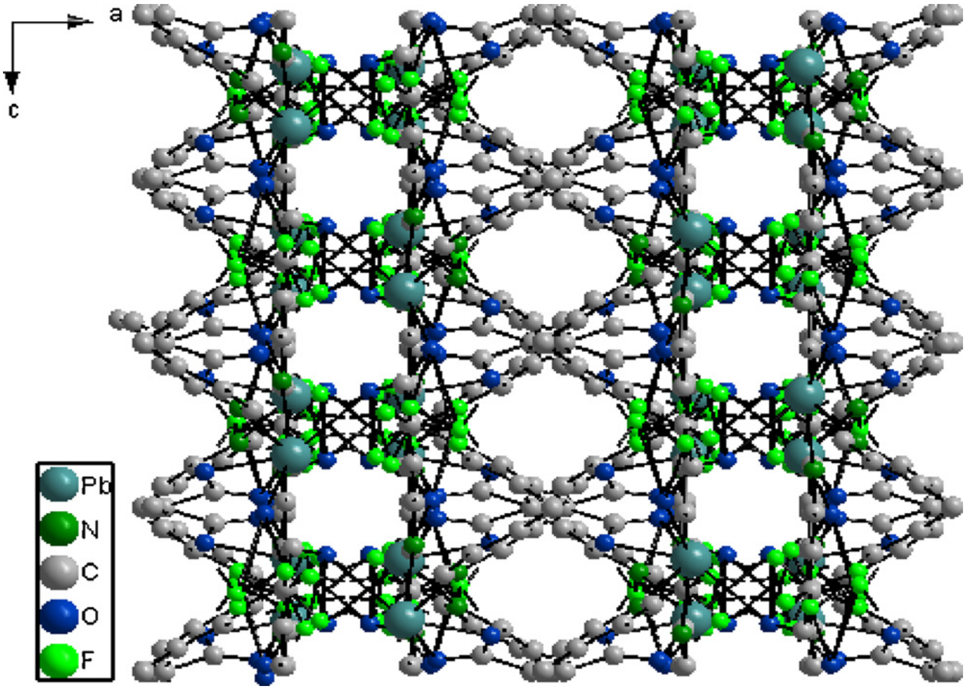


Fig. 55. Space-filling models showing the interlacing, looking down from the *b*-axis [164].

and compounds **88**, **254** and **169** are mixed–ligand compounds that one of them is acetate anion. However, the comparison of the mode of coordination acetate anions in lead(II) complexes containing acetate ligands may illustrate the influence of different ligands on the structural geometry. The [Pb(phen)(OAc)(O_2ClO_2)] [152] and [(phen)Pb(OAc)(O_2NO)] [151] are polymeric, the [Pb(phen)$(OAc)_2$] [236] and [(phen)Pb(OAc)(NCS)] [22] are dimeric whereas the [Pb$(bpy)_2$(OAc)](ClO_4) [236] and [Pb$(phen)_2$(OAc)](ClO_4) [93] are monomeric. The Pb_2O_2 rings which share edges with PbOCO quadrilaterals to make the dimer core are similar to the central Pb_2O_2 rings of dimeric [Pb(phen)$(OAc)_2$] [236], [(phen)Pb(OAc)(O_2NO)] [151], polymeric [Pb(phen)(OAC)(O_2ClO_2)] [152] and [(phen)Pb(OAc)(NCS)] [22], though the long edge of the rings in $[Pb(phen)(OAc)(O_2N)]_n$ (2.871 Å) is longer than in $[Pb(phen)(OAc)(O_2NO)]_n$ (2.804 Å) and $[Pb(phen)(OAc)(O_2ClO_2)]_n$ (2.736 Å), but considerably shorter than $[(phen)Pb(OAc)(NCS)]_2$ (3.190 Å) and $[Pb(phen)(OAc)_2]_2$ (3.366 Å). There is not any added interaction between oxygen atoms of the acetate ligands and neighboring lead(II) atoms in 1:2 adducts of the [Pb$(bpy)_2$(OAc)](ClO_4) and [Pb$(phen)_2$(OAc)](ClO_4) and these are monomers. This is consistent with the supposition that the nitrite anion should be a stronger ligand than nitrate and perchlorate and a weaker ligand than thiocyanate and acetate ligands ($phen > OAc^- > NCS^- > NO_2^- > NO_3^- > ClO_4^-$). It is very interesting, when that stronger ligands such as OAc^- and NCS^- are coordinated to lead(II) ion in the [(phen)Pb(OAc)X] ($X = OAc^-$ and NCS^-), the structures are dimeric and acetate ligand is bridged only from one side, whereas when weaker ligands such as NO_3^- and ClO_4^- are coordinated to lead(II) ion in the [(phen)Pb(OAc)X] ($X = NO_3^-$ and ClO_4^-), the structures would be polymeric and acetate ligand could bridge from each of the two sides. In the [Pb(phen)(OAc)(O_2N)], the acetate ligand has bridged only from one side. However, this point shows that the coordination mode of acetate anions in the lead(II) coordination polymers can affect by the other ligand in the lead(II) coordination sphere.

In compound **147** the 1,3-bdc ligand coordinates to the lead(II) atom, acting as a μ_5-bridge. One carboxylate group is in a chelating mode, while the other is in a chelating, bridging mode. The bridging property of the carboxylate group results in a one-dimensional ladder chain (Fig. 56). In the chain, bridged carboxylate groups construct a four-membered ring, [Pb_2O_2], with a Pb···Pb distance of 4.3475 (5) Å and a [$Pb_2(mbdc)_2$] box. In the box motif, two 1,3-bdc ligands are parallel and the separation of Pb···Pb by 1,3-bdc is 10.2706 (9) Å. The lone pair of electrons on the Pb(II) atom is stereochemically active and it occupies one site of the dodecahedron.

In the complex **151**, the Pb1 atom is coordinated by seven oxygen atoms and one fluore atom from five 2-fluorobenzoate ligands to complete a significantly distorted PbO_7F polyhedron.

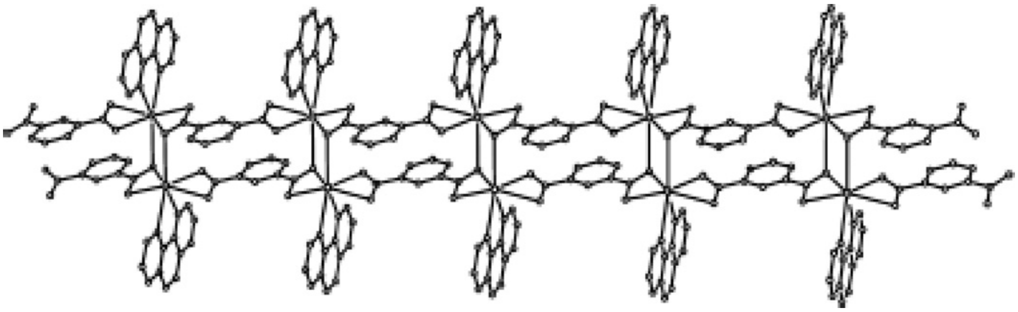


Fig. 56. View of the one-dimensional ladder chain of compound **147**. H atoms have been omitted for clarity [165].

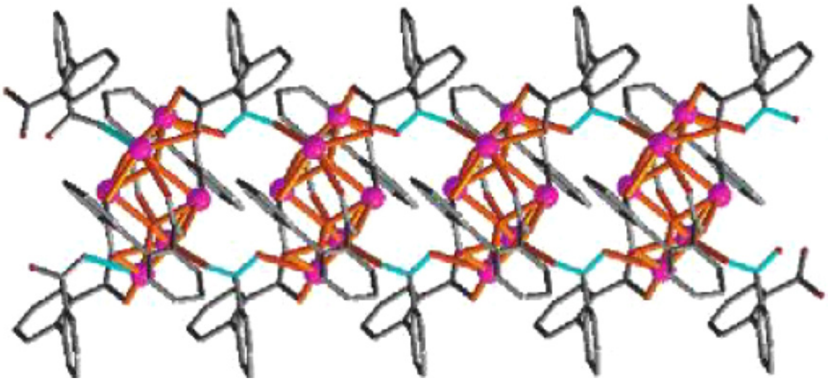


Fig. 57. View of the one-dimensional chain in the complex **160** along the *a*-axis[174].

The Pb2 atom is coordinated by five oxygen atoms from four 2-fluorobenzoate ligands and three water molecules to complete a significantly distorted PbO_8 polyhedron. The 2-fluorobenzoate ligands bridge the Pb(II) atoms, giving rise to a one-dimensional chain structure extending along the [100] direction. The polymeric chains are connected via weak C–H···O hydrogen bond and π–π stacking interactions into a two-dimensional supramolecular structure. In this compound the carboxylate groups have three different coordination modes. One of them is a tetra-donor chelating, bridging (μ_3-η^1:η^2:η^1) mode, while the other two are in a bi-donor {chelating (η^2) and bridging (μ_2-η^1:η^1)} coordination mode. The asymmetric unit for complex **153** includes four independent Pb(II) atoms coordinated to ten valine ligands, eight free perchlorate ions and four uncoordinated water molecules. The structure of the complex is a 1D polymer formed by $[Pb_2(Hval)_5]^{4+}$ monomeric species. However, along this polymer, a variety of coordination modes is present for ligands, due to the duplicated $[Pb_2(Hval)_5]^{4+}$ moiety in the asymmetric unit. Each coordination mode has a specific role in the building of the polymeric structure. μ-Hval-O,O,O′ essentially connects metal centers within the asymmetric unit; the unique μ-Hval-O,O′ connects asymmetric units; and finally, nonbridging Hval-O,O′ ligands complete the coordination spheres of two of the four independent Pb(II) atoms. Complex **160** is composed of one-dimensional chains of $[Pb_6(dpa)_4O_2]$. Two carboxylate groups of each bpdc ligand are deprotonated and the bpdc ligands adopt two types of coordination modes. One carboxylate group is in a bridging (μ_2-η^1:η^1) mode while the other is in a mono-donor (η^1) mode. The asymmetric unit of **160** consists of three crystallographically independent Pb(II) ions. Two such asymmetric units are linked by two μ_4-oxygen atoms to form a $\{Pb_6O_{18}\}$ SBU. This is the interesting $\{Pb_6O_{18}\}$ SBU formed by polycarboxylate ligands. The adjacent SBUs are linked by carboxylate groups to form an interesting one-dimensional structure along the *a*-axis (Fig. 57).

The carboxylate groups of H_2NDC are all deprotonated in compound **163** and exhibit different coordination modes. In mode I, the two carboxylate moieties of NDC^{2-} link to two Pb(II) ions, while in mode II, each carboxylate moiety of NDC^{2-} is bonded to one Pb(II) ion. Each NDC^{2-} ligand connects two Pb(II) centers in mode I or mode II, leading to zigzag chains. More interestingly, the lateral dpp ligands from adjacent chains are paired with C–H–π interactions and the 1D chain becomes a 2D network (Fig. 58).

6.3. Two-dimensional coordination polymers

Compounds $\{Pb(HIda)_2\cdot H_2O\}_n$ (**164**), $[Pb(Heida)H_2O]_n$ (**165**) [57], $[Pb(L^{22})_2]_n$ (**166**) [176], $[Pb(2,6\text{-pydc})]_n$ (**167**) [50], $[Pb(2,6\text{-pydc})]_n$ (**168**) [177], $\{[Pb_4(BTC)(L^{23})(OAc)(H_2O)_2]\cdot 1.5H_2O\}_n$ (**169**) [178], $[Pb(tsgly\text{-}O)_2(bpy)]_n$ (**170**) [119], $\{[Pb_4(\mu\text{-}3,4\text{-}TDTA)_4(H_2O)_2]\cdot 4H_2O\}_n$ (**171**) [179], $\{[Pb_3BTC_2]\cdot H_2O\}_n$ (**172**) [180], $[Pb(HIDC)]_n$ (**173**) [181], $\{[Pb_2(HNTP)_2(NTP)(CHZ)(H_2O)_2]\cdot 2.5H_2O\}_n$ (**174**) [182], $\{[Pb(Hile)_2(NO_3)(H_2O)_2]NO_3\}_n$ (**175**) [124], $[Pb_2(1,4\text{-}NDC)_2(phen)]_n$ (**176**) [183], $\{[Pb(3,5\text{-pydc})(H_2O)]\cdot(H_2O)\}_n$ (**177**) [184], $[Pb_2(4\text{-hyda})_4((dmphen)_2]_n$ (**178**) [185],

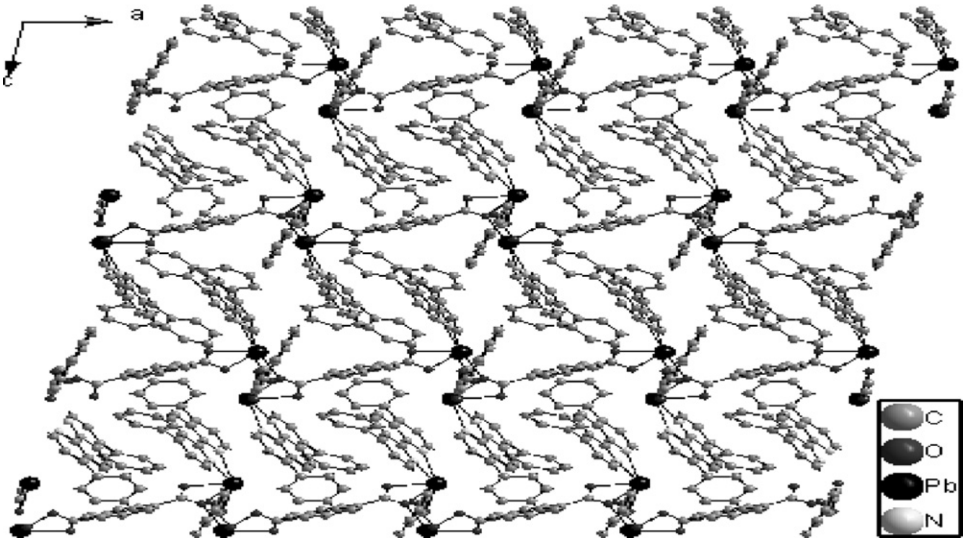


Fig. 58. The 2D layer structure of compound **163** formed by interchain C–H–π interactions [175].

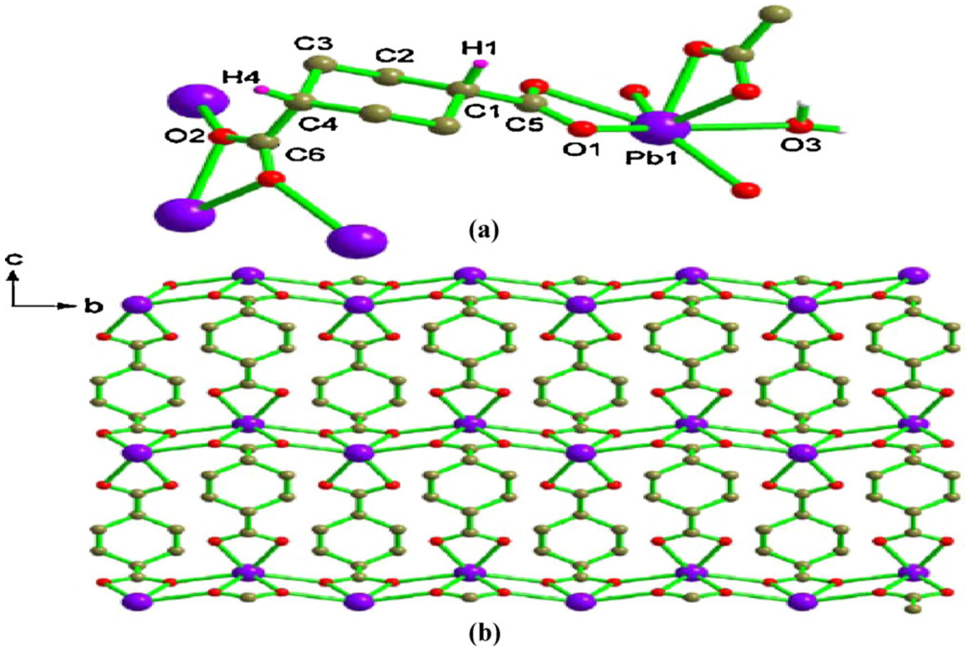


Fig. 59. (a) A view of **186** showing the coordination sphere of Pb(II) and conformation/coordination modes of chdc with atom labeling of the asymmetric unit and (b) 2D close-knit layered structure of **186** [6].

$\{Pb_4O[L^{24}]_2\}_n$ (**179**) [186], $[Pb_3(dnob)_2(phen)_3(H_2O)]_n$ (**180**) [187], $[Pb(hca)_2{\cdot}DMF]{\cdot}DMF\}_n$ (**180**) [160], $[Pb(trans\text{-}1,4\text{-}CHDC)(H_2O)]_n$ (**182**) [29], $\{[(OPb_4)_2(OH)_2(C_2O_4)(1,3\text{-}CHDC)_4]{\cdot}H_2O\}_n$ (**183**) [188] and $[Pb_2(ndc)_2(tcpp)]$ (**184**) [175] are two-dimensional layers with single type ligands or mixed ligands. In all the upper compounds the carboxylate groups act as at least two different coordination modes. In compounds **164**, **172**, **174**, **176** and **183** carboxylate groups have three different coordination modes. In compounds **164** and **174** the carboxylate groups act as not only mono-donor (η^1) and bi-donor (η^2) but also as $\mu_2\text{-}\eta^1:\eta^1$ coordination modes and in compound **172** as tetra-donor $(\mu_3\text{-}\eta^1:\eta^2:\eta^1)$, tri-donor $(\mu_2\text{-}\eta^2:\eta^1)$ and $(\mu_3\text{-}\eta^1:\eta^2)$ coordination modes. In compound **176** the carboxylate groups act as tri-donor $(\mu_2\text{-}\eta^2:\eta^1)$, bi-donor (η^2) and $(\mu_2\text{-}\eta^1:\eta^1)$ coordination modes and in compound **183** act as bi-donor $(\mu_2\text{-}\eta^1:\eta^1)$, tetra-donor $(\mu_3\text{-}\eta^1:\eta^2:\eta^1)$ and $(\mu_3\text{-}\eta^2:\eta^1:\eta^1)$ coordination modes. In compounds **175**, **177** and **184** the carboxylate groups act as bi-donor (η^2) and mono-donor (η^1) coordination modes and in compounds **169**, **173** and **180** as bi-donor (η^2) and tri-donor $(\mu_2\text{-}\eta^2:\eta^1)$ coordination modes. In compounds **161** and **168** the carboxylate groups act as tri-donor both $\mu_2\text{-}\eta^2:\eta^1$ and $\mu_3\text{-}\eta^1:\eta^2$ coordination modes and in compounds **170** and **178** as bi-donor (η^2) and tri-donor $(\mu_2\text{-}\eta^2:\eta^1)$ coordination modes. Carboxylate group in compounds **165**, **166**, **171**, **179**, **181** and **182** has two types of coordination modes. In compound $[Pb(C_6H_6O_7)]_n{\cdot}nH_2O$ (**185**) [189], the geometry around Pb(II) appears to be distorted trigonal bipyramidal with Pb–O distances ranging from 2.397(7) to 2.527(6) Å and the lone pair on Pb(II) occupies one of the three basal plane positions. The carboxylate group adopts two types of coordination modes. One carboxylate group is in a bi-donor bridging $(\mu_2\text{-}\eta^2)$ mode, while the other is in a mono-donor (η^1) mode. There is an extensive network of hydrogen bonding in the crystal structure of **185**. Coordination polymer $[Pb(chdc)(H_2O)]_n$ (**186**) [6] represents a lead(II) complex of H_2chdc in which the Pb(II) centers are connected by chdc anions to afford a 2D close-knit structure (Fig. 59b). As shown in Fig. 59(a), the local crystallographic unit, with a mirror symmetry passing through C5–C1–C4–C6, comprises one Pb(II) center, a doubly deprotonated chdc anionic ligand and a water ligand. Each chdc binds to four Pb(II) atoms, and two different coordination modes of the carboxylate groups. One of them is a tetra-donor chelating, bridging $(\mu_3\text{-}\eta^1:\eta^2:\eta^1)$ mode and other is in a bi-donor chelating (η^2) coordination mode. Compound $[Pb(5\text{-}FUOAc)_2]_n$ (**187**) [190], is a 2D polymeric lead(II) complex containing the Pb–O═< bond (Fig. 60). The coordination number of Pb(II) atoms is seven, PbO_7, with "stereo-chemically active" electron lone pairs, and the coordination sphere is hemidirected. Carboxylate groups act as two different tri-donor modes, chelating, bridging $(\mu_2\text{-}\eta^2:\eta^1)$ and bridging $(\mu_3\text{-}\eta^1:\eta^2)$.

In compound $[PbC_2H_2(CO_2)_2]_n$ (**188**) [88] a two-dimensional structure of lead(II) maleate and double layers are arranged parallel to the bc plane. Each maleate ligand is bonded to four Pb(II) atoms. In this complex the carboxylate group has two different coordination modes. One of them is a tetra-donor chelating, bridging $(\mu_3\text{-}\eta^1:\eta^2:\eta^1)$ mode and the other is in a tri-donor chelating, bridging $(\mu_2\text{-}\eta^2:\eta^1)$ coordination mode (Fig. 61).

In complex $[Pb(L\text{-}C_4H_4O_5)]$ (**189**) [191], the coordination number of Pb(II) is eight with an irregular geometry. The inert lone pair is buried inside to make the structure holodirectional. In compound **189** the malic acid acts as a quinque-dentate ligand and binds to the Pb(II) atoms with one hydroxyl and four carboxylate oxygen atoms. The carboxylate group of malic ligand has two types of coordination modes. One of them is a tetra-donor chelating, bridging $(\mu_3\text{-}\eta^1:\eta^2:\eta^1)$ mode while the other is in a tri-donor chelating, bridging $(\mu_2\text{-}\eta^2:\eta^1)$ coordination mode. Consecutive Pb(II) atoms are connected by carboxylate and hydroxyl oxygen atoms of the ligand to form a chiral zigzag double layer containing Pb–O–Pb two-dimensional infinite network (Fig. 62). The chiral double layers are stacked in a zigzag fashion with an inter-layer separation of half of the unit cell length along the c-axis. The presence of 2_1 screw axes in all the three directions can clearly be observed.

Single-crystal X-ray analysis reveals that compound $[Pb_3(NNO)_4(NO_3)_2H_2O]_n$ (**190**) [68], is a 2D layer built by two kinds of Pb–O chains and NNO ligands. Three independent Pb(II) centers display different coordination geometries with pentagonal–bipyramidal and trigonal–bipyramidal geometries. Four crystallographically unique NNO ligands in complex

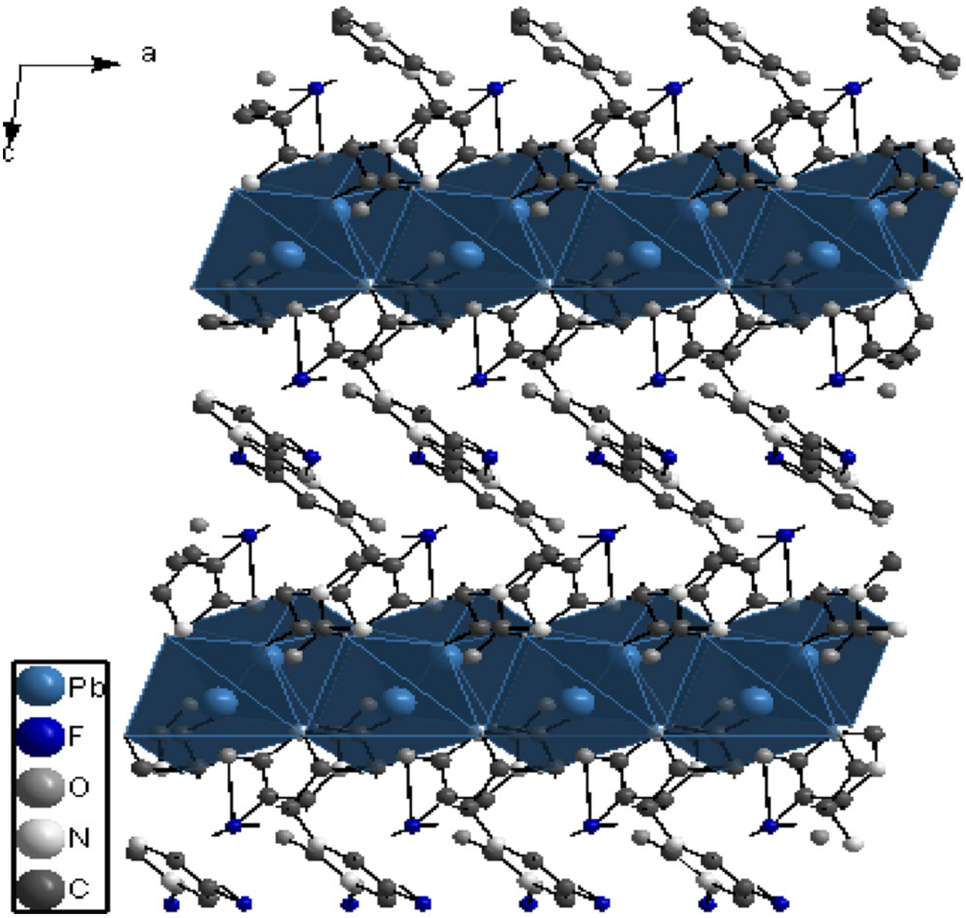


Fig. 60. Fragment of compound **187**, showing the 2D coordination polymer [190].

190 adopt three different types of coordination modes. Two of them act as bi-donor chelating (η^2), one of them as tri-donor chelating, bridging (μ_2-η^2:η^1) and the last one as mono-donor (η^1) coordination mode and all form 2D network (Fig. 63).

Compound $[Pb(HPHT)]_n$ (**191**) [192], is a two-dimensional layer structure containing one-dimensional lead-oxide chains. In this compound the HPHT ligand has two carboxylate groups that are in two different coordination modes, tetra-donor chelating, bridging (μ_3-η^1:η^2:η^1) and bi-donor bridging (μ_2-η^1:η^1) modes. Compound $[Pb(1,3\text{-}CHDC)(H_2O)]_n$ (**192**) [188] has a two-dimensional structure and there are two crystallographically distinct Pb(II) ions, two CHDC anions, and two terminal water molecules in the asymmetric unit. One of Pb(II) atoms is hemidirected and is coordinated

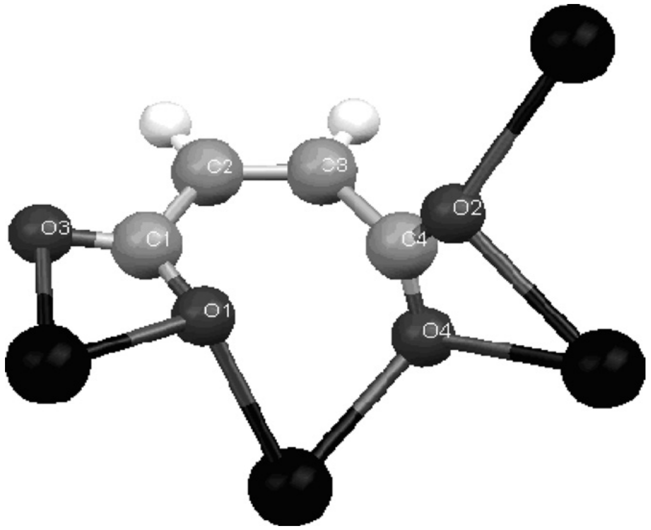


Fig. 61. Tetra-donor maleate ligand in compound **188** [88].

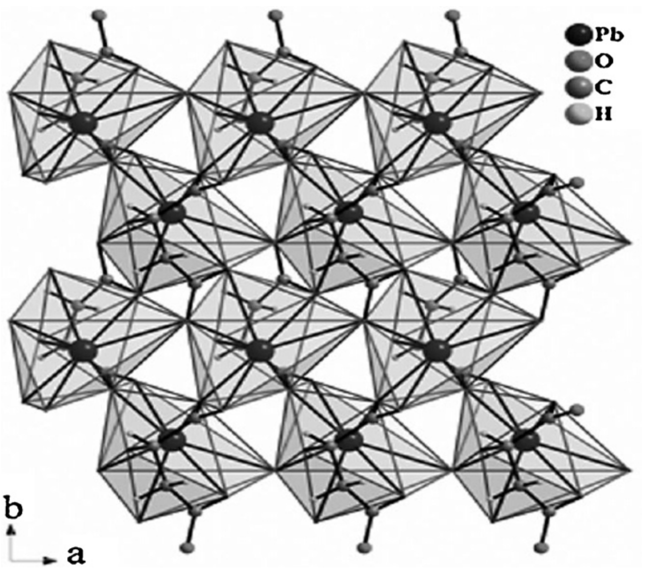


Fig. 62. Two-dimensional double-layers and polyhedral view of the layer in **189** [191].

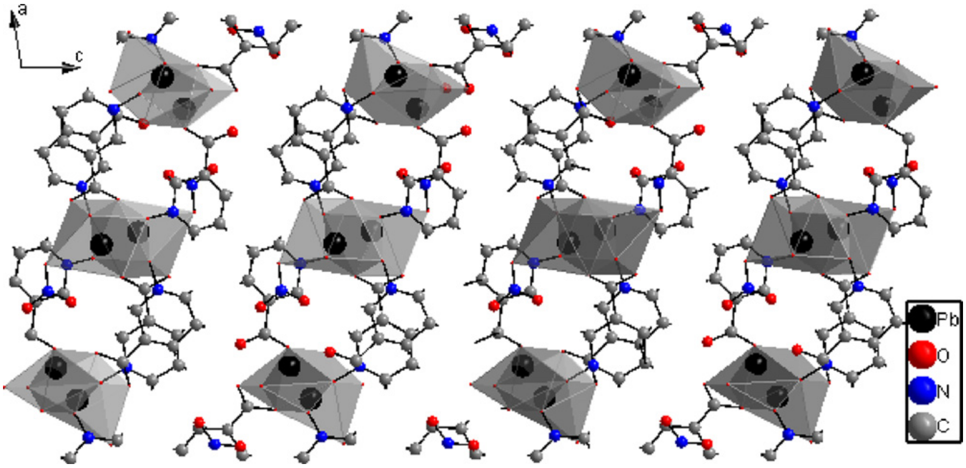


Fig. 63. View of the 2D layer in compound **190** [68].

by five oxygen atoms (PbO_5) from four different CHDC anions. The second type of Pb(II) atoms is eight-coordinated (PbO_8) and has a holodirected geometry. The anions exhibit two types of coordination modes. One is bi-donor bridging (μ_2-η^1:η^1) mode and the other is tri-donor chelating, bridging (μ_2-η^2:η^1) coordination mode (Fig. 64).

Recently, a nano-sized lead(II) maleate coordination polymer, $[Pb(\mu_7\text{-Mal})]_n$ (**193**) [193], has been synthesized by sonochemical method. Determination of the structure of compound **193** shows the complex in the solid state is a 2D polymeric network (Fig. 65a). Compound **193** is coordinated by seven oxygen atoms of Mal^{2-} anions, resulting in a seven-coordinate complex with a PbO_7 chromophore. One of carboxylate moiety of the Mal^{2-} ligand acts as both bidentate, and bridging group (totally tri-donor) in a chelating, bridging (μ_2-η^2:η^1) coordination mode and the other one as both bidentate, and bridging group (totally tetra-donor) in a chelating, bridging (μ_3-η^1:η^2:η^1) coordination mode, yielding a two-dimensional network. Fig. 65b indicates the original morphology of the nanoplate flower-like structure with the diameter varying between 40 and 70 nm.

6.4. Three-dimensional coordination polymers

Compound $Pb_3[L^{25}][BTS][H_2O]\cdot H_2O$ (**194**) [194] is a 3D coordination polymer and there are three unique Pb(II) ions in the asymmetric unit of this compound. The inter-connection of the Pb(II) ions via chelating and bridging L^{25} ligands leads to the formation of $Pb_6(L^{25})_2$ unit, whereas the inter-connection of the Pb(II) ions via bridging BTS anions resulted in a 1D double chain along the *c*-axis. The carboxylate group acts as tri-donor chelating, bridging (μ_2-η^2:η^1) and mono-donor (η^1) coordination modes. The cross-linkage of the two building blocks leads to a complicated 3D network. Two novel porous carboxylate-phosphonate hybrids, $\{[Pb_4(BTC)(HBTC)(HL^{26})]\cdot 3H_2O\}_n$ (**195**), and $\{[Pb_6(BTC)_2(HBTC)(H_2L^{27})]\cdot 4.5H_2O\}_n$ (**196**) [195] have three-dimensional structures. The structure of **195** is built from a 3D porous network of lead(II) tricarboxylate and 1D double chains of lead(II) aminodiphosphonate. The structure of compound **196** contains lead(II) carboxylate–phosphonate hybrid layers, cross-linked by 1D double chains of lead(II) phosphonate through the organic groups of both types of ligands, resulting in the formation of a 3D porous network. The lattice water molecules in both compounds

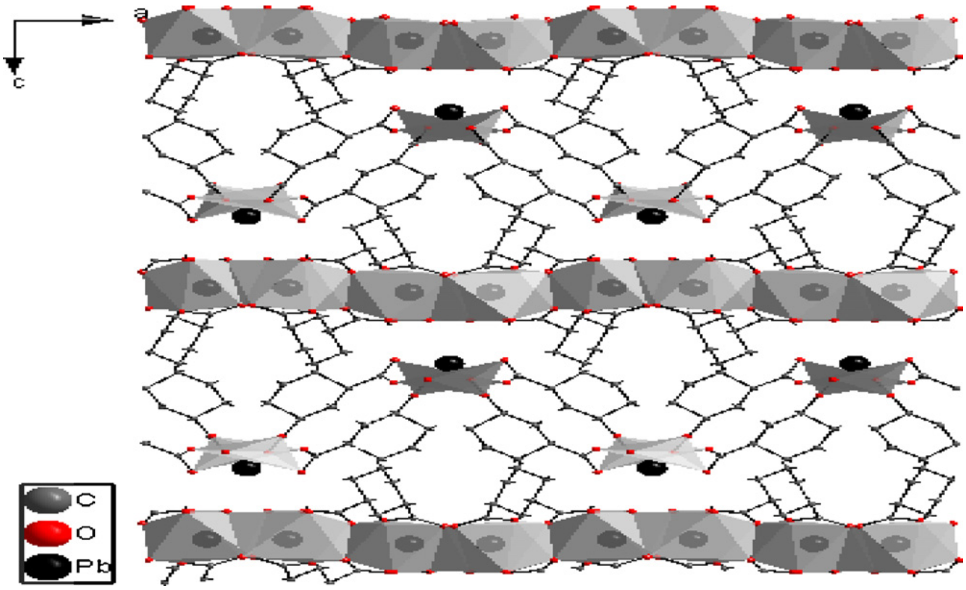


Fig. 64. The layers and the infinite Pb–O–Pb linkage in compound **192** [188].

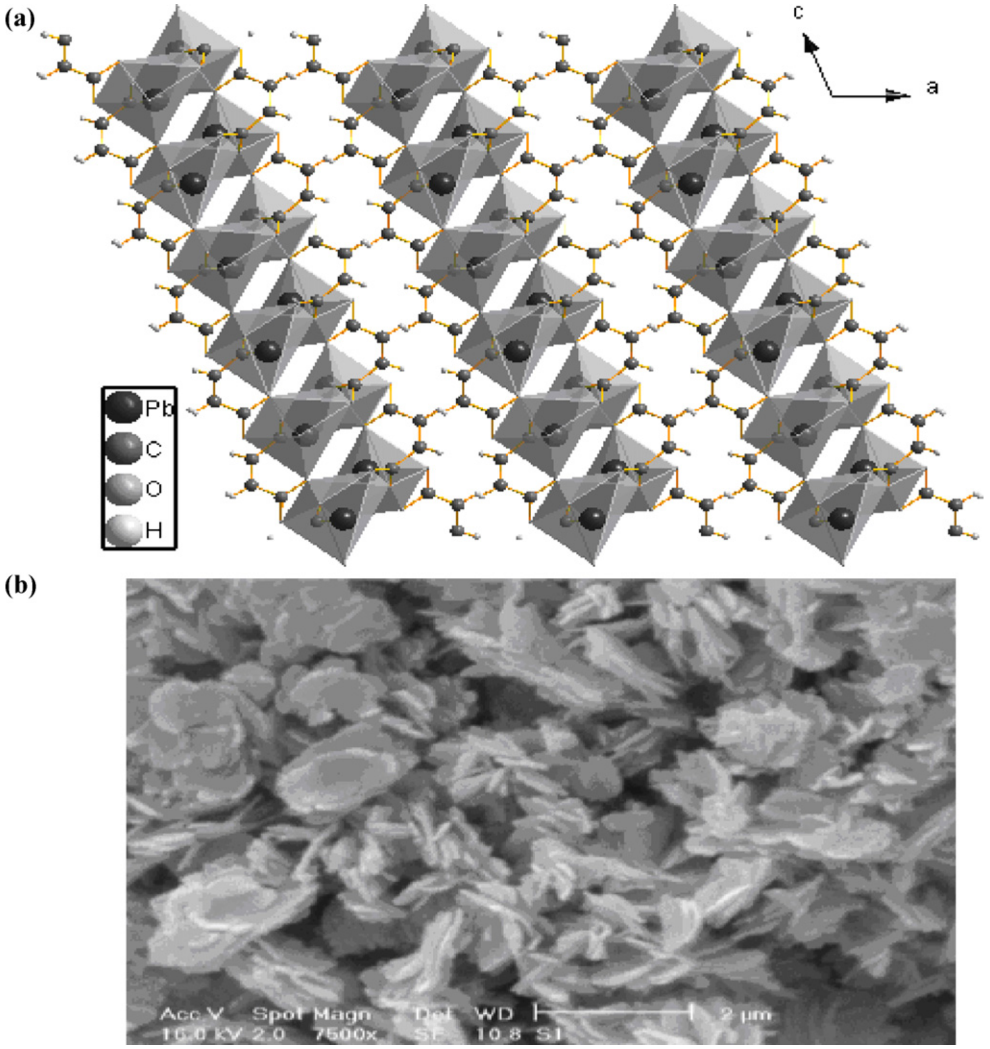


Fig. 65. (a) A fragment of the two-dimensional network in compound **193** and (b) SEM photograph of compound **193** nano-flower formed by nano-plate [193].

are located at the micropores of the structures. The carboxylate groups have more than two different coordination modes in these compounds. In compound $\{[Pb_2(PMIDA)]\cdot 1.5H_2O\}_n$ (**197**) [13], the inter-connection of Pb(II) ions by bridging carboxylate and phosphonate groups results in a 3D network with large tunnels along the *c*-axis (Fig. 66). The diameter of the pore is estimated to be slightly larger than 5 Å, thus it is of the micropore type. These micropores are hydrophilic due to the amine, carboxylate and phosphonate groups. The cavity of the tunnels is occupied by the lattice water molecules inter-linked through hydrogen bonding.

In complex $[Pb(glu)]_n$ (**198**) [129], the Pb(II) atom is hemidirected and seven coordinated (PbO_7) from five different glutarate anions. A PbO_7 polyhedron shares its two corners with two different PbO_7 polyhedra and two edges with two other PbO_7 forming an infinite 2D Pb–O–Pb layer of the I^2O^0 type, with a (4,4) net topology (Fig. 67a). This layer can be viewed as chains of edge shared PbO_7 polyhedra connected through the corners of PbO_7 polyhedra of the adjacent chains. The layers get further connected to each other through glutarate anions into a 3D structure of the I^2O^1 type (Fig. 67b). One of carboxylate moiety of the glu ligand acts as tridonor chelating, bridging (μ_2-η^2:η^1) coordination mode and the other one as tetra-donor chelating, bridging (μ_3-η^1:η^2:η^1) coordination mode.

Complex $[Pb(Adi)]_n$ (**199**) [129] has a 3D structure with an asymmetric unit of eleven non-hydrogen atoms. A PbO_7 polyhedron

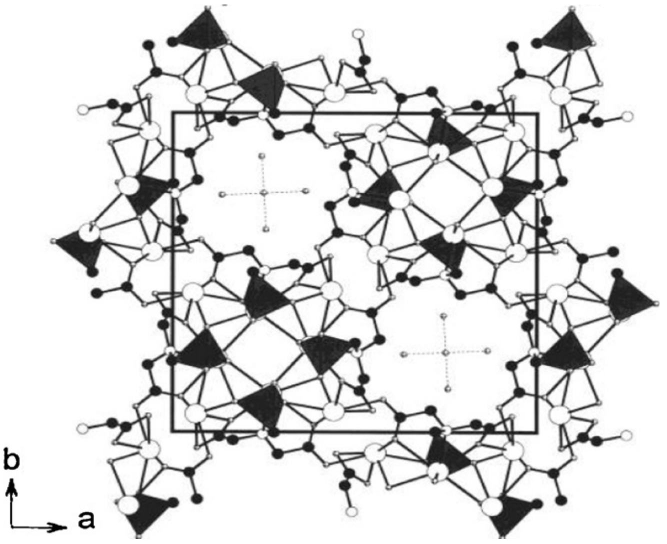


Fig. 66. View of structure of compound **197** along the *c*-axis showing the micropores. C–PO_3 tetrahedra are shaded in black. Pb, N, C, and O atoms are shown as open (large), open (small), black, and crossed circles, respectively [13].

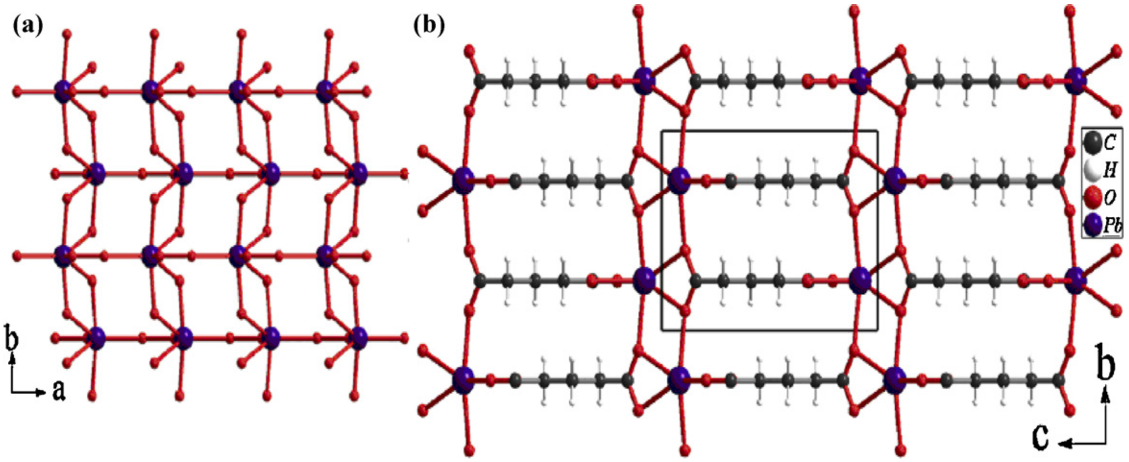


Fig. 67. (a) View of the inorganic layer with the infinite Pb–O–Pb linkages of the I^2O^0 type in **198** and (b) the 3D structure viewed along the *a*-axis [129].

shares its two corners with two PbO_7 polyhedra and two of its edges with other two PbO_7 forming an infinite 2D Pb–O–Pb layer of the I^2O^0 type. This layer contains PbO_7 polyhedra connected to each other through edges and corners. The layers are further connected to each other through the adipate anions into a 3D structure of the I^2O^1 type. In $[Pb_2(ox)(suc)]_n$ (**200**) [129], the Pb(II) atom is holodirected and coordinated by oxygen atoms from two oxalate and three succinate anions. Each PbO_7 polyhedron shares four of its corners with four other PbO_7 polyhedra forming an infinite 2D Pb–O–Pb layer of the I^2O^0 type, with a (4,4) net topology very similar to that in **199**. Two of these layers are connected to each other through the oxalate anions into a bilayer structure (Fig. 68a). These bilayers are further connected to each other through succinate anions into a 3D structure of the I^2O^1 type (Fig. 68b).

Complex $[(OPb_3)(1,3\text{-CHDC})_2]_n$ (**201**) [188] has a three-dimensional structure without any inorganic connectivity (I^0O^3). There are three Pb(II) atoms in three crystallographically distinct positions, two CHDC anions, and one independent oxo dianion in the asymmetric unit. Both the CHDC anions are in the cis conformation and the Pb(II) atoms have a hemidirected geometry. These connectivities lead to the formation of a SBU of Pb_6O_{18}, which includes two edge-shared OPb_4 tetrahedra. A carboxylate group connects the adjacent SBUs to form an infinite 1D chain, and the chains are connected to four other adjacent chains by CHDC anions to form the infinite three-dimensional structure (I^0O^3) (Fig. 69).

In the 3D coordination polymer of $[Pb_2(1,3\text{-CHDC})_2(H_2O)]_n$ (**202**) [188] there are two crystallographically distinct Pb(II) atoms, two CHDC anions, and one terminal water molecule. On the basis of the coordination modes, the carboxylate group can be classified into three types: (a) tetra-donor chelating, bridging (μ_3-η^1:η^2:η^1), (b) tri-donor bridging (μ_3-η^1:η^2) and (c) bi-donor bridging (μ_2-η^1:η^1). The layers can also be viewed as a (4,4) square lattice consisting of tetranuclear SBU of Pb_4O_{18}. The layers are further connected to each other and form a three-dimensional structure with the I^2O^1 type (Fig. 70).

The anhydrous complex $[Pb(fum)]_n$ (**203**) [196] adopts a 3D structure wherein 1D channels are arranged along the c direction (Fig. 71a) [21]. The coordination sphere around the Pb(II) is asymmetric and hemidirected. Also, nano-structured three-dimensional of this compound was synthesized by sonochemical method. The morphology and size of compound **203** shows that it is composed of particles with sizes of about 70 nm (Fig. 71b).

Also compounds $\{[Pb_3(3,5\text{-pdc})_2(NO_3)_2]\cdot 4H_2O\}_n$ (**204**) [197], $\{[Pb_2(HL^{28})(BTS)]\cdot H_2O\}_n$ (**205**) [194], $[Pb(HNta)]_n$

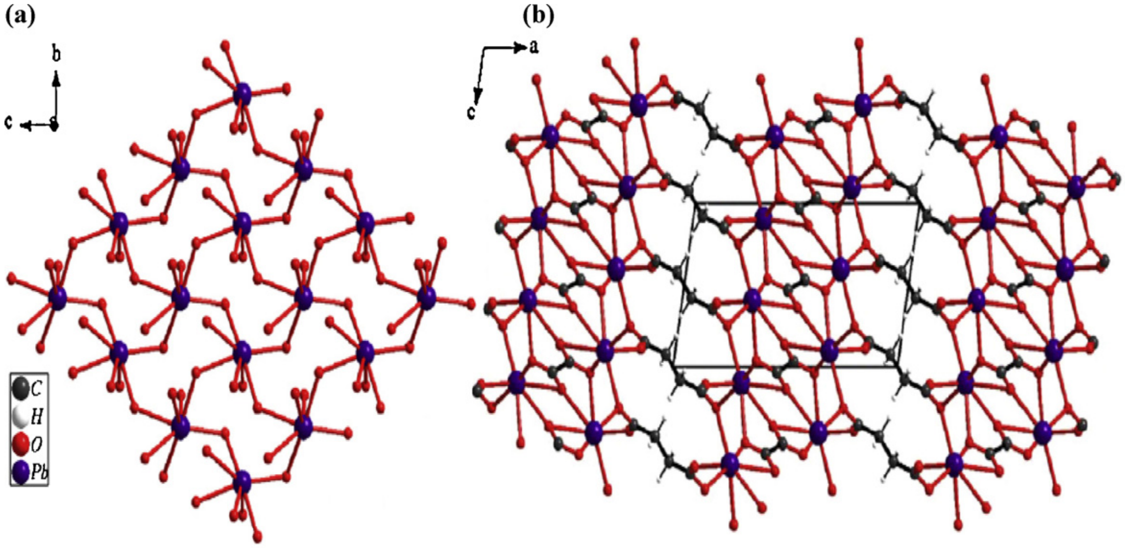


Fig. 68. (a) View of the inorganic layer with the infinite Pb–O–Pb linkages of the I^2O^0 type in **199** and (b) the 3D structure viewed along the *b*-axis [129].

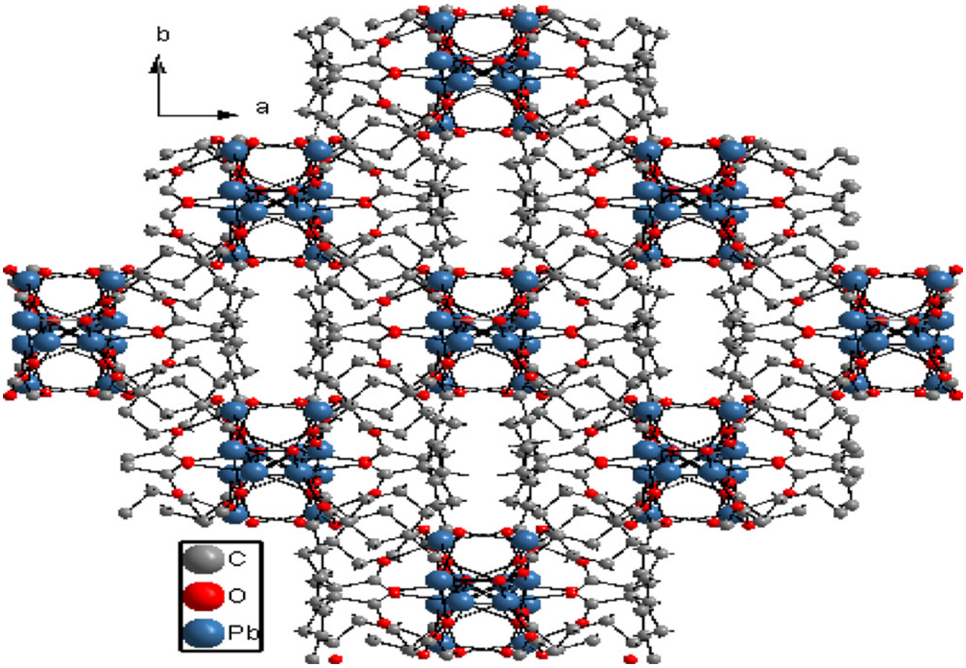


Fig. 69. The Pb_6O_{18} secondary building unit and the 3D structure of **201** [188].

(**206**) [57], $[Pb(1,4\text{-bdc})(H_2O)]_n$ (**207**) [198], $\{Pb[C_9H_{14}O_4]\}_n$ (**208**) [199], $\{[Pb(GEH)(H_2O)_{1/2}]ClO_4\}$ (**209**) [200], $[Pb(L^{29})_2]_n$ (**210**) [201], $\{[Pb_3(phen)_3(H_2O)_2(SIP)_2]\cdot 3H_2O\}_n$ (**211**) [202], $\{[(Pb_4O)Pb(OH)(bet)_8(Tf_2N)_3][Tf_2N]_4\cdot MeOH\}_n$ (**212**) [203], $[Pb_2(1,2,3,4\text{-BTC})]_n$ (**213**) [204], $[Pb_5(SIP)_2(L^{30})_2(H_2O)]_n$ (**214**) [205], $[Pb(Adi)]_n$ (**215**), $Pb_2(ox)(Adi)$ (**216**) [129], $[Pb_4(\mu_4\text{-}O)(ip)_3(H_2O)]_n$ (**217**) [206], $[Pb(PYDC)(H_2O)]_n$ (**218**) [192], $[Pb_2(bdc)_2(nmp)_2]_n$ (**219**) [207], $\{Pb_4(ip)_3(\mu_4\text{-}O)(H_2O)\}_n$ (**220**) [208], $[Pb_2(1,4\text{-NDC})_2(bpy)]_n$ (**221**) [209], $[Pb(C_5H_4NCOO)_2(H_2O)]_n$ (**222**) [210], $[Pb(1,4\text{-NDC})(DMF)]_n$ (**223**) [211], $[Pb(2,3\text{-pydc})]_n$ (**224**) [85], $[Pb(1,4\text{-bdc})]_n$ (**225**) [212], $[Pb(HIDC)(H_2O)]_n$ (**226**) [14], $[Pb_2(NNO)(BTC)]$ (**227**) [3], $[Pb(4\text{-pya})_2]_n$ (**228**) [213], $[Pb(1,2\text{-CHDC})]_n$ (**229**) [154], $[Pb_3(bpy)(H_2O)_5(SIP)_2]_n\cdot 0.5bpy\cdot 2H_2O$ (**230**) [214], $[Pb(ndc)(dma)]_n$ (**231**), $[Pb(1,4\text{-bdc})(dma)]_n$ (**232**), $\{[Pb_2(cis\text{-}1,4\text{-CHDC})_2]\cdot NH(CH_3)_2\}_n$ (**233**) [129], $[Pb(\mu\text{-}4\text{-pyc})(\mu\text{-}Br)]_n$ (**234**) [215] and $\{[Pb_2(1,3,5\text{-HBTC})_2(H_2O)_4]\cdot H_2O\}_n$ (**235**) [216] are three-dimensional framework with different ligands.

In all the upper compounds the carboxylate groups act as at least two different coordination modes. In compounds **212**, **213**, **218** and **229** the carboxylate group has four types of coordination modes; mono-donor (η^1), bi-donor (μ_2-η^1:η^1), tri-donor (μ_2-η^2:η^1) and tetra-donor (μ_3-η^1:η^2:η^1) in compound **212**, tri-donor (μ_2-η^2:η^1), tetra-donor (μ_3-η^1:η^2:η^1), bi-donor (μ_2-η^1:η^1) and (η^2) in compound **213**, mono-donor (η^1), tri-donor (μ_2-η^2:η^1), bi-donor (μ_2-η^2) and (μ_2-η^1:η^1) in compound **218** and mono-donor (η^1), tri-donor (μ_2-η^2:η^1), bi-donor (μ_2-η^2) and (μ_2-η^1:η^1) in compound **218** as well as tri-donor (μ_2-η^2:η^1), bi-donor (η^2) and (μ_2-η^1:η^1) in compound **227**. In compounds **206**, **216**, **217**, **219**, **220**, **226** and **233** the carboxylate groups have three types of coordination modes; mono-donor (η^1), bi-donor (μ_2-η^1:η^1) and tri-donor (μ_2-η^2:η^1) in compounds **206** and **217**, tri-donor (μ_2-η^2:η^1), bi-donor (μ_2-η^1:η^1) and (η^2) in compounds **219** and **233**, tri-donor (μ_2-η^2:η^1), bi-donor (η^2) and (μ_2-η^1:η^1) in compound **214**, tri-donor (μ_2-η^2:η^1), bi-donor (μ_2-η^2) and (μ_2-

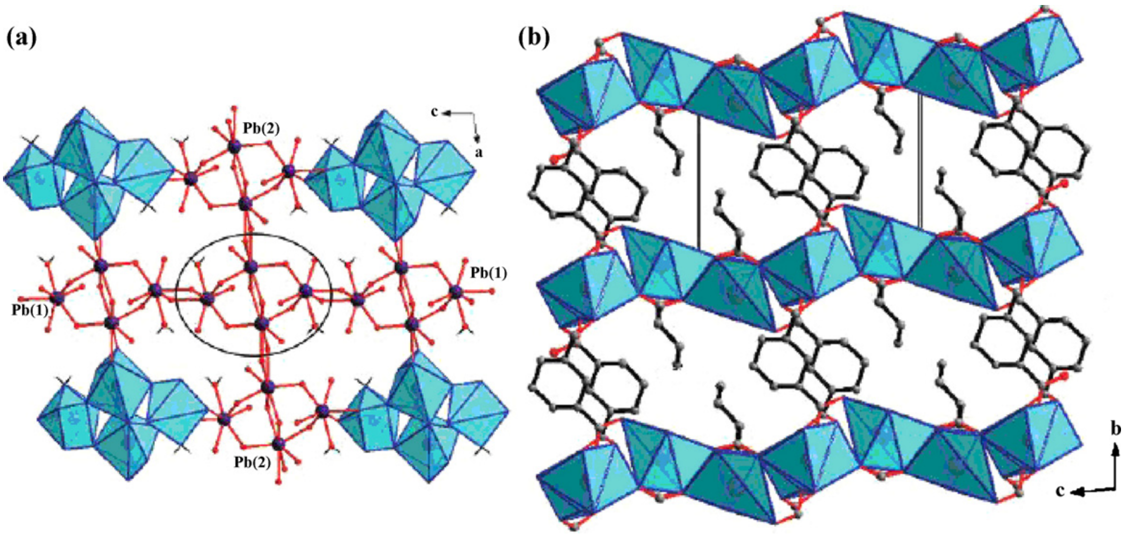


Fig. 70. (a) A view of the layer with infinite Pb–O–Pb linkages in **202** and (b) 3D structure, viewed along the *a*-axis [188].

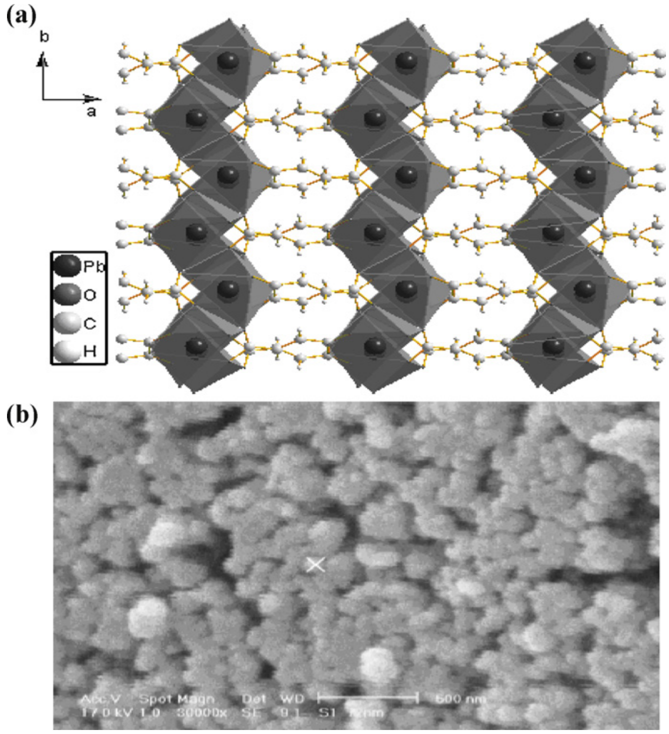


Fig. 71. (a) A fragment of the three-dimensional network in compound **203** and (b) SEM photograph of nano-particles of compound **203** prepared by sonochemical method [196].

η^1:η^1) in compound **220** and bi-donor (μ_2-η^1:η^1), tetra-donor (μ_3-η^1:η^2:η^1) and tri-donor (μ_2-η^2:η^1) in compound **221**. The carboxylate groups act as tetra-donor (μ_3-η^1:η^2:η^1) and tri-donor (μ_2-η^2:η^1) coordination modes in compounds **208**, **215**, **225**, **228** and **229** and as bi-donor (η^2) and tri-donor (μ_2-η^2:η^1) in compounds **205**, **209**, **222** and **230** and as tri-donor both (μ_2-η^2:η^1) and bridging (μ_2-η^1:η^1) in compounds **226** and **231** and bi-donor (η^2), tetra-donor chelating, bridging (μ_3-η^1:η^2:η^1) and tri-donor (μ_3-η^1:η^2) in compounds **204** and **216**. Carboxylate groups in compounds **207**, **210**, **211**, **223**, **224**, **232**, **234**, and **235** also have two types of coordination modes.

7. Heterometallic lead(II) coordination polymers

In this section the heterometallic lead(II) carboxylate compounds with different metal ions such as compounds $[PbZr_3(\mu_4\text{-}O)(m\text{-}OAc)_2(\mu\text{-}OPr^i)_5(OPr^i)_5]_n$ (**236**) [217], $\{Sr[Pb(Nta)]_2{\cdot}7.5H_2O\}_n$ (**237**), $\{Ba[Pb(Nta)NO_3]{\cdot}1.5H_2O\}_n$ (**238**) [57], $[Pb\text{-}(FcCOO)(\mu_2\text{-}FcCOO)(bpe)]_n$ (**239**) [218], $\{K_2[Pb(EDTA)]{\cdot}4H_2O\}_n$ (**240**) [219], $[Pb_2Cu(O_2C{-}CH_2{-}NH_2)_2Br_4]_n$ (**241**) [220], $[PbNa(NTA)]_n$ (**242**) [221] and $MnPb(Edta){\cdot}4H_2O$ (**243**) [222] were taken into account. All of them form bimetalic carboxylate coordination polymers by mono-donor (η^1) coordination modes. In the structure of complex **241**, the adjacent lead(II) halide layers are linked by trans-$Cu(Gly)_2$ to form 3D frameworks. These layered structures can be considered as a result of the inter-calation of neutral trans-$Cu(Gly)_2$ entities in the PbX_2 layered network. Copper(II) ions are at the center of a symmetrical unit consisting of two glycinato ligands, and all non-hydrogen atoms approximately lie in a plane that contains the *c*-axis (Fig. 72).

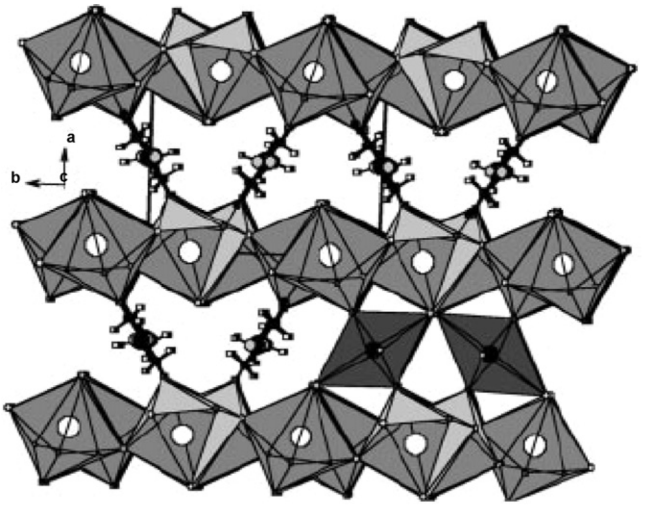


Fig. 72. Structure of **241** viewed along the *c*-axis showing layers of lead(II) polyhedra linked by pillars formed by trans-$Cu(Gly)_2$ entities. Two copper(II) [4 + 2] coordination polyhedra, with the weakly bonded bromide atoms, are shown in deep grey [220].

Compounds $\{Na[Pb(Nta)]\}_n$ (**244**) [57], $[Pb_2Al_5(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OiPr)_9(OiPr)_3(\mu\text{-}OAc)_3]_n$ (**245**) [223], $\{[PbZr_2(O)(OOCCH_3)_2(OCH_2CH_3)_6]_2\}_n$ (**246**) [224], $Pb(Hsal)_2(Cu(salen))_2$ (**247**) [225], $Pb_2Ti_2(\mu_4\text{-}O)(\mu\text{-}OAc)_2(\mu\text{-}OPri)_5(OPri)$ (**248**) [217], $\{Pb(OAc)_2[Cu(salen)]\}_n$ (**249**) [225], $\{[CuPb(L^{31})(BzO)(DMF)]ClO_4\}_n$ (**250**) [226], $\{[Ph_2Pb(OAc)(FEtTSC)]{\cdot}MeOH\}_n$ (**251**), $\{[Ph_2Pb(OAc)(FMeTSC)]{\cdot}MeOH\}_n$ (**252**) [227], $\{[Pb(OAc)(Ni(salen)_2](OAc)\}_n$ (**253**) [225], $\{[M_2Cr_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2(nta)_4 7H_2O]{\cdot}14H_2O\}_n$ (**254**) [228], $[Pb(\eta^1\text{-}\mu_2\text{-}OOCCH{=}CHFe)_2(phen)]_n$ (**255**) [229] and $[Pb_2Cu(O_2C{-}CH_2{-}NH_2)_2Cl_4]_n$ (**256**) [220] form carboxylate coordination polymers by bi-donor coordination modes and compounds $\{[Pb(\mu_2\text{-}\eta^2\text{-}OOCCH{=}(CH_3)CFc)_2]{\cdot}MeOH\}_n$ (**257**) [10], $[Pb\{(CO)_9Co_3(\mu_3\text{-}OAc)\}_2]_n$ (**258**) [230] and $\{[Pb(\mu_2\text{-}\eta^2\text{-}OOCH_4C_6Fe)_2]{\cdot}(CH_3OH)_2\}_n$ (**259**) [231] form carboxylate coordination polymers by tri-donor coordination modes.

Complexes $\{Pb(ip)_2[Cu^{II}_2(obpy)_2][Cu^{I}_2(obpy)_2]\}_n(H_2O)_{2n}$ (**260**) [232], $\{[Pb_2(FcCOO)(\eta^2\text{-}FcCOO)(\mu_2\text{-}\eta^2\text{-}FcCOO)(\mu_3\text{-}\eta^2\text{-}FcCOO)(CH_3OH)]{\cdot}1.5CH_3OH{\cdot}H_2O\}_n$ (**261**) [218], $[Pb(o\text{-}OOCC_6H_4COFc)(\mu_2\text{-}o\text{-}OOCC_6H_4COFc)(bpe)]_n$ (**262**) [10], $K[Pb(Nta)]$ (**263**), $Ca[Pb(Nta)]_2{\cdot}2H_2O$ (**264**) [57], $Na_{1.5}[Pb_2(INO)_5]{\cdot}0.5NO_3$ (**265**) [68], $Pb_2Zr(ox)_4{\cdot}6H_2O$ (**266**) [233], $CuPb(2,5\text{-}pydc)_2$ (**267**) [234] and $[KPb(AcO)_2(SCN)]_n$ (**268**) [235], form carboxylate coordination polymers with more than one type coordination modes. In compounds **262** and **265**, the carboxylate group acts as mono-donor (η^1) and bi-donor chelating (η^2) coordination mode and in compounds **263** and **264**, carboxylate groups act as mono-donor (η^1) and bi-donor bridging (μ_2-η^2) coordination mode. In compounds **260** and **262** the carboxylate group has three different coordination modes, mono-donor (η^1), bi-donor bridging (μ_2-η^1:η^1) and chelating (η^2) coordination modes in compound **261** and tri-donor chelating, bridging (μ_2-η^2:η^1), bi-donor chelating (η^2) and mono-donor (η^1) coordination modes in compound **261**. In compound **266**, one of the carboxylate groups acts as tri-donor chelating, bridging (μ_2-η^2:η^1) coordination mode. The other one acts as tetra-donor chelating, bridging (μ_3-η^1:η^2:η^1) coordination mode. In compounds **267** and **268**, the carboxylate group has two types of coordination modes, tri-donor chelating, bridging (μ_3-η^1:η^2) and bi-donor bridging (μ_2-η^1:η^1) in compound **267** and tri-donor chelating, bridging (μ_2-η^2:η^1) and tetra-donor chelating, bridging (μ_3-η^1:η^2:η^1) in compound **268**. In compound **265**, there are two additional kinds of coordination modes with Pb(II) atoms: one acts as a diconnector to link with two Pb2 centers through a chelating carboxylate group and N-oxide O atom and the other being a terminal ligand coordinated with the Pb2 center through a mono-donor carboxylate group like a dancing arm. As shown in Fig. 73a, each $[Pb_2O_2]$ unit is bridged to one Pb2 by two parallel INO ligands along the [0 0 1]-direction, and then is bridged

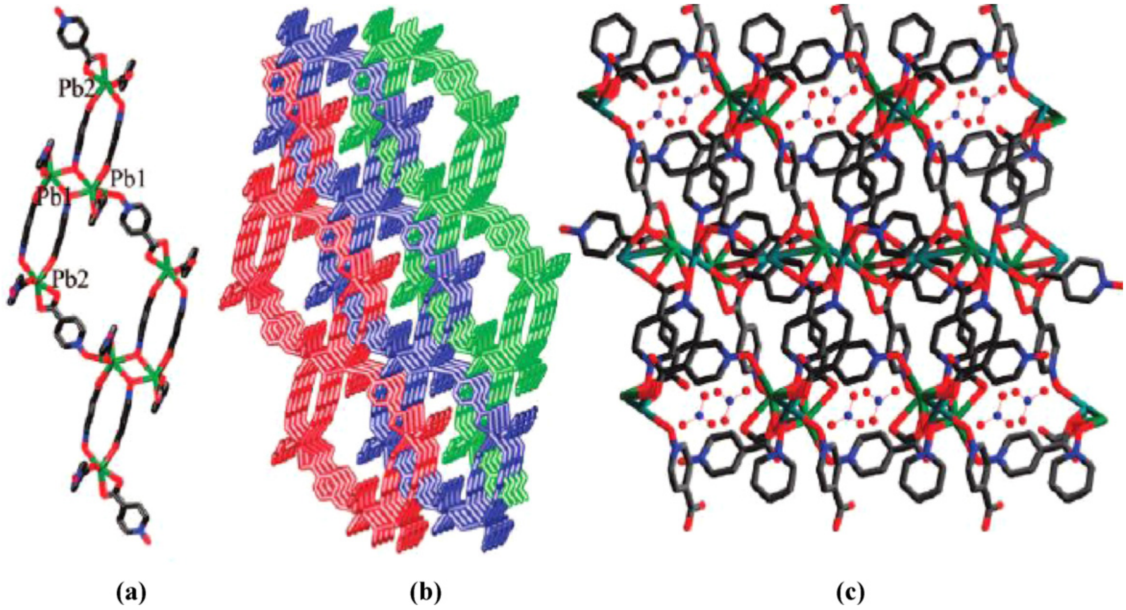


Fig. 73. (a) View of 1D chain, showing the [Pb$_4$(INO)$_4$] unit, (b) view of the mutual polythreading of the 2D sheets in **265** and (c) view of the 3D supramolecular network, where the parallelogram channels located guest nitrate anions are created by stacking of 2D layer along the *b*-axis [68].

to the second Pb2 through another two parallel INO ligands from the opposite direction yielding [Pb$_4$(INO)$_4$] unit. Likewise, two INO ligands connect with a [Pb$_4$(INO)$_4$] unit to give a 1D motif with very large rhombic windows (dimensions 9.99 × 7.53 Å^2) along the *c*-axis, which is then further extended into a 2D layer by bridging INO ligands. The dancing mono-donor INO ligands and Pb2 centers of each 2D layer are threaded into a 1D rhombic channel with each square penetrated oppositely by two INO lateral arms belonging to two different layers, as shown in Fig. 73b. It is noteworthy that one-dimensional rectangular channels also exist with the dimension of ca. 4.25 × 2.68 Å^2 running along the *b*-axis direction, which are occupied by anions (Fig. 73c).

8. Additional remarks

Several different synthetic approaches have been offered for the preparation of lead(II) coordination compounds. Some of them are (1) slow diffusion of the reactants into a polymeric matrix, (2) diffusion from the gas phase, (3) evaporation of the solvent at ambient or reduced temperatures, (4) precipitation or recrystallization from a mixture of solvents, (5) temperature controlled cooling and (6) hydrothermal synthesis. Also in this review, we reported nano-sized lead(II) coordination polymers synthesized by sonochemical method.

Compounds **2–4**, **11**, **13**, **16**, **17**, **23**, **25-27**, **48**, **55**, **63**, **64**, **67**, **72–77**, **82**, **85**, **87**, **93**, **94**, **101**, **103**, **109**, **112**, **118**, **134**, **135**, **139**, **142**, **144**, **146**, **148**, **155**, **159**, **181**, **188**, **209**, **236**, **239**, **249**, **253**, **255**, **257**, **259**, **261** and **262** have been prepared through slow evaporation of the solvent at ambient or reduced temperatures. Compounds **21**, **49**, **88**, **91**, **94**, **126**, **129**, **170**, **191**, **204**, **223** and **247** have been produced by slow diffusion. Complexes **9**, **10**, **14**, **18**, **20**, **24**, **28**, **30**, **32**, **37**, **38**, **40–42**, **47**, **50**, **51**, **56-61**, **65**,**66**, **70**, **78**, **79**, **84**, **96–100**, **104**, **117**, **119**, **123**, **133**, **147**, **151**, **154**, **156**, **157**, **160-163**, **166-169**, **172**, **173**, **176**, **177**, **182-184**, **186**, **187**, **189**, **190**, **192**, **194**, **202**, **205**, **211**, **213-220**, **225-227**, **229-233**, **260**, **265** and **266** have been synthesized by the hydrothermal method. Compound **29**, **80**, **81** and **258** have been prepared through the layering technique. Only compound **19** has been produced by photodimerization. Colorless single crystals of **171** have been grown by recrystallizing the white powder from hot water. Single crystals of **43**, **106**, **212**, **250** and **266** are recrystallized at low temperature (compounds **44** and **110** at 6 °C, **141** at −20 °C, **185** at 4 °C, **245** at −15 °C and **248** at 5 °C). Single crystals of compounds **31**, **33**, **34**, **45**, **68**, **69**, **90**, **92**, **95**, **102**, **107**, **108**, **111**, **114**, **115**, **120–122**, **24**, **128**, **130**, **132**, **136**, **140**, **193**, **203**, **234** and **235** as well have been formed using a heat gradient applied to a aqueous solution of the reagents (the branched tube method) and finally nano-sized compounds **33**, **34**, **88**, **90**, **95**, **102**, **107**, **108**, **115** **120–122**, **193** and **203** have been synthesized by sonochemical method.

9. Conclusions

Lead(II), with its large radius, flexible coordination environment and various stereo-chemical activities, provides unique opportunities for formation of unusual network topologies with interesting properties. Lead(II) compounds are a potential class of functional materials and ideal systems for investigation of structure–property relationships. The largest class of coordination polymers are those containing carboxylate ligands and until now a variety of hybrid materials with different dimensions has been designed with the use of carboxylate groups. The carboxylate group due to its rich coordination modes usually binds either a mono-donor, a bi-donor, a tri-donor or a tetra-donor to a metal ion and lead(II) forms discrete, one-, two- and three-dimensional coordination polymers. Also lead(II) can form one-, two- and three-dimensional coordination polymer via secondary interactions such as, hydrogen-bonding, π–π stacking interactions and non-covalent bonding. The different coordination modes of carboxylate groups increase the strength and stability of the resulting architectures. Carboxylate groups in the lead(II) coordination polymers have been coordinated in binding modes ranging from η^1, bridging (μ^2-η^1:η^1), chelating (η^2), bridging (μ_2-η^2), bridging (μ_3-η^1:η^2), bridging (μ_3-η^1:η^2), chelating, bridging (μ_2-η^2:η^1) to chelating, bridging (μ_3-η^1:η^2:η^1) and chelating, bridging (μ_4-η^2:η^2). In this study, the researchers found that carboxylate groups in many of lead(II) coordination polymers form more than one type of coordination mode and among all of these modes maximum number belonged to chelating (η^2) mode.

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