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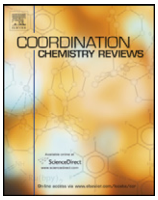

Review

Structures and properties of mercury(II) coordination polymers

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Abbreviations: amoimy, 1-(9-anthracenylmethyl)-3-octylimidazol-2-ylidene; ampa, aminomethylphosphonic acid; azobpy, 3,3′-azobispyridine; 4,4′-azpy, 4,4′-azopyridine; bbimms, 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene; bbsb, 1,4-bis(benzylsulfanyl)butane; bbsp, 1,5-bis(benzylsulfanyl)pentane; 4-bedpef, 9,9-bis-ethyl-2,7-di-(4-pyridyl)ethynylfluorene; besb, 1,4-bis(ethylsulfanyl)butane (C_4H_9S); besp, 1,3-bis(ethylsulfanyl)propane; bib, 1-bromo-3,5-bis(imidazol-1-ylmethyl)benzene; bidtp, bis(isopropyl)dithiophosphate $\{S_2P(OPr^i)_2\}$; bin, 1,5-bis(isonicotinamido)naphthalene; 2,2′-bipy, 2,2′-bipyridine; 4,4′-bipy, 4,4′-bipyridine; bipyP$_2$, tetraethyl 2,2′-bipyridyl-4,4′-diphosphonate; 2-bmps, bis(2-methylpyridyl) sulfide; bnbap, binaphthyl-bis(amidopyridyl); bpa, 1,2-bis(4-pyridyl)ethane; bpba, N,N′-bis(4-pyridyl)-1,4-benzenedicarboxamide; 2-bpdb, 1,4-bis(2-pyridyl)-2,3-diaza-1,3-butadiene; 3-bpdb, 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene; 4-bpdb, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene; 2-bpdh, 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene; 3-bpdh, 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene; 4-bpdh, 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene; bpe, 1,2-bis(4-pyridyl)ethane; bpen, 1,2-bis(4-pyridyl)ethylenediamine; 4-bpet, 2,2′-bis-(4-pyridylethynyl)tolane; bpfb, N,N′-bis(4-pyridyl formamide)-1,4-benzene; bpfp, N,N′-bis(3-pyridylformyl)piperazine; 4-bpmape, bis[4-(4-pyridylmethyleneamino)phenyl] ether; 4-bpmbdt, 2,6-bis(4-pyridinylmethyl)-benzo[1,2-c:4,5-c′]dipyrrole-1,3,5,7(2H,6H)-tetrone; 3-bpmd, N,N′-bis(3-pyridylmethyl)-diphthalic diimide; 4-bpmp, N,N′-bis(4-pyridylmethyl)piperazine; 4-bpmpd, N,N′-bis(4-pyridylmethyl)pyromellitic diimide; 3-bpo, 2,5-bis(3-pyridyl)-1,3,4-oxadiazole; 4-bpo, 2,5-bis(4-pyridyl)-1,3,4-oxadiazole; bpp, 1,3-bis(4-pyridyl)propane; 4-bpt, 2,5-bis(4-pyridyl)-1,3,4-thiadiazole($C_{12}H_8N_4S$); bptb, 1,4-bis(phenylthio)butane ($PhS(CH_2)_4SPh$); bpu, 1,3-bis-pyridin-4-ylmethyl urea; bpytm, bis(2-pyridylthio)methane; 3,5-Br$_2$py, 3,5-dibromopyridine; btan, 9,10-bis(triazol-1-ylmethyl)anthracene; ^{n}Bu, n-butyl; bzim, benzimidazole; bzimtH$_2$, benzo-1,3-imidazole-2-thione; caf, caffeine; cht, cyclohexanethiolate; 3,5-Cl$_2$py, 3,5-dichloropyridine; 2-cpa, (2-chlorophenoxy)acetate; cryptand5, 1,13-bis(8-chinolyl)-1,4,7,10,13-pentaoxatridecane; Cy, cyclohexyl; dedtp, diethyldithiophosphinate; 1,9-DiMeG, 1,9-dimethyl-guanine; DLMD, 1,3,6,7-tetramethyllumazine; dmap, 4-(dimethylamino)pyridine; dmdp, O,O′-dimethyl dithiophosphato; 2,5-dmpyr, 2,5-dimethylpyrazine; 2,6-dmpyr, 2,6-dimethylpyrazine; Dmt$^-$, dimethyl-1,2,4-triazolate; dpb, 2,3-di (4-pyridyl)-2,3-butanediol; Dpc, 6,7-dimethyl-2,3-di-(2′-pyridyl)-chinoxaline; 3-dpcpdo, achiral 2,5-diphenyl-3,4-di(3-pyridyl)cyclopenta-2,4-dien-1-one; dpp, diphenylphosphinate; dppeO, 1,2-bis(diphenylphosphino)ethane monoxide; dps, 4,4′-dipyridylsulfide; 2,2′-dpyds, 2,2′-dipyridyl disulfide; dsep, $\{Se_2P(OPr^i)_2\}$; 2-ebpec, 9-ethyl-3,6-bis[2-(2-pyridyl)ethenyl]carbazole; 4-ebpec, 9-ethyl-3,6-bis[2-(4-pyridyl)ethenyl]carbazole; HaaiEt, 1-ethyl-2-(phenylazo)imidazole; HAm4DH, 2-pyridineformamide Tthiosemicarbazone; H$_4$bpb, N,N′-bis(3-pyridylmethyl)-1,4-benzenedimethylamine; hmt, hexamethylenetetramine; 2-Hoz, 2-oxazolidone (1,3-oxazolidin-2-one, $C_3H_5NO_2$); 3-Hpapap, 2-[3-(pyridylamino)-phenylazo]pyridine); HpicOH, 3-hydroxypicolinic acid; Hpyta, 4-pyridylthioacetic acid; Htrz, 1,2,4-triazole; iimb, 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene; LBA, D-lactobionates; MB, methylene blue; mbpa, meso-2,5-bis(pyridinio)adipate; mbtma, meso-2,5-bis(trimethylammonio) adipate; mebta, 2-methyl-1,3-benzothiazole; Me$_2$dmit, 4,5-bis(methylthio)-1,3-dithiole-2-thione; 9-MeDP, 9-methyl-1-deazapurine; meimtH, 1-methyl-1,3-imidazole-2-thione; 3,5-Me$_2$py, 3,5-dimethylpyridine; Mmt$^-$, monomethyl-1,2,4-triazolate; 3-mpdp, 2-[(E)-2-(3-methylphenyl)-1-diazenyl]pyridine; mpy, 2-pyridylmethanol; 1-MH, 1-methylhydantoin; N-BBzBimCH, 1,4-bis(1-benzyl-benzimidazol-2-yl)cyclohexane; nbs, *p*-nitrobenzoxasulfamate; NicH, pyridine-3-carboxylic acid or nicotinic acid; NIT-Ph, 2-(phenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide; OAc, acetate; PBz$_3$, tribenzylphosphine; PCy$_3$, tricyclohexylphosphine; pds, peroxodisulfate (S_2O_8); PEDT, 4,5-(phenyl-ethylenedithio)-1,3-dithiole-2-thione; pehc, 2-[1-(pyrrol-2-yl)ethylidene]hidrazine carbothioamide; Pip, piperazine; pipdtc, piperidinecarbodithioate; 3-pmbz, N-(3-pyridylmethyl)benzimidazole; pom, 3-methyl-4-nitropyridine 1-oxide; ptr, (m-phenol)-1,2,4-triazole; py, pyridine; pya, 4-pyridylacetate; pyda, 2,6-pyridinediamine; pydc·H$_2$, 2,6-pyridinedicarboxilic acid; 4-pye, 4-pyridylethynyl; pyia, pyridinioacetate; pym, pyrimidine (1,3-diazine); Pyo, pyridazine (1,2-diazine); 2pypo, (2-pyridyl)phosphonicacid; pyr, pyrazine (1,4-diazine); 18S6, 18-membered saturated thiacrown ether; sac, saccharinate anion; TCE, 1,1,2,2-tetrachloroethane; tcm$^-$, tricyanomethanide; terpy, 2,2′,2″-terpyridine; tfms, trifluoromethanesulfonate; 4-tfp, 4-tetrafluoropyridyl; tib, 1,3,5-tris(1-imidazolyl)benzene; tempt, 2,4,6-tris[4-(imidazol-1-ylmethyl)phenyl]-1,3,5-triazine; titmb, 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene; tmaa, trimethylammonioacetate; Tmac, trimethylammonio-carbonamidate; 2-tmmpio, 4,4,5,5-tetramethyl-2-(6-methyl-2-pyridyl)-2-imidazoline N^1-oxyl N^3-oxide; 3-tmpio, 4,4,5,5-tetramethyl-2-(3-pyridyl)-2-imidazoline N^1-oxyl N^3-oxide; toacpd, 1,4,7,10-tetraoxa-13-azacyclopentadecane; tpmb, 1,3,5-tris(4-pyridylmethoxyl)benzene; 4-tpstmb, 1,3,5-tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene; tpt, 2,4,6-tri(4-pyridyl)-1,3,5-triazine; TPyP, tetrapyridylporphyrin; ttb, 3,4-ethylenedithio-1,3-dithiole-2-thione ($C_5H_4S_5$); tzdSH, 1,3-thiazolidine-2-thione; L1, rac-1,1′-$C_{20}H_{12}(OCH_2\text{-}3\text{-}C_5H_4N)_2$; L2, 1,2-$C_6H_4\{CH_2C(O)NHCH_2\text{-}4\text{-}C_5H_4N\}_2$; L3, rac-1,1′-$C_{20}H_{12}(OCH_2\text{-}4\text{-}C_5H_4N)_2$; L4, $PPh_2CH_2CH_2PPh_2{=}C(H)C(O)Ph$; L5$^-$, $O_2CCH_2N^+Me_2(CH_2)_2N^+Me_2CH_2CO_2^-$; L6$^-$, $O_2CCH_2N^+Me_2(CH_2)_3N^+Me_2CH_2CO_2^-$; L7$^-$, $O_2CCH_2N^+Me_2(CH_2)_4N^+Me_2CH_2CO_2^-$; L8, 1,2-$C_6H_4\{C(O)\text{-}NHCH_2\text{-}4\text{-}C_5H_4N\}_2$.

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ABSTRACT

During the last two decades, coordination polymers have received much attention and the number of synthesized compounds is still growing, which is mainly due to their potential application in such fields as microelectronics, nonlinear optics, molecular selection, ion exchange and catalysis. In contrast, coordination polymers of transition metals ions, the formation of polymers with main group metal ions such as mercury(II) is disproportionately sparse when compared with those of other metals. Because of the effects of mercury on environment and its polymers' applications, it is necessary to understand mercury's ability to bind donors and form complexes or coordination polymers. This review provides an overview of all the reported coordination polymers of mercury(II) after 1990 and a summary of their properties. One-dimensional polymers, constituted the majority of the mercury(II) coordination polymers and the most frequent coordination number for mercury(II) is four.

1. Introduction

Coordination polymer is a general term used to indicate an infinite array composed of metal ions which are bridged by certain ligands among them. This is a general term that incorporates a wide range of architectures including simple one-dimensional chains with small ligands to large mesoporous frameworks [1,2]. Generally, the formation process proceeds automatically and, therefore, is called a self-assembly process.

In general, the type and topology of the product generated from the self-assembly of inorganic metal nodes and organic spacers depend on the functionality of the ligand and valences and the geometric needs of the metal ions used. Organic ligands are very important in design and construction of desirable frameworks, since changes in flexibility, length, and symmetry of organic ligands can lead to the formation of a class of materials with diverse architectures and functions [3].

Depending on the metal element that is used in the polymer, and its valence, different geometries may be created, e.g., linear, trigonal-planar, T-shaped, tetrahedral, square-planar, square-pyramidal, trigonal-bipyramidal, octahedral, trigonal-prismatic, pentagonal-bipyramidal, and their distorted forms [4]. Organization of building blocks can lead to the formation of metal-organic frameworks of various dimensions: one-, two- or three-dimensional architectures. Dimension is usually determined through the nodes (metal centers) [5].

Metal coordination polymers have been studied widely as they represent an important interface between synthetic chemistry and materials science, and they have specific structures, properties, and reactivities that are not found in mononuclear compounds. They may have potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing. In the last two decades, rapid developments in the crystal engineering of metal-organic coordination polymers have produced many novel materials with various structural features and properties.

The group 12 elements are rather a special case when considering the chemistry of the main group elements. Supramolecular structures that contain mercury(II) seem to have much more in common with main group elements, in part because they tend to form structures with low-coordinate linear or other distorted coordination geometries [6]. The spherical d^{10} configuration is associated with a flexible coordination environment so that the geometries of these complexes can vary from tetrahedral to octahedral and severe distortions in the ideal polyhedron occur easily. Furthermore, due to the general lability of the d^{10} metal ion complexes, the formation of coordination bonds is reversible, which enables metal ions and ligands to rearrange during the process of polymerization to give highly ordered network structures. Consequently, Zn, Cd and Hg can readily accommodate all kinds of architectures and a selection of the topological types of 1D, 2D and 3D polymers is given [7].

In spite of attractive properties of mercury(II) compounds in terms of their potential applications in paper industry, paints, cosmetics, preservatives, thermometers, manometers, energy efficient fluorescent light bulbs and mercury batteries (although somehow limited due to mercury's toxicity), formation of polymers with Hg^{2+} ion is disproportionately sparse when compared with that of Zn^{2+} and Cd^{2+} metals.

Grednic [8] defines the nearest neighbours of mercury in a crystal structure as those which are in "contact" with it. In a free molecule (e.g. in the vapor state) these contacts are chemical bonds and their number is defined by valency or coordination number. With a crystal structure the position is less clear, and it is necessary to restrict the consideration of nearest neighbours (the atoms in the coordination sphere) of mercury to those within a defined distance. All atoms surrounding mercury at a distance of less than the sum of van der Waals radii are considered to belong to the mercury coordination sphere [8]. Mercury(II) has atomic, ionic, covalent (tetragonal) and van der Waals radii of

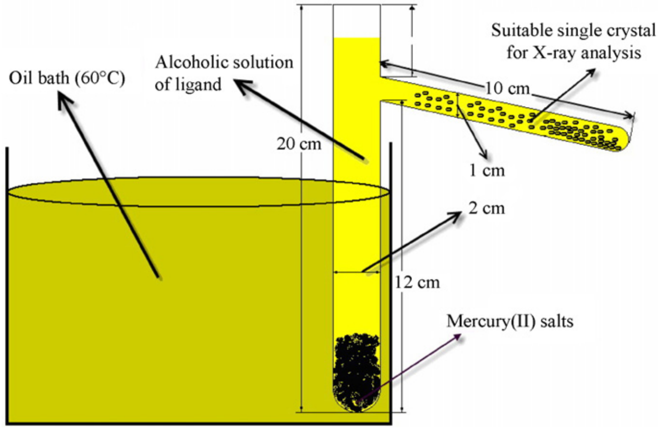


Fig. 1. Depiction of the branched tube for syntheses and isolation of single crystals of multi-dimensional mercury(II) coordination polymers.

$1.50 < r(\mathrm{Hg}) < 1.73$, 1.04, 1.48 and 1.50 A°, respectively [8]. In addition van der Waals radii 1.55 [9], 1.75(7) [10] and 1.71–1.76 Å [11] have been cited. In this review, distances smaller than the sum of van der Waals radii, are taken as effective coordination number.

Several different synthetic approaches have been offered for the preparation of mercury(II) coordination polymers. Some of them are (1) slow diffusion of the reactants into a polymeric matrix (e.g. compounds **4**–**5**, **20**, **74**–**75**, **77**–**78**, **80**, **135**, **190** and **250**), (2) layering technique (e.g. compounds **54**, **97**–**101** and **227**), (3) evaporation of the solvent at ambient or reduced temperatures (e.g. compounds **12**–**17**, **51**–**52**, **125**–**127**, **233**, **240**, **243**, **255** and **258**), (4) precipitation or recrystallisation from a mixture of solvents (e.g. compounds **1**, **10** and **11**), (5) temperature controlled cooling (e.g. compounds **116**, **173**, **188** and **246**), (6) hydrothermal synthesis (compounds **188** and **249**) and (7) gel growth crystallization technique (compound **215**). In our reported compounds (e.g. **31**, **34**–**38**, **40**, **44**–**47**, **50**, **140**–**141**, **147**, **186** and **237**), we have shown another new and simple method for the construction of multi-dimensional mercury(II) coordination polymers, the branched tube method (Fig. 1). The new method is straight forward, cheap and trouble-free and can be used for the preparation of other types of mercury(II) coordination polymers.

2. One-dimensional coordination polymers

One-dimensional (1D) complexes which are the simplest topological type of coordination arrays represent a good starting point for modeling and investigating infinite polymeric compounds to develop strategies for engineering supramolecular polymers [12]. In one-dimensional motifs the metal ion is coordinated with two ligand molecules, metal ions and organic ligands alternate "infinitely", leading to a chain [5]. The most important motifs among one-dimensional coordination polymers are linear chains, zigzag chains, double chains, ladder-like chains, fish-bone, railroad and helix.

2.1. Coordination number 3

In compounds $[\mathrm{Hg(4\text{-}pye)_2}]_n$ **(1)** [13] and $[\mathrm{Hg(4\text{-}tfp)_2}]_n$ **(2)** [14], Hg(II) centers are coordinated by two C atoms and one N atom in a T-shaped geometry to give infinite zigzag polymeric chains (Fig. 2). In the complex $[\mathrm{Hg(2\text{-}cpa)_2}]_n$ **(3)** [15] mercury is bonded linearly to two carboxylate oxygen atoms to form a polymer link to a third oxygen giving triangular coordination about the mercury.

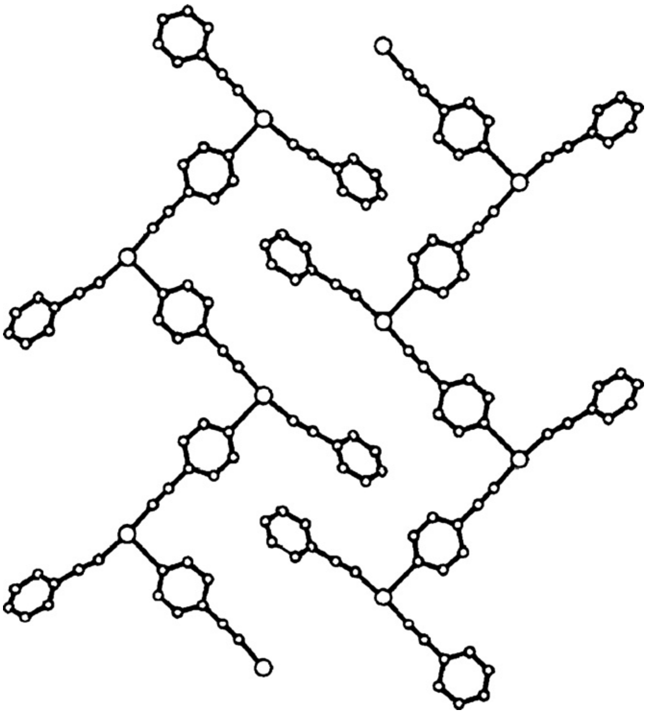


Fig. 2. Zigzag chain structure of $[\mathrm{Hg(4\text{-}pye)_2}]_n$ **(1)** [13]. Reproduced with permission of Elsevier.

2.2. Coordination number 4

Combination of neutral tetrakis-monodentate tecton **I** (Fig. 3) and $\mathrm{HgCl_2}$ leads to the formation of a 1D coordination polymer (compound **4** [16]). The empty spaces in the network are occupied by $\mathrm{C_2H_2Cl_4}$ and $\mathrm{H_2O}$ solvent molecules without any specific interactions with the networks. Connection between the organic bis-monodentate tectons **II** and **III** (Fig. 3) and $\mathrm{HgCl_2}$ (compounds **5** [17] and **6** [18]) and tecton **IV** (Fig. 3) with $\mathrm{HgX_2}$ (X = Cl, Br, I) (compounds **7**, **8** and **9** [18]) leads to the formation of zigzag polymeric chains. When tecton **IV** is combined with $\mathrm{HgX_2}$ (X = Cl, Br, I), two 1D chains have opposite directions and packed orthogonally leading to the formation of a 2D network with basket wave type. The formation of the overall structure results from the parallel packing of braided sheet (Fig. 4) [18]. Again, connection between the organic tecton **V** (Fig. 3) and $\mathrm{HgCl_2}$ leads to an enantiomerically pure neutral single stranded infinite helix (compound **10**) with P helicity [19]. In **11,** 1D chains resulting from reaction between tecton **VI** (Fig. 3) and $\mathrm{HgCl_2}$ [20] are interconnected through H bonds between the C=O groups belonging to one strand and the NH moieties belonging to the consecutive strand and lead to the formation of a 2D network. In all the compounds above the coordination sphere around Hg(II) is composed of two halide anions and two N atoms belonging to two consecutive tectons in a distorted tetrahedral coordination geometry.

The structures of $[\mathrm{Hg(4,4'\text{-}bipy)I_2}]_n$ **(12)** [21,22], $[\mathrm{Hg(4\text{-}bpmp)I_2}]_n$ **(13)** [23], $[\mathrm{Hg(4,4'\text{-}azpy)I_2}]_n$ **(14)** [24], $[\mathrm{Hg(bpfp)I_2}]_n$ **(15)** [25], $[\mathrm{Hg(bpfb)I_2}]_n\cdot\mathrm{2DMF}$ **(16)** [26], $[\mathrm{Hg(bpfb)I_2}]_n$ **(17)** [27], $[\mathrm{Hg(azobpy)I_2}]_n$ **(18)** [28], $[\mathrm{Hg(4\text{-}bpt)I_2}]_n$ **(19)** [29], $[\mathrm{Hg(hmt)I_2}]_n$ **(20)** [30], $\{[\mathrm{Hg(bpba)I_2}]\cdot\mathrm{1.5CH_3OH}\}_n$ **(21)** [31], $\{[\mathrm{Hg(3\text{-}bpmd)I_2}]\cdot\mathrm{0.4CH_3OH}\}_n$ **(22)** [32], $[\mathrm{Hg(4\text{-}bpmbdt)I_2}]_n$ **(23)** [33], $[\mathrm{(HgI_2)_2(dpb)_2(DMSO)_2}]_n$ **(24)** [34], $[\mathrm{Hg(iimb)I_2}]\cdot$0.5acetone **(25)** [35], $[\mathrm{Hg(4\text{-}bpo)I_2}]\cdot\mathrm{CH_3CN}$ **(26)** [36], $[\mathrm{Hg(3\text{-}bpdb)I_2}]_n$ **(27)**, $[\mathrm{Hg(3\text{-}bpdh)I_2}]_n$ **(28)** [37] and $[\mathrm{Hg(4\text{-}bpdb)I_2}]_n$ **(29)** [37,38], $[\mathrm{Hg(4\text{-}bpet)I_2}]_n$ **(30)** [39], $[\mathrm{Hg(\mu\text{-}bpen)I_2}]_n$ **(31)** [40] and $[\mathrm{Hg(\mu\text{-}bin)I_2}]_n$ **(32)** [41] consist of one-dimensional zigzag chains and the Hg

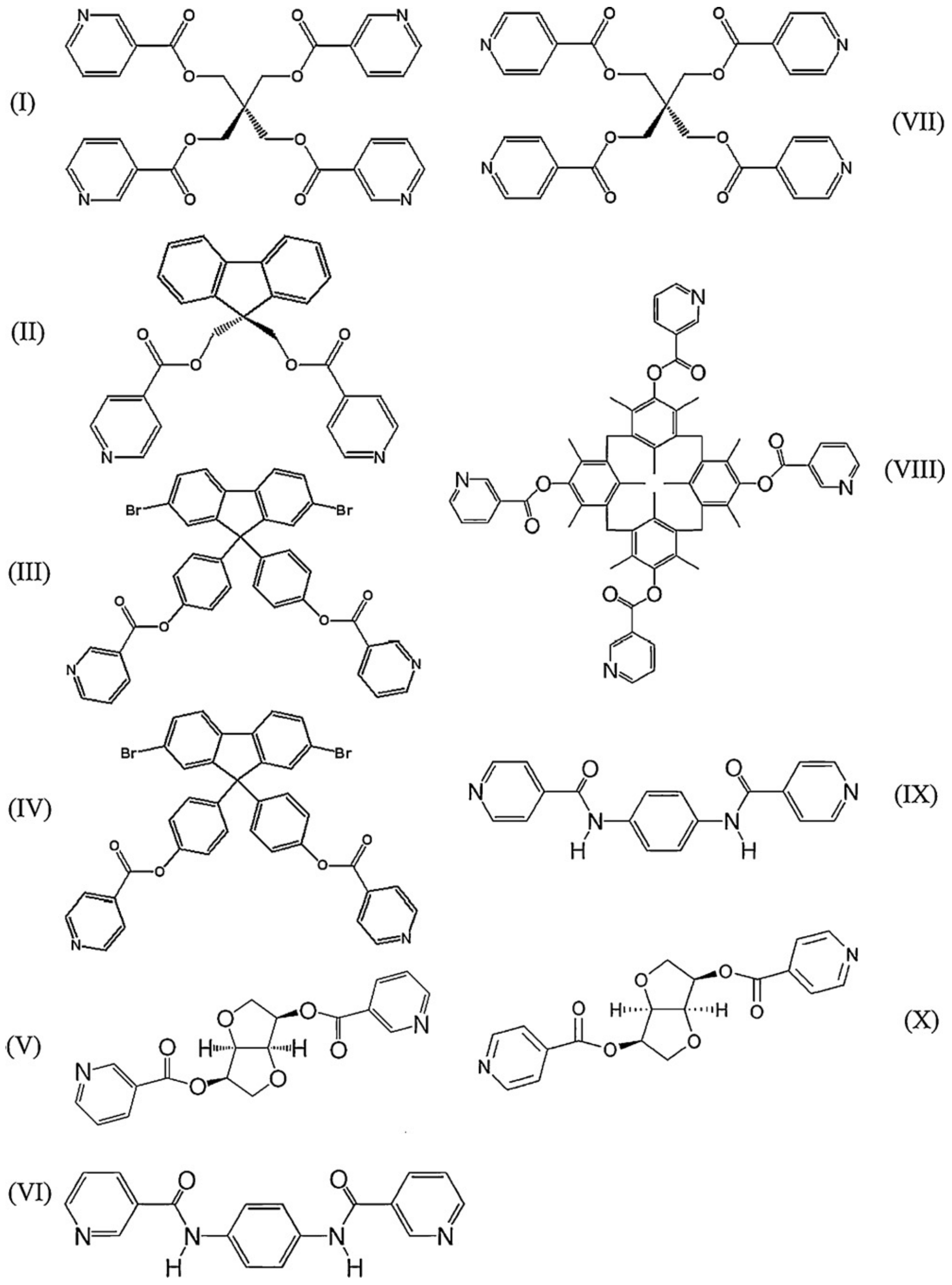


Fig. 3. Tectons used in mercury(II) coordination polymers.

atoms are in a distorted tetrahedral environment, coordinated by two nitrogen atoms from different N-donor bifunctional ligands and two iodide atoms. Complex **14** exhibits considerable NLO absorption properties in solution, NLO properties are also observed in complexes **15**, **16** and **18**. In compound **17** intermolecular hydrogen bonds, between the N atoms and the O atoms of adjacent ligands link the chains into a 2D network. In compound **18** the I atoms exhibit weak interactions with Hg atoms from neighbouring chains. These weak interactions resulted in a final 3D supramolecular motif. In complex **19**, through weak I···I interactions, 1D zigzag chains are extended into a two-dimensional double layer structure. This compound exhibits intense green-blue photoluminescence in the solid state. In compound **23**, both 4-bpmbdt ligands adopt a distorted ‘Z’ conformation. The unusual feature of this material is the zigzag chains of $[Hg(4\text{-bpmbdt})I_2]_n$ running in perpendicular directions, which enable them to interweave in a 2O/2U (two-over/two-under) fashion to create the cloth-like sheet structure (Fig. 5). Representations of 1O/1U (one-over/one-under) and 2O/2U (two-over/two-under) cloth-like interwoven sheets are given in Fig. 6. In compound **25**, infinite 1D chains are joined together by I···I interactions (3.90 Å) to lead to the formation of an infinite 1D ladder. Each chain contains hexagons that are large enough to allow other hexagons to pass through. In this way, 1D ladders form a 3D framework structure (Fig. 7). The maximum emission wavelength of this complex is at 450 nm. Despite the fact that I^- are only in a monodentate coordination mode in the above compounds, in polymeric complex, $[Hg(bzim)I_2]_n$ **(33)** [42], one I^- anion is in a monodentate coordination mode and the others bridge neighbouring Hg atoms to form a zigzag polymeric chain. The Hg atom is coordinated by one N atom from bzim ligand and three I^- anions in a distorted tetrahedral geometry. Adjacent polymeric chains

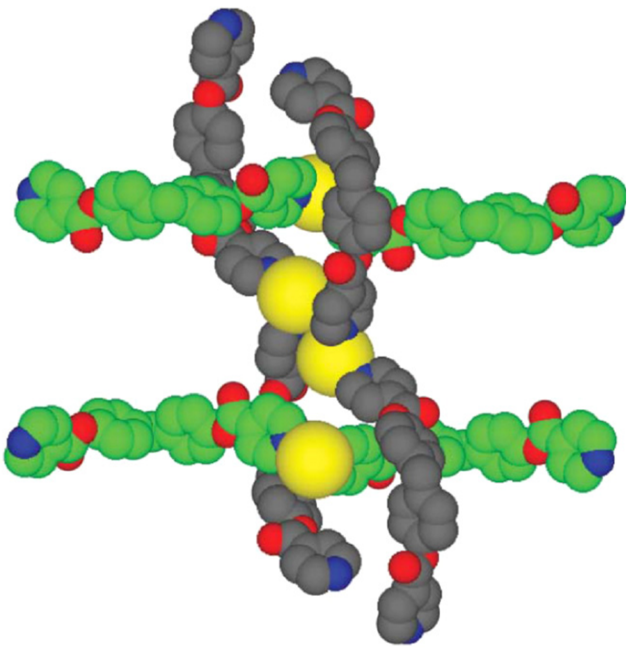


Fig. 4. A portion of the structure of 1D coordination polymer obtained upon combining tecton **IV** with $HgCl_2$ showing the almost perpendicular packing of 1D networks leading to the formation of a braided sheet [18]. Reproduced by permission of The Royal Society of Chemistry.

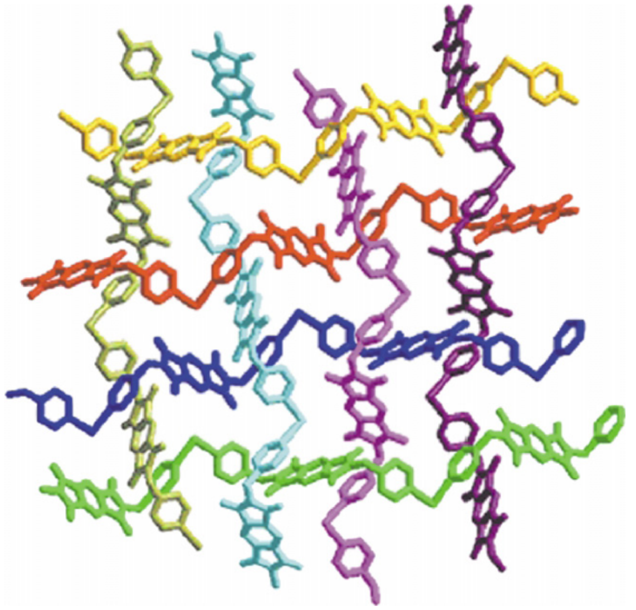


Fig. 5. 2O/2U interwoven 2D network in $[Hg(4\text{-bpmbdt})I_2]_n$ **(23)** [33]. Reproduced by permission of The Royal Society of Chemistry.

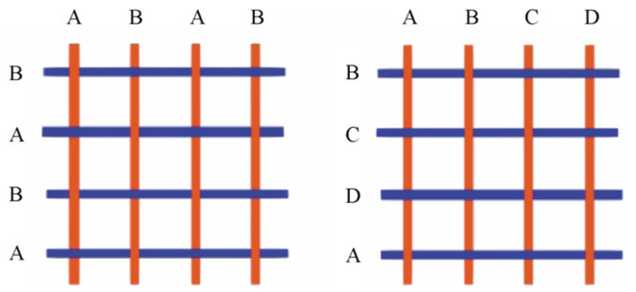


Fig. 6. 1O/1U (left) and 2O/2U (right) cloth-like interwoven sheets [33]. Reproduced by permission of The Royal Society of Chemistry.

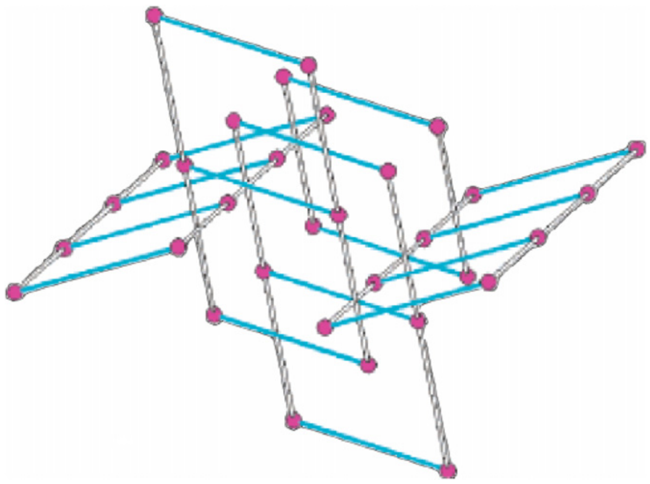


Fig. 7. A schematic drawing of polycatenated 1D polymers of $[Hg(iimb)I_2]\cdot0.5acetone$ **(25)** [35]. Reproduced with permission of American Chemical Society.

are linked by N–H···I hydrogen bonds to form 2D supramolecular layers.

The crystal structures of compounds $[Hg(\mu\text{-4-bpo})Br_2]_n$ **(34)** [7], $[Hg(4\text{-bpdb})Br_2]_n$ **(35),** $[Hg(3\text{-bpdb})Br_2]_n$ **(36)** [43], $[Hg(3\text{-bpdh})Br_2]_n$ **(37)**, $[Hg(4\text{-bpdh})Br_2]_n$ **(38)** [44], $[Hg(4\text{-bpet})Br_2]_n$ **(39)** [39], $[Hg(\mu\text{-bpen})Br_2]_n$ **(40)** [40], $[Hg(2,2'\text{-dpyds})Br_2]_n$ **(41)** [45], $[Hg(btan)Br_2]_n$ **(42)** [46] and $[Hg(N\text{-BBzBimCH})Br_2]_n$ **(43)** [47] consist of one-dimensional zigzag chains in which the nitrogen atoms of N-donor bifunctional ligands are linked to two different mercury atoms and also the bromide atoms are coordinated to a mercury atom and are not bridged to two mercury atoms. The Hg(II) ions are in a distorted tetrahedral geometry. The individual 1D chains in compounds **34, 35**, **36, 42** and **43** are further linked by weak hydrogen bonds into two-dimensional networks among which, compound **34** has a honeycomb topology. Complex **42** has two emission bands at 470 and 530 nm.

The crystal structures of $[Hg(4\text{-bpdb})(SCN)_2]_n$ **(44),** $[Hg(3\text{-bpdb})(SCN)_2]_n$ **(45)** [43], $[Hg(4\text{-bpdh})(SCN)_2]_n$ **(46)** [48], $[Hg(\mu\text{-bpa})(SCN)_2]_n$ **(47)**, $[Hg(\mu\text{-bpe})(SCN)_2]_n$ **(48)**, $[Hg(\mu\text{-bpp})(SCN)_2]_n$ **(49)** [49], $[Hg(4,4'\text{-bipy})(SCN)_2]_n$ **(50)** [22,49] and $Hg(Pip)(SCN)_2$ **(51)** [50] consist of 1D zigzag chains. In these compounds, the coordination environment of the Hg atoms is a distorted tetrahedron, except for **51** that has a tetrahedral Hg(II) sphere. The nitrogen atoms of N-donor bifunctional ligands are linked to two different mercury atoms and the thiocyanate atoms are coordinated to mercury via S atoms but are not bridged to two mercury atoms. Structures **44**, **45** and **46** can be seen as grown from 1D structures to hybrid 2D networks by weak π–π stacking and H-bonding interactions. Also in compounds **47–49**, C–H···S and C–H···N interactions grow the 1D structure into hybrid two- and three-dimensional networks, respectively. Compounds **46**, **48** and **50** display photoluminescence emission bands with the maximum intensities at 363, 468 and 430 nm, respectively.

In complex $[(Hg(SCN)_2)_2(Pip)]_n$ **(52)** [50] a double chain polymer is obtained through combination of the dimers $(NCS)_2$–Hg–Pip–Hg–$(SCN)_2$ through the terminal N atom of one neighbouring SCN^- ion and Hg(II) centers which are in a distorted tetrahedral environment. In the structure of complex $[Hg_2(N\text{-BBzBimCH})Cl_4]_n$ **(53)** [47] the Hg(II) are coordinated by three chlorine atoms and one nitrogen atom in a highly distorted tetrahedral coordination geometry, while two coordinated chlorine atoms act as μ-linker to bridge two Hg atoms to form a 1D chain. A hydrogen bond links the adjacent chains to form a 2D structure. Also in the structure of $[Hg(bpu)Cl_2]_n$ **(54)** [51],

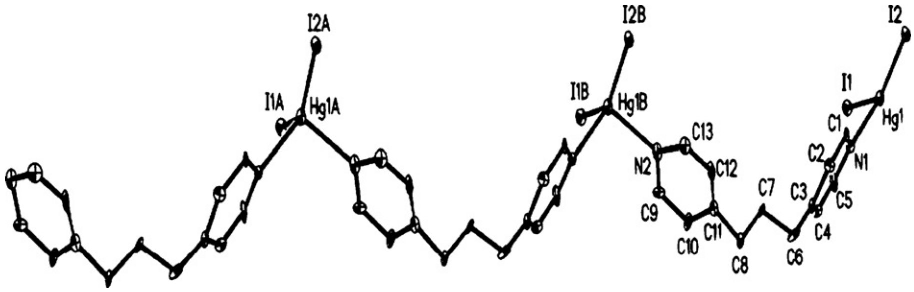


Fig. 8. The wave-shaped structure connected through bpp ligands with anti–anti conformation in $[Hg(bpp)I_2]_n$ **(60)** [28]. Reproduced with permission of Elsevier.

typical amide–amide hydrogen bonds extend the 1D chain to a 2D herringbone-like hydrogen-bonded framework.

In the linear polymeric complex $[Hg(dps)I_2]_n$ **(55)** [52], the flexibility of dps together with the weak interchain C–H···I interactions give 3D supramolecular conformation. The Hg(II) centers are in a distorted tetrahedral geometry. In the polymeric complex of $[Hg(\mu\text{-bin})Cl_2]_n$ **(56)** [41] the mercury(II) center having roughly tetrahedral $HgCl_2N_2$ coordination. The conformation of the ligand and the opening of the N–Hg–N angle above the tetrahedral value combine to give minimum distortion from a linear polymeric structure. Complex $[Hg(\mu\text{-bin})Br_2]_n$ **(57)** [41] is isostructural and isomorphous to **56**. In complex $[Hg_2(\mu\text{-pyr})(\mu\text{-I})_2I_2]_n$ **(58) [**53,54] one I^- anion acts as a terminal monodentate ligand, whereas the other forms a full halogen bridge to a mercury atom of an adjacent $I_2Hg(pyr)$ moiety. The geometry is a distorted octahedron with one pyrazine nitrogen, two bridging iodide, one terminal iodide atom, and two vacant spaces at the mercury(II) ion. The individual 1D chains in compound **58** are linked by weak I···π···I interactions into a 2D network.

The structure of complexes $[Hg(bib)Br_2]\cdot 0.5THF$ **(59)** [35], $[Hg(bpp)I_2]_n$ **(60)** (Fig. 8) [28], $[Hg(bpp)Br_2]_n$ **(61)** [55] and $[Hg(ptr)Cl_2]_n$ **(62)** [56] are 1D wave like chains in which Hg(II) atoms are in a distorted tetrahedral coordination environment with two N atoms from two consecutive N-donor ligand and two halide atoms. In complex **59** the disordered THF molecules are located at the border of the chains and connect the neighbouring chains through C–H···O hydrogen bonds to generate a 3D framework. Compound **60** shows NLO properties. The molecular structure of $[Hg(ptr)(CN)_2]_n$ **(63)** [56] is isomorphous with **62**, with similar cell parameters, but different anions. The neighbouring arciform chains of **62** and **63** interconnect to form 18-membered rings through hydrogen bonds and result in a 2D wavy layer along the bc plane. Compounds **62** and **63** show blue fluorescent emission with two bands near 450 and 415 nm where the former may originate from the π–π* transition of the triazole rings and the latter may originate from ligand-to-metal transfer (LMCT) [57,58]. There also exists a wave-like structure in $[Hg(3\text{-pmbz})Cl_2]_n$ **(64)** [59] in which each Hg(II) atom completes its tetrahedral geometry with two terminal Cl^- and two nitrogen atoms from different 3-pmbz, one of which comes from imidazole ring of 3-pmbz, and the other comes from pyridine ring of 3-pmbz. Each 3-pmbz ligand has two types of π–π interactions, one being generated among benzimidazole rings and another between two pyridine rings. In this compound, one chain is connected with two other chains through π–π interactions of pyridine rings to form a 2D structure. Then along the *a*-axis the interaction fashion, results in an infinite 3D stacking structure among linear complexes. This complex exhibits intense photoluminescence emission at 536 nm in the solid state. In the wave-like structures of complexes $[Hg_2(titmb)Br_4]$ **(65)** and $[Hg_2(titmb)Cl_4]$ **(66)** [35], the Hg(II) atoms are not only linked by titmb ligands but also bridged by Br atoms within the 1D chain. Therefore, the Hg and Br atoms also form an infinite Br···Hg···Br···Hg inorganic chain linked by Hg–Br···Hg interactions. The 1D chains range along the *ac* plane to form a 3D framework, and the structure is stabilized by a C–H···Br hydrogen bond.

The structure of compounds $[Hg(bbimms)I_2]_n$ **(67)** [60], $[Hg(3\text{-bpo})I_2]_n$ **(68)** [61], $[Hg(3\text{-bpo})Br_2]_n$ **(69)** [36], $HgCl_2(Caf)$ **(70)** [62] consist of 1D helical chains and each Hg atom is joined to two different N-donor ligands and further bound by two terminal halide atoms in a distorted tetrahedral geometry. In complex $\{[Hg(4\text{-bpmape})I_2]\ 0.5H_2O\}_n$ **(71)** [32], combination between the organic ligand 4-bpmape and HgI_2 leads to a helical strand. Hg(II) center adopts a tetrahedral geometry. A double stranded helical arrangement is formed from a weak hydrogen bond between I atom and H atom of the phenyl unit (Fig. 9). When taking into account the lateral interconnections between double helices, the overall structure is a 3D network. Meanwhile, in $[Hg(2\text{-ebpec})I_2]_n$ **(72)** and $[Hg(4\text{-ebpec})(SCN)_2]_n$ **(73)** [63] adjacent single stranded helical chains, one exhibiting left-handedness and the other right-handedness, interact through π–π stacking interactions, to generate a compact double stranded helical chain. These double-stranded helical chains are further extended into the 2D architecture by hydrogen bonding and π–π stacking interactions. Because left-handed and right-handed helical chains coexist in the crystal structures, the crystals are mesomeric and do not exhibit chirality. Complexes $[Hg(\mu\text{-}\mathbf{L1})Cl_2]_n$ **(74)** and $[Hg(\mu\text{-}\mathbf{L1})Br_2]_n$ **(75)** [64] are isostructural and exist as helical homochiral polymers $[Hg(\mu\text{-R-}\mathbf{L1})Cl_2]_n$ and $[Hg(\mu\text{-S-}\mathbf{L1})Cl_2]_n$ with distorted tetrahedral stereochemistry at the mercury(II) centers. The polymers associate through a combination of secondary Cl–Hg···Cl and Br–Hg···Br interactions and π–π stacking interactions between aryl rings of the naphthyl groups to form a 2D sheet of polymers. The polymer chains alternate in chirality, ···*R*···*S*···*R*···*S*, so that each sheet is racemic. Coordination polymer $[Hg(3\text{-dpcpdo})Br_2]_n$ **(76)** [65] consists of exclusively achiral building blocks, and shows helical chirality with spontaneous chiral resolution. This behaviour reveals that locally one enantiomer in **76** is formed in excess, probably even exclusively. Bending of the

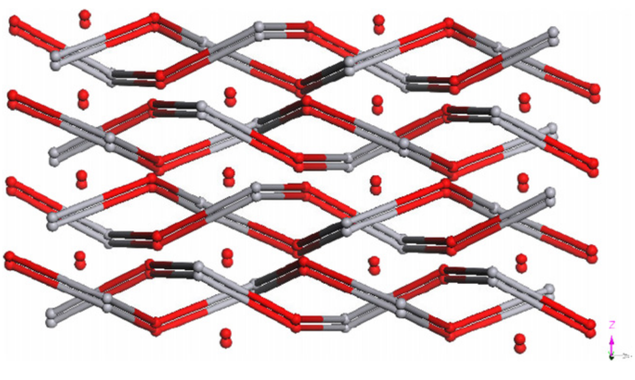


Fig. 9. Schematic representation of double stranded helices in $\{[Hg(4\text{-bpmape})I_2]\cdot 0.5H_2O\}_n$ **(71)** [32].

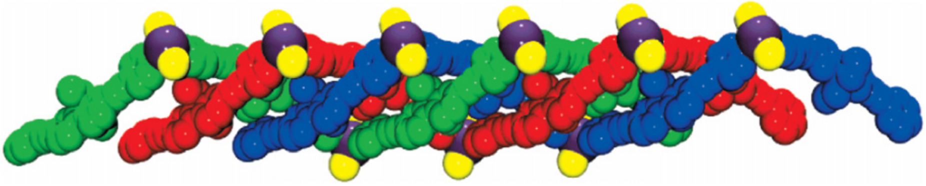
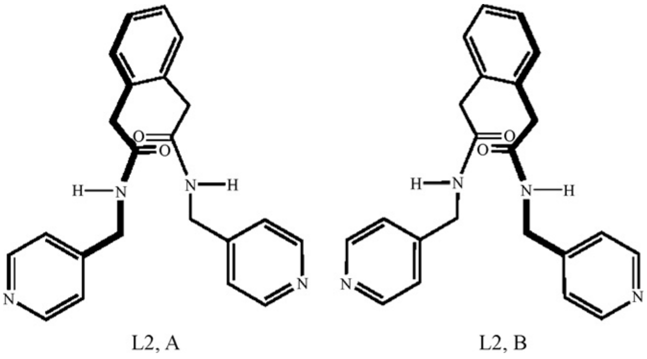


Fig. 10. Triple-helix structure of HgX_2(4-bedpef)·CH_2Cl_2 (X = Cl, Br) [66]. Reproduced with permission of American Chemical Society.

ligand and its coordination at the Hg center in isostructural compounds $HgCl_2$(4-bedpef)·CH_2Cl_2 **(77)** and $HgBr_2$(4-bedpef)·CH_2Cl_2 **(78)** [66] results in zigzag chains that adopt a helical twist and again the mercury atom is in a distorted tetrahedral environment. Three such helical zigzag chains intertwine to form the triple-helix structure (Fig. 10). These compounds exhibit photoluminescence properties.

The structure of complex $[(HgI_2)(\mu\text{-}\mathbf{L2})]_n$ **(79)** [67] exists as the one-dimensional polymer with tetrahedral mercury(II) centers bridged by the ligand **L2**, which are present in the chiral conformations ***A*** and ***B*** (Fig. 11). The polymers are packed parallel to each other to give a sheet structure, in which all the polymer chains have the ligand in the same conformation ***A*** or ***B***. The complex $[Hg(\mu\text{-}\mathbf{L3})Cl_2]_n$, **(80)** [64] exists in the form of zigzag homochiral polymers $[Hg(\mu\text{-R-}\mathbf{L3})Cl_2]_n$ or $[Hg(\mu\text{-S-}\mathbf{L3})Cl_2]_n$, in which the Hg(II) ions adopt tetrahedral geometry. Two crystalline forms of the mercury(II) chloride complex, $[Hg(\mu\text{-rac-bnbap})Cl_2]_n$ **(81)** [68], is containing a racemic mixture of homochiral (···*RRR*···, ···*SSS*···) polymers, but **81A** contains zigzag polymers, whereas **81B** contains helical polymers. In complex **81A**, Hg(II) ions are in a roughly tetrahedral geometry. Adjacent chains self-assemble through intermolecular N–H···O=C hydrogen bonds between ligands of opposite chirality (···*R*···*S*···) to give a 2D sheet structure. In addition, pairs of ···*RRR*··· and ···*SSS*··· chains from adjacent sheets form double-stranded polymers through weak Hg···O interactions, and these secondary bonds link the sheets together to form a 3D network. The helical chains in complex **81B** are further associated through intermolecular hydrogen bonding between amide groups of ligands of opposite chirality (···*R*···*S*···) and form a sheet of chiral helical channels. The bromide complex $[Hg(\mu\text{-}rac\text{-bnbap})Br_2]_n$, **(82)** is isostructural with the analogous chloride complex **81B** [68], and the iodide complex $[Hg(\mu\text{-}rac\text{-bnbap})I_2]_n$, **(83)**, exists as a heterochiral ···*RSRS*··· polymer $[(HgI_2)_2(\mu\text{-}R\text{-bnbap})(\mu\text{-}S\text{-bnbap})]_n$. There is an additional twist to the polymer chains of **83** when compared to **81A**. In contrast to the previous examples, the association of chains of **83** occurs through hydrogen bonding between amide groups of ligands of like chirality (···*R*···*R*···, ···*S*···*S*···) to form a 2D sheet of polymers. Furthermore, the association of polymer chains through hydrogen bonding creates small pockets in the sheet structure in which dichloromethane solvent molecules are encapsulated (Fig. 12) [68]. Crystallization of complexes **82** and **83** in the presence of a large excess of mercury halide resulted in the conversion of the polymers into 34-membered meso macrocycles $[(HgX_2)_2(\mu\text{-R-bnbap})(\mu\text{-S-bnbap})]\cdot HgX_2$ (**84**, X = Br; **85**, X = I) that encapsulate a single linear mercury(II) halide molecule inside the ring [68]. While, crystallization of complex **83** in the presence of a small excess of mercury(II) iodide gave the unusual polymeric compound $[\{(HgI_2)(\mu\text{-bnbap})\}_{12}]_n\cdot(HgI_2)_n$ **(86)**, with 1 guest HgI_2 molecule for every 12 $[HgI_2\cdot\mu\text{-bnbap}]$ units. In this intricate network material, six polymer chains surround each guest HgI_2 molecule (Fig. 13). Complex **86** exists as a one-dimensional heterochiral polymer $[(HgI_2)_2(\mu\text{-R-bnbap})(\mu\text{-S-bnbap})]_n$ with tetrahedral mercury(II) centers bridged by alternating enantiomers of the ligand *rac*-bnbap [68]. The structure of the enantiopure complex $[Hg(\mu\text{-R-bnbap})I_2]_n$ **(87)** exists as helical chiral polymers that further associate with four other chains through intermolecular amide hydrogen bonding to form a 3D network [68].



L2, A L2, B

Fig. 11. Ligand L2 in conformations *A* and *B*.

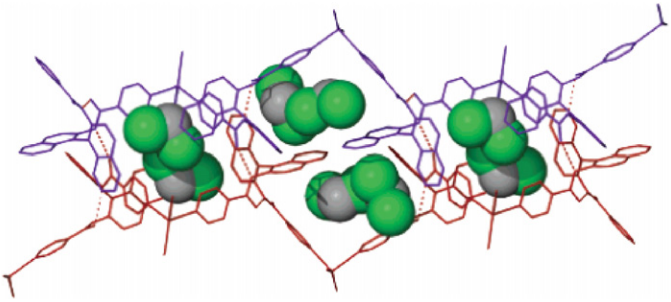


Fig. 12. View of the solvent encapsulated within the cavities formed by hydrogen bonding between two polymer chains in compound **83** [68]. Reproduced with permission of American Chemical Society.

In compounds $[Hg_3(tpmb)_2I_6]\cdot H_2O$ **(88)** [69], $[Hg_3(tib)_2I_6]\cdot 2DMF$ **(89)**, $[Hg_3(timpt)_2I_6]\cdot 4H_2O$ **(90)** [35] and $[Hg(4\text{-tpstmb})I_2]$ **(91)** [70] coordination geometry around each Hg(II) center is distorted tetrahedral with two N atoms from two different N-donor ligands and two iodide anions. Each N-donor ligand in turn connects three Hg(II) atoms to give 1D chains containing M_2L_2 macrocycles (Fig. 14). In **88** and **89** 1D chains connect by π–π and C–H···O interactions to form 2D and 3D structures, respectively. Both compounds **88** and **90** show photoluminescence

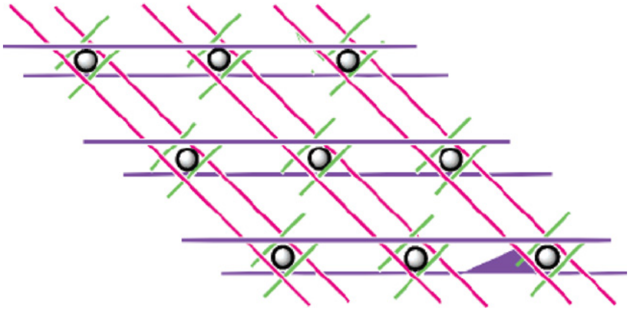


Fig. 13. Drawing representing the grid structure formed around free HgI_2 molecules in compound **(86)** [68]. Reproduced with permission of American Chemical Society.

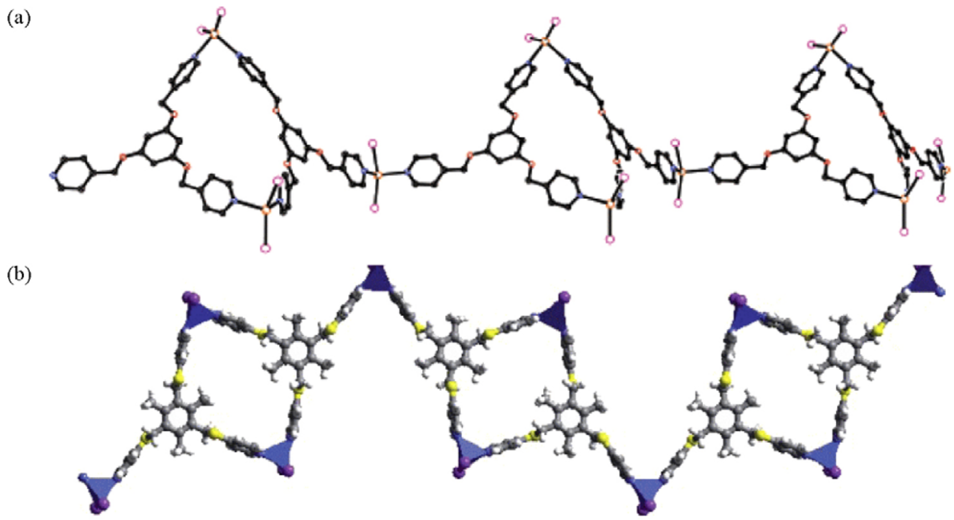


Fig. 14. (a) Infinite 1D pearl-like chain structure of $[Hg_3(tpmb)_2I_6]\cdot H_2O$ **(88)** [69]. Reproduced with permission of American Chemical Society. (b) Square-grid network coordination polymers in the crystal structure of **91** and **92** [70]. Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

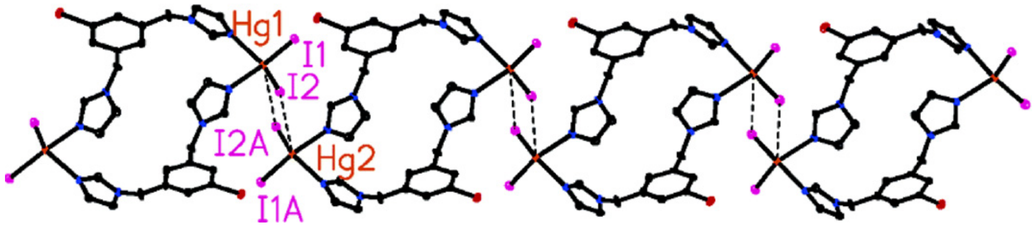


Fig. 15. A view of 1D chain of $[Hg(bib)I_2]$ **(94)** through Hg–I···Hg interactions [35]. Reproduced with permission of American Chemical Society.

emission. Similar conditions are observed in $[Hg(4\text{-}tpstmb)Br_2]$ **(92)** [70] and $[Hg_3(titmb)_2Br_6]_n$ **(93)** [71] in which the only difference is the substitution of bromine instead of iodine. However, in $[Hg(bib)I_2]$ **(94)** [35], the M_2L_2 macrocyclic rings are further connected by weak Hg···I interactions to form an infinite 1D supramolecular chain (Fig. 15). Two compounds **93** and **94** generated 3D framework structures by C–H···Br and C–H···I interactions. In $[Hg(4\text{-}tpstmb)Br_2]\cdot(dmso)$ **(95)** and $[Hg(4\text{-}tpstmb)Br_2]\cdot(dmf)$ **(96)** [70] the ligand 4-tpstmb from three available pyridyl moieties only two interact with Hg(II) to yield an infinite coordination polymer chain. Also, each Hg(II) is bonded to two Br atoms in a distorted tetrahedral geometry. Such adjacent chains are held together by C–H···N hydrogen bonds, as observed in the structure of the free ligand and form cavities of dimension 11 Å × 16 Å, which are aligned in a three-dimensional arrangement to yield channels. The channels are occupied by the solvent molecules dmso and dmf in **95** and **96**, respectively.

Compound $[(HgI_2)_2TPyP]\cdot 2TCE$ **(97)** [72] has a nanoporous 1D polymeric architecture with each HgI_2 tetrahedrally coordinated by a pyridyl moiety of two TPyP molecules. A supramolecular cavity is formed between the linked porphyrins with an effective cavity size of 2.5 Å × 7.7 Å. The 1D coordination polymers are arranged in layers inducing another supramolecular cavity (effective cavity size, 2.4 Å × 3.0 Å). The 2D layers are offset stacked at 5.5 Å and form a partially open porous network. The TCE molecules are sandwiched between the layers and cap the supramolecular cavities. In complex $[(HgBr_2)_2TPyP]\cdot 6TCE$ **(98)** [72], there are three TCE molecules per TPyP between the layers, and the 1D polymers stack (porphyrin cavity directly over supramolecular cavity) at an 8.1 Å separation. Complex $[(HgI_2)_2TPyP]\cdot 4TCE$ **(99)** [72], is a 1D polymer and has a bilayer structure identical to **97**, which exhibits solvation and stacking features of both **97** and **98**; but is solvated with four TCE molecules per formula rather than two as in **97**. Alternating layers have either one (between offset stacked layers as in **97**) or three

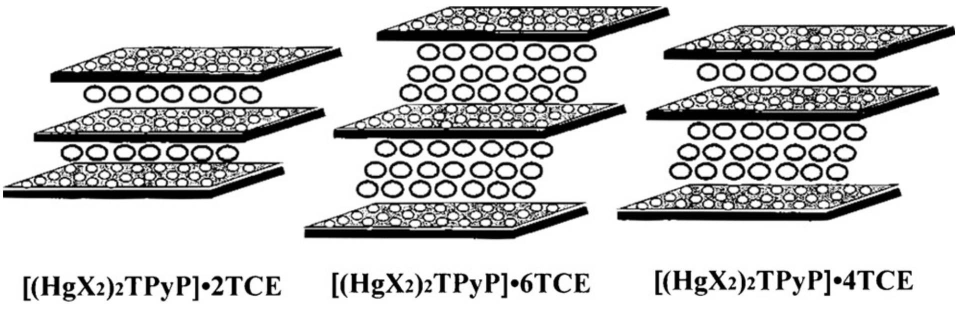


Fig. 16. Identical neutral guest molecules in crystal structures of **97**, **98** and **99** [72].

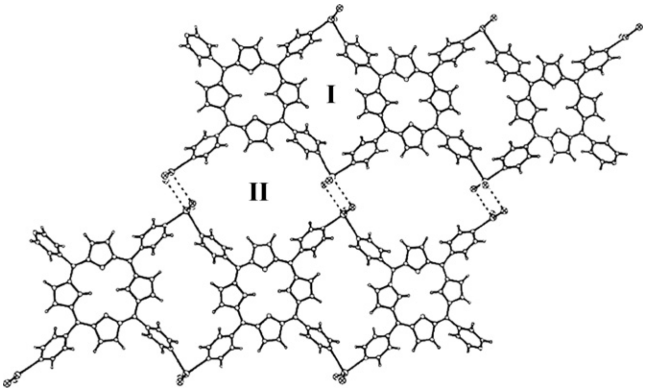


Fig. 17. 1D coordination polymer of [$(HgBr_2)_2$TPyP]·2TCE (polymorph **100A**) with supramolecular cavities (I) [73]. Reproduced with permission of Elsevier.

(between stacked layers as in **98**) TCE molecules per TPyP with interlayer separations of 5.4 and 8.3 Å, respectively (Fig. 16). Indeed, these two stacking distances correspond to the interlayer stacking distances of **97** (5.5 Å) and **98** (8.1 Å). The crystal structures of **97**, **98** and **99** demonstrate an interesting ability to include variable numbers of identical neutral guest molecules by subtle rearrangement of the stacking of layers (Fig. 16).

Compound [$(HgBr_2)_2$TPyP]·2TCE **(100)** [73] has two polymorphic structures. Polymorph **100A** has a supramolecular cavity (2.5 Å × 7.7 Å) that is constructed by TPyP molecules bridged with two $HgBr_2$ units (Fig. 17). The 1D chains in **100A** cross-linked through Hg···Br and Br···Br interactions (3.289(11) and 3.857(10) Å, respectively) to form 2D polymeric steplike structure with additional cavities (cavity II, effective cavity size 4.6 Å × 9.0 Å). The 1D polymers are stacked at an interplanar distance of 3.725 Å and form a continuous open porous structure. Polymorph **100B** exhibits the same 1D coordination polymer as observed in **100A**, but these 1D polymers form a herringbone-type structure and not the open porous structure observed for **100A**. In complex [$(HgBr_2)_2$TPyP]·$2CHCl_3$ **(101)** [74], the Hg(II) center is bonded to two bromides and two pyridyl nitrogen atoms in a distorted tetrahedral geometry. This results in relatively large inter-porphyrin cavities in the extended chain. Solvent ($CHCl_3$) molecules partially fill the interchain space, and they are not included in the inter-porphyrin cavities. When removed from the mother liquor, crystals of [$(HgBr_2)_2$TPyP]·$2CHCl_3$ lose $CHCl_3$ and collapse rapidly. The resultant solid does not absorb CH_2Cl_2, $CHCl_3$, CH_3OH or benzene to form inclusion compounds. It seems that crystallinity of the one-dimensional [$(HgBr_2)_2$TPyP]·$2CHCl_3$ cannot be sustained after loss of interchain space-filling solvent of crystallization [74].

There are two crystallographically independent Hg atoms in $[Hg(1\text{-}MH)_2]_n$ **(102)** [75] in which each Hg atom are bound by two N and two O atoms of deprotonated hydantoin anions to form a polymeric chain. In compound $[Hg(pyta)Cl]_n$ **(103)** [76], Hg(II) ions are connected by the bridging pyta ligands to form a 1D box-like coordination framework (Fig. 18) which has dimeric Hg_2O_2 subunits as the nodes in which each carboxylate group of pyta behaves as a μ-O,O bridging coordination mode. Self-assembly by interchain H-bond interactions of the adjacent 1D arrays affords a 2D hydrogen-bonded layer. Additionally, these parallel 2D layers are combined into the final 3D supramolecular network through interlayer hydrogen bonds as well as weak S···S interactions.

In the crystal structure of $[Hg(CF_3)_2(Pip)]_n$ **(104)** [50], the piperazine molecules are in the chair conformation and bridge between two $Hg(CF_3)_2$ molecules such that a zigzag chain is built. Hg(II) is in a heavily distorted tetrahedral coordination geometry. In complex Hg(*p*-MeC_6H_4)($O_2CC_6F_5$) **(105)** [77], mercury(II) is bonded to the C atom of an aryl group and O atom of a perfluoroaryl group in a near linear C–Hg–O arrangement in which C–Hg–O units stack into columns with intermolecular Hg–O bonding. In this complex, the stereochemistry about mercury is distorted square-planar. Also in the structure of Hg(C_6H_4OMe-*p*)($O_2CC_6F_4$OMe-*p*) **(106)** [78] *p*-anisylmercury unit is coordinated by a carboxylate through one oxygen and having a near linear C–Hg–O arrangement which form stacks through Hg···O carboxylate interactions. Again the stereochemistry at mercury is distorted square-planar. The carboxylate ligands are μ_3-tridentate with the oxygen strongly bonded to Hg also bridging to a further mercury atom. The other carbonyl oxygen binds a single mercury atom. The solid state structure of $[Hg(\mu_2\text{-dpp})_2]_n$ **(107)** [79] shows four-coordinate mercury centers asymmetrically bridged by two dpp ligands to form polymeric chains.

In compound $[HgCl_2{\cdot}DMSO]_n$ **(108)** [41] two O atoms of DMSO have joined $HgCl_2$ units to give a polymeric chain. The structure of the compound $(HgCl_2)_3(DMSO)_2$ has been determined previously and contains a mixture of $[(HgCl_2)_2(DMSO)_2]$, and $HgCl_2$ [80]. Compounds $[HgCl_2{\cdot}DMSO]_n$ and $[(HgCl_2)_2(DMSO)_2]$ are isomeric with polymeric and dimeric structures. The zigzag chain in $Hg[C_6H_4(CHO)\text{-}2]Cl$ **(109)** [81] is formed through two interactions between O atoms of two different aldehyde and an Hg atom, in which one is intramolecular, and the other is intermolecular, from a neighbouring molecule. The Hg atom is also bonded both by a chloride and an *o*-formylphenyl group in a linear arrangement. In the crystal structure of $[Hg(meimt)_2]_n$ **(110)** [82], the mercury atom is coordinated by two sulfur atoms and two nitrogen atoms from four meimt ligands. Two centrosymmetrically related meimt ligands bridge two mercury atoms forming polymeric chains.

In complex [HgMe{S(O)PPh_2}] **(111)** [83], the Hg atom is bonded by a methyl group and the sulfur atom of the thiophosphorus ligand; it further forms a dimer by Hg···O interactions. The dimers are then connected into a supramolecular ribbon structure through additional Hg···O interactions. The coordination geometry around the metal atom is distorted ψ-trigonal bipyramidal, with the sulfur atom and methyl group in axial and two Hg···O interactions in equatorial positions. In complexes $[Hg(dppeO)Br_2]_n$ **(112)** and $[Hg(dppeO)I_2]_n$ **(113)** [84] both P and O atoms of the ligand dppeO are coordinated to Hg atoms to form one-dimensional pseudo-

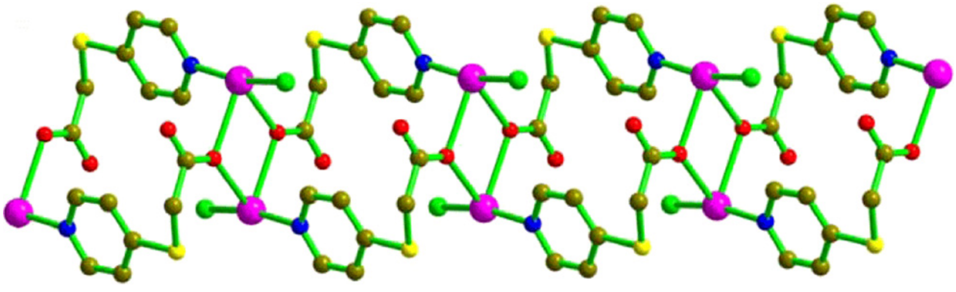


Fig. 18. 1D box-like coordination motif with dimeric nodes in $[Hg(pyta)Cl]_n$ **(103)** [76]. Reproduced with permission of Elsevier.

helical and linear zigzag polymeric chains. The geometries around the Hg centers are highly distorted tetrahedral.

In the crystal structure of complexes $[Hg(\mathbf{L4})I_2]_n$ **(114)** [85], $[Hg(pehc)I_2]_n$ **(115)** [86] and $[Hg(Me_2dmit)I_2]_n$ **(116)** [87] mercury atoms have bonded to three iodine atoms, two of which form bridges to neighbouring mercury atoms forming polymeric chains, among which complex **115** has a linear structure. The coordination sphere of Hg atoms are completed by contact to P atom of **L4** and S atoms of pehc and Me_2dmit ligands in a distorted tetrahedral geometry. In compounds $[Hg(\text{-}SCH_2CH_2NH_2)Cl]\cdot NaOH\cdot 2H_2O$ **(117)** [88] and $[HgCl(SCH_2CH_2NH_2)(H_2O)_2]_n$ **(118)** [89], the mercury atom has a distorted tetrahedral geometry, and infinite chains resulting from Hg–S bridges between $Hg(\text{-}SCH_2CH_2NH_2)Cl$ units. In complex **118** the one-dimensional polymeric chains are held together *via* intermolecular hydrogen bonding involving an NH_2 group, Cl and water molecules generates a 3D structure. The tetranuclear repeating unit in $[Hg_4I_8(SCH_2CH_2NH_3)_2]_n\cdot nH_2O$ **(119)** [90], $[Hg_4I_8(SCH_2CH_2NH_3)_2]\cdot 2H_2O$, consists of three independent Hg centers, namely HgI_3S, HgI_2S_2, and HgI_4, and is connected through bridging S atoms to form a one-dimensional polymeric chain. Hg(1) and Hg(2) are quite similar and bonded to one bridging S, one terminal I, and two bridging I atoms; Hg(3) is bonded to two bridging S and I atoms, and Hg(4) is attached to two bridging and two terminal I atoms. Hg(4) is quite unique in being coordinated by four I atoms. The geometry around all the Hg atoms is a distorted tetrahedral.

$[PhHg(3\text{-}SC_6H_4NH_2)_2]$ **(120)**, $[MeHg(3\text{-}SC_6H_4N{=}CHC_6H_4OH)]$ **(121)** and $[MeHg(4\text{-}SC_6H_4N{=}CHC_6H_4OH)]$ **(122)** [91] have two crystallographically independent molecules in an asymmetric unit. Each mercury atom is bonded linearly by C and S atoms and has two weak $Hg\cdots S$ interactions and the result is a linking of the individual molecules into a polymeric zigzag ladder. The ladder may be considered as composed of pseudo-cubanes, each having one face opened up by lengthening of two opposite $Hg\cdots S$ edges, and sharing opposite faces. Structure of complex $[Hg(\mu\text{-}cht)_2]_n$ **(123)** [92], exists as a linear-chain with highly distorted tetrahedral mercury(II) centers that are doubly bridged by two S atoms from cht ligands. Complex $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2\cdot 1/2[S(CH_2)_3NMe_3]$ **(124)** [93] contains one-dimensional cationic chains of formula $[Hg\{S(CH_2)_3NMe_3\}_2]_n^{2n+}$. The mercury atoms are tetrahedrally coordinated by the doubly bridging sulfur atoms. The aminothiolate ligands radiate from the core of the $Hg(\mu\text{-}SR)_2Hg$ chains, providing them with a positively charged environment. The hexafluorophosphate anions, balancing this charge, are positioned so as to separate the positive charges from each other, both within and between the cation chains. In this complex, however, additional zwitterionic $S(CH_2)_3NMe_3$ molecules apparently lie in the wide channels running parallel to the c axis and to the cation chains.

Ligands bbsb and besp link $(HgBr_2)_2$ dimers to form polymeric chain structures of $[Hg_2(bbsb)Br_4]_n$, **(125)** [94] and $[Hg_2(besp)Br_4]_n$ **(126)** [95], respectively. The Hg(II) ion is coordinated by three Br atoms and one S atom from the bbsb and besp ligands in a distorted tetrahedral geometry. These complexes have dinuclear structures with different structural parameters. This can be attributed to the difference in the spacer lengths of the two dithioether ligands. In compound $[Hg(bbsp)Br_2]_n$ **(127)** [96] polymeric chain is built of bbsp ligands bridged between Hg(II) centers, in which Hg(II) atom has a distorted tetrahedral coordination environment. In each chain the coordinating S centers have the same chirality, S (or R), which leads to each chain being chiral. However, crystal symmetry results in adjacent chains having opposite chirality, and thus the structure as a whole is racemic.

In the complexes $[Hg(\mu\text{-}SC_6H_4OCH_3\text{-}p)(2,2'\text{-}bipy)]_n[PF_6]_n$ **(128)** and $[Hg(\mu\text{-}SeC_6H_5)(2,2'\text{-}bipy)]_n[PF_6]_n$ **(129)** [97], S and Se atoms of their ligands, bridge between Hg(II) centers and form bonds with the average distances of 2.348(2) and 2.4571(8) Å, respectively, which are comparable to those of other related systems [98]. These complexes exhibit luminescence properties. In compound $[Hg(dsep)_2]_n$ **(130)** [99] dsep ligand bridges two Hg atoms, and the other chelates to the Hg atom and in this way a helical chain is formed. The chelating dsep ligands are oriented on both sides of the helical chain. Each mercury atom is coordinated by four selenium atoms from two bridging dsep ligands, and one chelating ligand. The coordination geometry around Hg is distorted tetrahedral. The complex $[(PhSe)_7Hg_4BrPy]_n$ **(131)** [100] exhibits polymeric zigzag assembling of the adamantane structures linked through selenium bridges (Fig. 19). In each single molecule of $[(PhSe)_7Hg_4BrPy]$ the Hg(II) ions present a distorted tetrahedral configuration and are linked through asymmetric $[\mu\text{-}(Ph)Se]^-$ bridges. The quasi-tetrahedral coordination of Hg(1) and Hg(3) is accomplished by one pyridine molecule (Hg1) and one bromide ligand (Hg3); this asymmetric neighbourhood allows attributing the formal oxidation states 2.5 and 1.5 to Hg(1) and Hg(3), respectively. The synthesis of $[(PhSe)_7Hg_4BrPy]_n$ also represent the first successful attempt to achieve a polymeric assembly of a $(\mu\text{-}Se)Hg$ cluster using a triazene as coordinating intermediary ligand [100].

The crystal of $[(o\text{-}C_6F_4Hg)_3Br]^-[PPh_4]^+$ **(132)** [101] is built of infinite zigzag chains which are formed of alternating molecules of $(o\text{-}C_6F_4Hg)_3$ and Br^- anions (Fig. 20a). This complex has an unusual structure of a polydecker bent sandwich in the solid state wherein every Br^- anion is coordinated to six mercury atoms of two neighbouring molecules of $(o\text{-}C_6F_4Hg)_3$. The unique feature of this complex is that the coordinating centers in its structure are not the metal atoms or cations as in the case of normal sandwich complexes but the anions of the metalloid. The complex $[(o\text{-}C_6F_4Hg)_3\cdot NIT\text{-}Ph]_n$ **(133)** [102] exhibits extended helical binary polymeric chains with alternating molecules of $(o\text{-}C_6F_4Hg)_3$ and NIT-Ph that propagate parallel to one another (Fig. 20b). The interactions responsible for the formation of these infinite chains involve the triple coordination of the oxygen atoms of the NIT-Ph molecule to the mercury centers of $(o\text{-}C_6F_4Hg)_3$. Also in complex $[(o\text{-}C_6F_4Hg)_3(SCN)]^-[^nBu_4N]^+$ **(134)** [103], helical chain of $[(o\text{-}C_6F_4Hg)_3(SCN)]_n^{n-}$ is made up of alternating molecules of $(o\text{-}C_6F_4Hg)_3$ and SCN^- anions in which every SCN^- ion is bonded to the mercury atoms of two neighbouring molecules of the macrocycle through the S atom and forms with

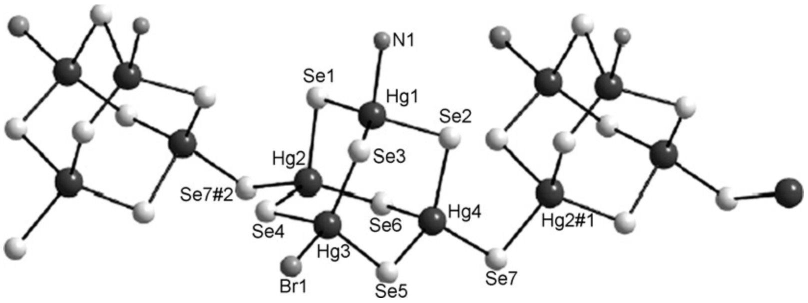


Fig. 19. Polymeric assembly of $[(PhSe)_7Hg_4BrPy]_n$ **(131)** through selenium bridges [100]. Reproduced with permission of Elsevier.

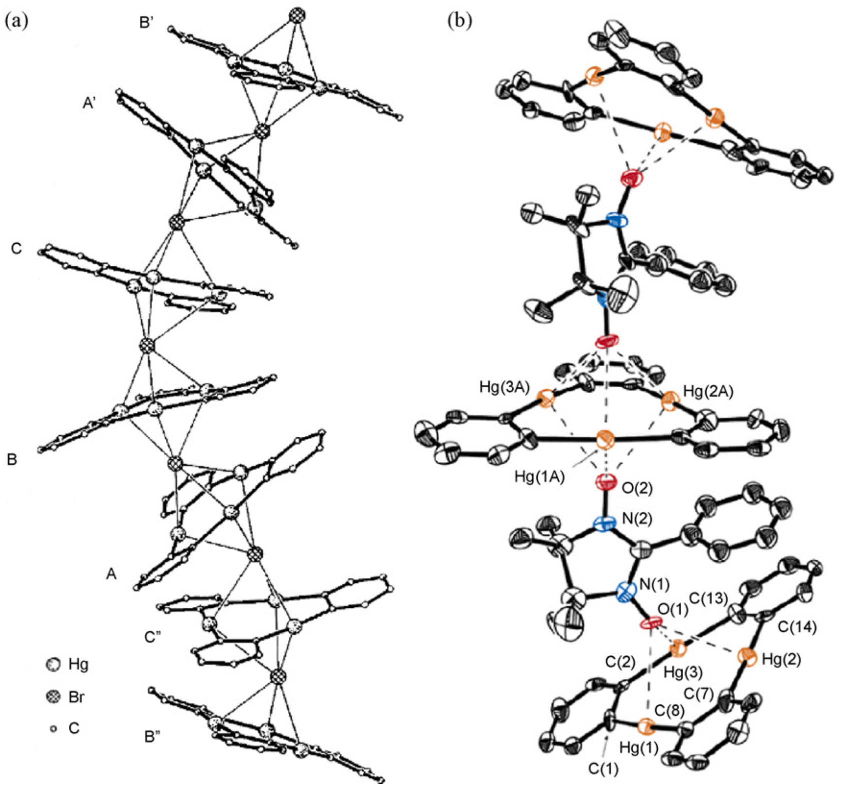


Fig. 20. (a) The fragment of infinite polyanionic chain [(O-C6F4Hg)3Br]$_n{}^{n-}$ **(132)** [101]. Reproduced with permission of Elsevier. (b) Portion of a polymeric chain observed in the structure of compound [(o-C_6F_4Hg)$_3$·NIT-Ph]$_n$ **(133)** [102]. Reproduced with permission of American Chemical Society.

each of these molecules two relatively short Hg···S bonds (3.06(1), 3.36(1) Å and 3.19(1), 3.36(1) Å) and one considerably longer Hg···S bond (3.74(1) and 3.87(1) Å). Thus this complex is considered as a supramolecular structure.

2.3. Coordination number 5

Complex [Hg(μ-**L3**)(O_2CCF_3)$_2$]$_n$ **(135)** [64] exists as homochiral polymers of [{Hg(μ-R-**L3**)(O_2CCF_3)$_2$}]$_n$ and [{Hg(μ-S-**L3**)(O_2CCF_3)$_2$}]$_n$. Pairs of homochiral chains (···RRR··· and ···SSS···) associate to form double-stranded polymers. These double-stranded polymers are held together by pairwise Hg···O interactions between the mercury(II) centers and oxygen atoms of the trifluoroacetate anions, and so the Hg(II) centers adopt a distorted trigonal bipyramidal geometry. In the structure of complex [Hg(3-papap)Cl]$_n$ **(136)** two 1D infinite zigzag chains that adopt a saw-tooth-like polymeric structure made of [Hg(3-papap)Cl]$_n$ units run anti-parallel along the *a* axis [104]. Each mercury atom is in a five-coordinated N_4Cl environment, and the geometry around each Hg(II) ion is distorted square pyramidal. The two independent polymeric chains are closely packed/locked through Hg–π interactions along with face-to-face π–π ring interactions. The secondary interactions in this structure work together to bring the two consecutive chains close together to form a 3D structure. This complex has micrometer size and shows emission and poor adsorption properties. In complexes [Hg(4-tpstmb)Cl_2]·(dmso)$_2$ **(137)** and [Hg(4-tpstmb)Cl_2]·(dmf)$_2$ **(138)** [70], each Hg atom is connected to three bridging 4-tpstmb ligands and two terminal Cl atoms, thus, each Hg(II) with five-coordination has a square-pyramidal geometry. This interaction results in the formation of a cavity of dimension 9 Å × 12 Å and each cavity is created by two molecules of 4-tpstmb and Hg(II) (Fig. 21). The cavities are further aligned in a three-dimensional arrangement to yield channels which are occupied by solvent molecules.

In complexes [Hg_2(2-bpdh)I_4]$_n$ **(139)** [37], [Hg_2(2-bpdb)Br_4]$_n$ **(140)** [43] and [Hg(2-bpdh)(SCN)$_2$]$_n$ **(141)** [48], 2-bpdh and 2-bpdb ligands are chelating with each nitrogen atom of the pyridyl and diaza groups on one side of the molecule coordinating to a mercury(II) ion. In compounds **139** and **141** one counter ion acts as monodentate ligand, whereas two others form a doubly bridged between two Hg atoms to generate one-dimensional double chains that in **141** is heterochiral (Fig. 22). But in complex **140,** each one of the Br^- anions acts as a monodentate ligand, whereas the other forms a Hg–μBr–Hg bridge. In these complexes the geometry is a distorted tetragonal pyramid. In complexes **140** and **141** individual 1D double-chains further link by weak hydrogen bonding and grow into a 2D network. The replacement of an H atom of a diaza group in **140** by $-CH_3$ in **141**, as a bulk group, cause the achiral species to form chiral dimers, possibly due to steric effects of bulky methyl groups.

Compounds [Hg_2(μ-2,5-dmpyr)(μ-Cl)$_4$]$_n$ **(142)** and [Hg_2(μ-2,5-dmpyr)(μ-Br)$_4$]$_n$ **(143)** [54], while crystallizing in different space groups, show very similar structural motifs and packing characteristics. They are one-dimensional double chain metallopolymers and consist of mercury(II) ions bridged by both 2,5-dmpyr ligands and chloride or bromide ions. The geometry around the mercury ion is a distorted square pyramid. Weak Hg···Cl and Br···H–C interactions further link the individual parallel 1D double chains in **142** and **143** with each other and grow the 1D double chains into 2D networks. The compound [Hg(SBz)$_2$]$_n$ **(144)** [105,106] forms a polymeric chain by intermolecular Hg–S interactions. These chains are connected to each other by short Hg–S interactions (Hg–S = 3.15 Å) leading to the formation of a double chain structure. The coordination environment around the mercury atom is a distorted trigonal bipyramid.

In compounds [Hg(3-mpdp)Cl_2]$_n$ **(145)** [107] and [Hg(mebta)Cl_2]$_n$ **(146)** [108], chlorine atoms doubly bridge between mercury atoms to form polymeric chains, in which geom-

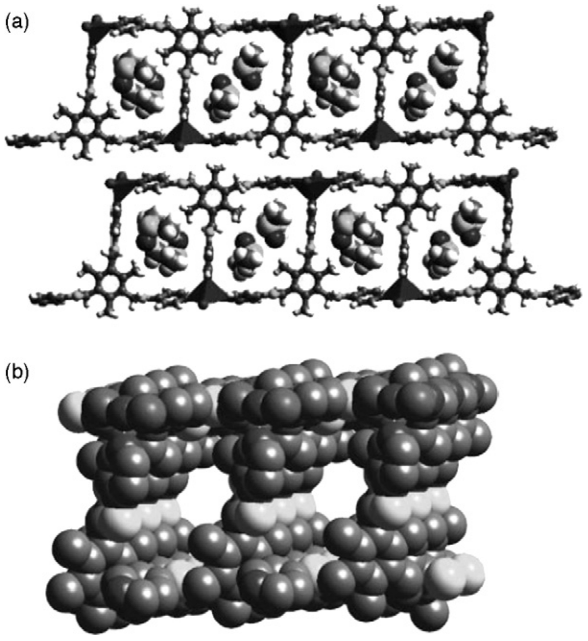


Fig. 21. (a) Presentation of the cavities occupied by dmso molecules in the crystal structure of $[Hg(4\text{-tpstmb})Cl_2]\cdot(dmso)_2$ **(137)**. (b) Three-dimensional formation of the channels; the alignment of the cavities is shown in (a) [70]. Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

etry around the Hg atoms is essentially that of a distorted trigonal bipyramid. Also in complex $[Hg(4\text{-bpo})(\mu\text{-SCN})]_n$ **(147)** [7] SCN doubly bridge between Hg atoms to constructed one-dimensional linear chains with a building block of $[Hg(SCN)_2]$. The coordination geometry around the mercury(II) ion is a distorted square pyramid. The one nitrogen atom of the 4-bpo ligand is not coordinated to the Hg atom and indeed this ligand acts as a less common unidentate ligand. The individual polymeric chains further linked by $N\cdots(H)C_{py}$ interactions to form a 2D framework.

Complexes $[Hg(3,5\text{-}Cl_2py)(\mu\text{-Br})_2]_n$ **(148),** $[Hg(3,5\text{-}Cl_2py)(\mu\text{-I})_2]_n$ **(149),** $[Hg(3,5\text{-}Br_2py)(\mu\text{-I})_2]_n$ **(150),** $[Hg(3,5\text{-}Me_2py)(\mu\text{-I})_2]_n$ **(151)** [109] and $[Hg(2,6\text{-dmpyr})(\mu\text{-Br})_2]_n$ **(152)** [54] represent 1D coordination polymers based on five-coordinated, halide-bridged mercury(II) cations. The coordination geometry around the mercury(II) in complex **148** is distorted tetragonal pyramid and in complex **152** is distorted square pyramidal, or octahedral with one vacant coordination site. By weak C–H hydrogen bonds, compound **152** forms a 2D network.

The one-dimensional ribbon in $[Hg(Me_2dmit)Cl_2]_n$ **(153)** [87] results from the bonding of the $HgCl_2$ units through two chlorine bridges, thus giving rise to centrosymmetric four-membered $Hg(\mu\text{-}Cl)_2Hg$ motif. Therefore, the coordination environment around the mercury centers is a distorted square pyramid. But in complex $[Hg(Me_2dmit)Br_2]_n$ **(154)** [87], the coordination mode around the mercury atoms is intermediate between the situations encountered for $[Hg(Me_2dmit)I_2]_n$ **(116)** [87] and $[Hg(Me_2dmit)Cl_2]_n$ **(153).** In complex $Hg(Tmac)Cl_2$ **(155)** [110], each mercury atom is coordinated by an N atom of ylide Tmac, one terminal Cl atom and three bridging Cl atoms (μ_3-Cl) in a distorted trigonal bipyramid environment and forms a 1D ladder like chain. In the complex $[Hg_2(2\text{-bmps})Cl_4]_n$ **(156)** [111], the thioether atom of 2-bmps forms a bridge between Hg(II) atoms resulting in linear Hg–S–Hg units, also two N atoms of 2-bmps connect two Hg atoms. These units are joined together with two bridging chloride ligands. Additional contact with a terminal Cl atom completes the coordination sphere of Hg atom in a distorted square pyramidal geometry.

Complex $[Hg_2(ttb)_2Cl_4]_n$ **(157)** [112], is formed by centrosymmetric binuclear subunits in which weak coordination of Hg–S constitutes a one-dimensional infinite chain. The mercury atoms in zigzag arrangement achieve five-coordination in a distorted trigonal bipyramidal geometry by bonding to two bridging Cl, a terminal Cl, a thione S and a thioether S atom of ttb. The $S\cdots S$ contacts between two nearby chains generate a 2D network and through $S\cdots S$ interactions between the 2D layers, a 3D supramolecular network is formed. In the complex $[Hg(bpytm)Br_2]_n$ **(158)** [113] bpytm is N-monodentate. The mercury atom is coordinated by N and three Br atoms, while two coordinated bromine atoms act as μ-linker to bridge two Hg atoms and form a 1D chain. With additional weak intramolecular $Hg\cdots S$ bond the coordination polyhedron around mercury(II) is a distorted trigonal bipyramid with a vacant equatorial position. In complex $[Hg(tzdSH)(\mu\text{-Br})Br]_2$ **(159)** [114] a centrosymmetrically double halogen bridged dimer is formed with the heterocyclic ligand η^1-terminally bonded via the exocyclic thione sulfur atom. The primary bonding arrangement around mercury is pseudo tetrahedral. Secondary $Hg\cdots Br$ interactions link the molecules together via double asymmetric bromide bridges into polymeric chains. In the structure of $[Hg(HpicOH)Br_2]_n$ **(160)** [115], there are two covalent bonds, forming the linear characteristic coordination, Br1–Hg–Br2. The effective coordination sphere of mercury is irregular 2 + 3, consisting of three weak additional contacts, two with bromine atoms from adjacent molecules, and one with the carboxylic oxygen of HpicOH in the zwitterionic form. The coordination polyhedron is a very deformed square-pyramid with an O atom at the apex. Two polymeric chains are mutually connected by intermolecular hydrogen bonds $N\text{–}H\cdots O$.

In the structure of $[Hg(bzimtH_2)I_2]_n$ **(161)** [116], the mercury atom is coordinated by two iodine atoms and one sulfur atom from $bzimtH_2$. It has a distorted trigonal geometry. Through $Hg\cdots I$ interactions with two neighbouring molecules which are related by mirror plane symmetry, the number of atoms coordinated

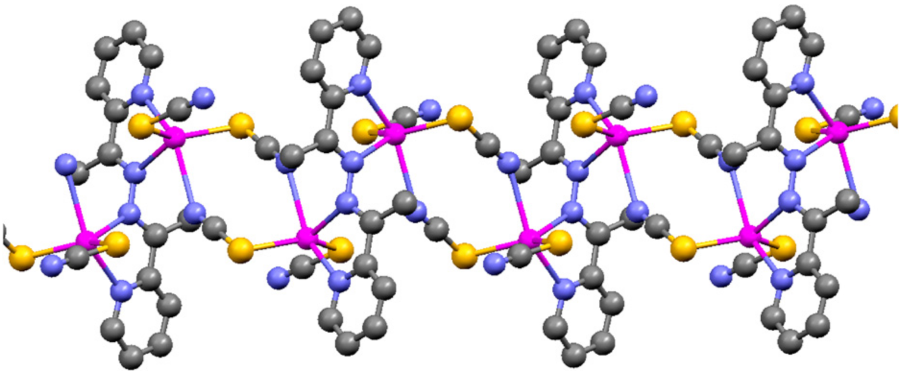


Fig. 22. Representation of the 1D hetrochiral coordination polymer in compound **141** [48]. Reproduced with permission of Elsevier.

to mercury increases to five, thus effectively forming a trigonal-bipyramidal (3 + 2) coordination sphere around the mercury center, elongated in the axial direction. The intermolecular hydrogen bonds and Hg···I contacts lead to the formation of a 2D network. The complex [$(HgI_2)_2$(cryptand5)] **(162)** [117] has symmetry C_i with the oxygen atom O(3) of the ether chain on a center of symmetry of the unit cell, each Hg atom is bound to the two I atoms, the N atom of the chinolyl residue, and one oxygen atom, O(1) and $O(1)^i$, respectively of the ligand; neighbouring complex units are connected via iodine bridges thus forming chains. In the structure of [Hg(μ-S-Am4DH)Br]$_n$ **(163)** [118] coordination around each mercury atom involves the NNS tridentate Am4DH and the thiolato sulfur bridges to the neighbouring Hg(II) atom in the chain. The coordination sphere of Hg atoms is completed by terminal Br atoms in a distorted trigonal bipyramidal geometry.

In the complex Hg(bidtp)$_2$ **(164)** [119] one phosphorodithioate group acts as a chelating group and the other as a bridging group between neighbouring mercury atoms giving rise to an infinite polymer. The coordination of the metal atom is fivefold. In complex [Hg($4-SC_6H_4NH_2)_2$] **(165)** [91], each Hg atom binds to five S atoms and adopts a square-based pyramidal geometry. The core of the chain contains parallel S–Hg–S primary units and is formed by fused Hg_3S_4 incomplete cubanes when the secondary interactions are also considered; it is surrounded by a sheath of radiating aromatic substituents, all approximately parallel (Fig. 23).

In complex [Hg(2-oz)$_2$]$_n$ **(166)** [120] each mercury atom is bound by two oxazolidone nitrogen atoms in a nearly linear arrangement. Each Hg(2-oz)$_2$ molecule is essentially planar and has its carbonyl groups in a syn orientation. Pairs of Hg(2-oz)$_2$ units are oriented face-to-face in an orthogonal relationship such that the carbonyl oxygen atoms of one Hg(2-oz)$_2$ are linked to the mercury atom of the other, and vice versa, to form a dimer. Two oxygen atoms, one from each Hg(2-oz), unit in the dimer, are bridging and serve to link adjacent dimers so as to form a polymeric chain. In the compound [Hg(DLMD)(NO_3)Cl] **(167)** [121], the coordination polyhedron of mercury(II) is a distorted trigonal bipyramid. The nitrate anion acts as bridging ligand between two mercury centers but only through one of their oxygen atoms, thus making a zigzag chain. In the compound [Hg(bipyP$_2$)Cl$_2$]$_n$ **(168)** [122] the coordination sphere of Hg(II) contains two Cl atoms, two N atoms from the bipyridine chelate and one O bridging atom from phosphonate group and thus, the coordination number is five. In three complexes [HgCl(NO_3)(PPh_3)] **(169)**, [HgBr(NO_3)(PPh_3)] **(170)** and [HgI(NO_3)(PPh_3)] **(171)** [123], the mercury atom environment is dominated by close associations with the halide and phosphorus atoms in a quasi-linear array. The nitrate moieties bridge successive mercury atoms to form polymeric chain structures.

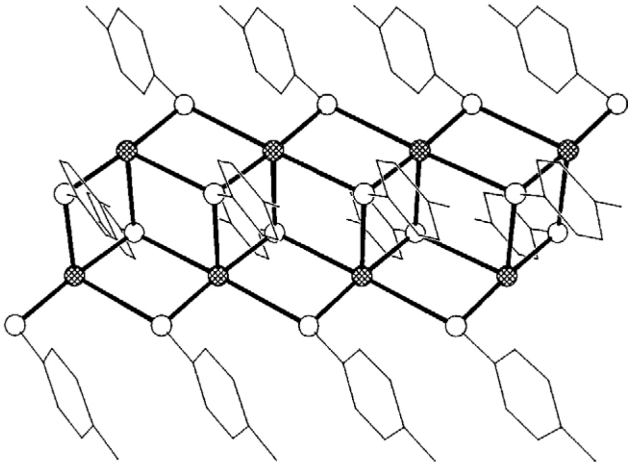


Fig. 23. A section of the polymeric chain of linked incomplete Hg_3S_4 cubanes in complex [Hg($4-SC_6H_4NH_2)_2$] **(165)** [91]. Reproduced with permission of Elsevier.

2.4. Coordination number 6

The structure of complex [Hg(HaaiEt)(μ-1,1-N_3)$_2$]$_n$ **(172)** [124] shows an end-on (μ-1,1-N_3) azido bridged Hg-HaaiEt polymer. The Hg is sitting in a distorted octahedral environment with HgN_6 coordination; four N centers come from four bridged N_3 and two N donor centers, N(imidazole), N(azo) come from chelated HaaiEt unit. A 2D network is generated by π–π interaction of aromatic rings. [Hg(pyr)$_2$Br$_2$]$_n$ **(173)** [125] consists of $HgBr_2$ units which are connected to the 1 and 4 positions of four pyrazine molecules forming double strands, while [Hg(μ-Pyo)(μ-Cl)$_2$]$_n$ **(174)** [126,127] and [Hg(μ-Pyo)(μ-Br)$_2$]$_n$ **(175)** [128], consist of strands of octahedrally coordinated mercuric centers symmetrically and asymmetrically bridged by chloride and bromide, respectively. Neighbouring mercuric centers are also connected by the two adjacent N atoms of pyridazine molecules. The structure of complex [Hg$_2$(bpytm)Cl$_4$]$_n$ **(176)** [113] consists of chains in which Hg atoms are alternately bridged by bpytm ligands and Cl atoms. Ligand bpytm is bis-monodentate, each of its N atoms binding one Hg atom. Each Hg atom is coordinated by one N-atom, one terminal Cl atom, and two Cl atoms bridging to one of the Hg atoms of a neighbouring molecule. Besides these strong bonds, there are also two weak intramolecular interactions: one with the nearest sulfur atom and the other with the terminal chlorine on the other Hg atom. If one takes into account all these interactions, the Hg atom has a very distorted octahedral environment.

The complexes [Hg(3,5-Cl_2py)$_2$(μ-Cl)$_2$]$_n$ **(177)**, [Hg(3,5-Br_2py)$_2$(μ-Cl)$_2$]$_n$ **(178)** and [Hg(3,5-Me_2py)$_2$(μ-Cl)$_2$]$_n$ **(179)** [109] have isomorphous infinite polymeric chains with six-coordinated mercury centers. Polymeric complex [Hg(3,5-Br_2py)$_2$(μ-Br)$_2$]$_n$ **(180)** has two symmetrically independent mercury(II) cations, both located in crystallographic inversion centers and each metal is coordinated in a pseudo-octahedral fashion [109]. Complexes [Hg(C_5H_4NCOOMe)(μ-Cl)$_2$]$_n$ **(181)**, [Hg(C_5H_4NCOOEt)(μ-Cl)$_2$]$_n$ **(182)** [129] and [Hg(MeC_5H_3NCOOEt)(μ-Cl)$_2$]$_n$ **(183)** [130] exist as polymeric chains with highly distorted octahedral mercury(II) centers that are doubly bridged by two Cl atoms. Picolinate ligands behave as chelates, whereas in complex [Hg(C_5H_4NCOO)$_2$]$_n$ **(184)** [130], 2-pyridinecarboxylate ligands behave as chelates and simultaneously bridge two consecutive mercury atoms to form one-dimensional chain (Fig. 24).

In complex [Hg(3-bpo)$_2$(SCN)$_2$]$_n$ **(185)** [131] Hg(II) ion is coordinated by four bridging SCN^- anions and two 3-bpo molecules to form a 1D linear chain. The coordination geometry around the mercury(II) ion is irregular as a distorted octahedron. The individual polymeric chains linked by N_{oxa}···HC(py) and N_{py}···HC(py) interactions, result in a 2D framework. The structure of complexes [Hg(μ-4-bpo)(NO_2)$_2$]$_n$ **(186)** [7], [Hg(μ-3-bpdb)(OAc)$_2$]$_n$ **(187)** [132] and [Hg(4,4′-bipy)(CN)$_2$(H_2O)$_2$]$_n$ **(188)** [133] is a 1D zigzag chain of mercury(II) bridged by N-donor ligands in which Hg(II) centers have a distorted octahedral environment. In compounds **186** and **187** individual 1D chains are linked by weak hydrogen bonds which grow the 1D chains into three- and two-dimensional networks, respectively. Also in complex **188** the chains link together via the π···π and O_{water}–H···π-electron interactions, forming layers which further stack on top of each other to complete a 3D structure. In the solid state this compound shows an intense emission at 433 nm.

In the polymeric complex {(pyda·H)$_2$[Hg(pydc)Cl]$_2$·2H_2O}$_n$ **(189)** [134,135] the Hg(II) atoms are located in the center of a distorted octahedral arrangement consisting of six donor atoms from two carboxylato oxygen, one pyridine nitrogen, one chlorine atom and two carbonyl oxygen atoms from two adjacent

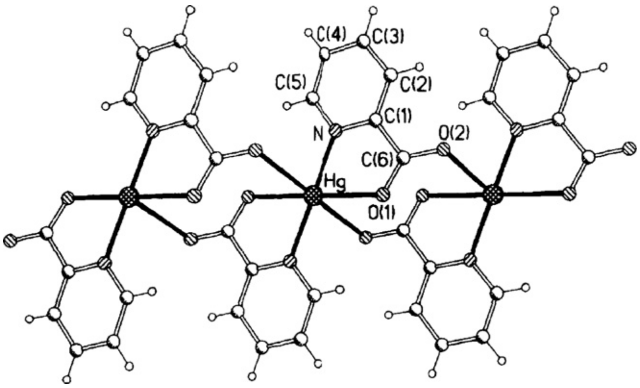


Fig. 24. Part of the polymeric chain structure of compound $[Hg(C_5H_4NCOO)_2]_n$ **(184)** [130]. Reproduced with permission of Elsevier.

carboxylato groups positioned at the two neighbouring layers. These two last oxygen atoms, in fact, act as bridges between Hg atoms. This polymeric complex provides relatively large pores within the structure and a 3D layered network is constructed by ion pairing, hydrogen bonding and π–π interactions. In the crystal structure of $\{[Hg(2,2'\text{-bipy})_2(pds)]\cdot 0.4H_2O\}_n$ **(190)** [136], the Hg(II) center coordinates to two 2,2′-bipy groups and then two pds O atoms link $[Hg(2,2'\text{-bipy})_2]$ centers together to form chains. A fractional hydration water molecule completes the structure. In complex $[Hg(\mu\text{-}2pypo)_2]_n\cdot 2H_2O$ **(191)** [137], the mercury center is coordinated by the N atom of the pyridyl group and O atoms of the phosphonate group. The phosphonate group enables the polymer to grow, as every phosphorus atom has two bridging oxygen atoms and a terminal double-bonded oxygen atom. The mercury center has a very slightly distorted octahedral geometry.

Complex $\{[Hg(smz)_2]\cdot 2DMSO\}_n$ **(192)** [138] consists of two smz ligands bridging between Hg(II) centers creating a one-dimensional chain. Coordination geometry around Hg(II) atoms is strongly distorted octahedral. The crystal structure contains dimethylsulfoxide solvent molecules which are involved in intermolecular hydrogen bonds. The structure of $[Hg_2(sac)_4(mpy)_2]_n$ **(193)** [139] consists mainly of the dimeric $[Hg_2(sac)_4(mpy)_2]$ units that are sequentially linked by the sulfonyl oxygen atoms of the sac ligands of the adjacent units forming a 1D polymeric chain. In polymeric complex $[Hg(\mu_2\text{-}dpp)_2(py)_2]_n$ **(194)** [79], two asymmetric dpp ligands, bridge between Hg(II) centers. Two trans pyridine molecules complete the coordination sphere around mercury in an octahedral geometry. In complexes $[Hg(PBz_3)(NO_3)Cl]_n$ **(195)**, $[Hg(PBz_3)(NO_3)Br]_n$ **(196)** and $[Hg(PBz_3)(NO_3)I]_n$ **(197)** [140] the nitrate anions bridge to adjacent mercury atoms via bidentate interactions to form polymeric chains. In complex $[Hg(PBz_3)(NO_3)(SCN)]_n$ **(198)** [140] SCN^- ions bridge the mercury atoms and constitute centrosymmetric dimers and nitrate anions connect adjacent dimers together to form a polymeric structure. In the structure of $[Hg(PCy_3)(NO_3)_2]_n$ **(199)** [141] two independent types of nitrato groups are present: a bridging group that is involved in the formation of the polymeric chain structure and a second, terminal, bidentate group. The crystal structure of $Hg[LBA]_2\cdot 2H_2O$ **(200)** [142] shows a grating-like polymeric structure. The array of sugar rings is almost the same and each major groove in $Hg[LBA]_2\cdot 2H_2O$ also contains two water molecules. The coordination geometry around the mercury atom is a distorted octahedron. In the structure of complex $[Hg_2(\mathbf{L5})Cl_4]_n$ **(201)** [143] the mercury atom is bonded by two terminal chloride atoms and a carboxyl oxygen atom in a nearly planar, distorted T-shaped coordination geometry. Another three weaker Hg···O bonds lead to six-coordination about the mercury. In complex $[Hg(\mu\text{-}tfms)_2(OH_2)_2]_n$ **(202)** [144] the mercury(II) ion binds strongly two water molecules in an almost linear ${Hg(OH_2)_2}^{2+}$ entity. Two oxygen atoms of each tfms ion bind to two different ${Hg(OH_2)_2}^{2+}$ ions forming double bridges in infinite chains. The water molecules form strong hydrogen bonds to the sulfonate oxygen atoms of neighbouring chains, giving rise to sheets from which the CF_3 groups protrude. These sheets are then held together only by van der Waals interactions between the fluorine atoms, which explains the ease with which the crystals split into flakes. In compounds $[Hg(Dpc)(CF_3)_2]_n$ **(203)** and $[Hg(Dpc)Br_2]_n$ **(204)** [145], Dpc ligands chelate to Hg(II) and bridge between mercury(II) centers to form 1D coordination polymers.

The complexes $[\{Si(CH_2SR)_4\}HgBr_2]_n$ (**205**, R = Me; **206**, R = Ph) [146] present in the solid state extended structures in which fairly linear $HgBr_2$ moieties are connected by doubly bidentate chelating thioether ligands. In complex $Hg^{II}(18S6)Cl_2$ **(207)** [147] the mercury atom is coordinated by four sulfur atoms of two different macrocycles to form a polymeric chain structure (Fig. 25). Each mercury atom is also coordinated by two chlorine atoms. Therefore, the mercury atom has a distorted six-coordinated square-bipyramidal arrangement.

2.5. Coordination numbers 7 and 8

In complex $[Hg(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}OAc)(OAc)]_n\cdot n/2H_2O$ **(208)** [148] each Hg(II) atom has a coordination number of seven and the environment is a distorted pentagonal bipyramid with an O_5N_2 coordination sphere. The carboxylate group of one acetate ligand acts only as a bidentate chelating group. In the second mode two OAc^- anions act as both a chelating and a bridging group (totally tridentate). These metallacycle nodes are connected through four 4,4′-bipy bridges to two other nodes, resulting in one-dimensional double-chains. Solvate water molecules are found in the lattice of this compound and are involved in a hydrogen bonding network. The coordinated water molecules are acting as hydrogen

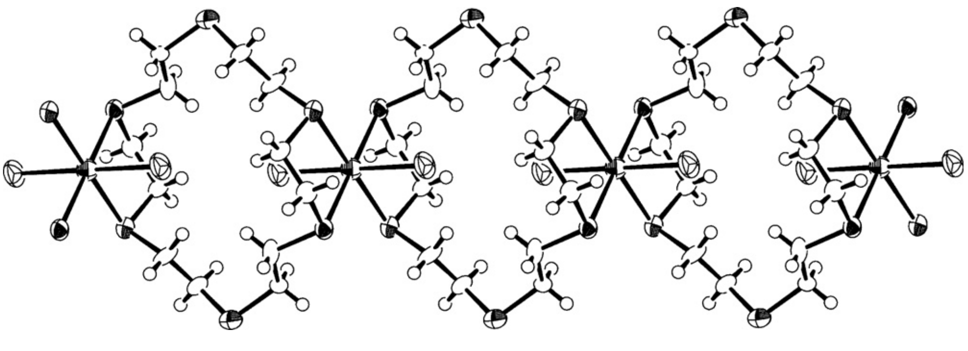


Fig. 25. Packing diagram showing one of the arrangements of the polymeric chain structure of the complex $Hg^{II}(18S6)Cl_2$ **(207)** [147]. Reproduced with permission of American Chemical Society.

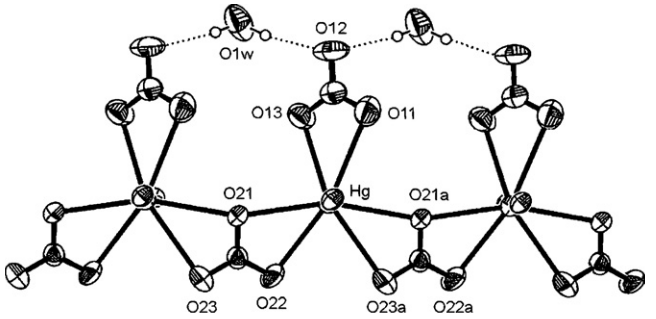


Fig. 26. Honeycomb-like chain structure of mercuric and nitrate ions in compound **212** The N–Hg–N axis is oriented perpendicular to the plane shown [151]. Reproduced with permission of Elsevier.

bond donors towards the O atoms of the coordinated acetate ligands. Consequently, the 1D structure is grown by the hydrogen bonds into a hybrid 2D network. The maximum emission of this compound in the solid state is in the blue region (446.4 nm) and the emission bands cover much of the blue region, giving the observed blue luminescence. Also in complex $[Hg(nbs)_2(H_2O)_3]_n$ **(209)** [149] the mercury(II) ion has a distorted pentagonal bipyramidal coordination environment. The HgN_2O_3 units, in which mercury(II) ion is coordinated by two nbs nitrogen atoms and three water oxygen atoms, are bridged by the nitro oxygen atoms of the adjacent units, forming polymeric chains. The water oxygen atoms form intermolecular hydrogen bonds with the sulfonyl and nitro oxygen atoms of the nbs ligands in the neighbouring units and the polymeric chains of HgN_2O_3 units are held together by these hydrogen bonds forming a 3D network. In the complex $[Hg_2(pds)(terpy)_2(OAc)_2]_n$ **(210)** [150] the peroxodisulfate group acts as a bridge, giving rise to linear chains. In complex $[Hg(Dpc)(NO_3)_2](H_2O)$ **(211)** [145] Dpc ligand chelates to seven-coordinate mercury(II) centers and bridges them to form a 1D coordination polymer.

In complex $[Hg(9\text{-}MeDP)_2](NO_3)_2{\cdot}H_2O$ **(212)** [151] Hg(II) is bound by two N atoms of two 9-MeDP ligands that are arranged approximately trans to each other. One nitrate anion acts as a bidentate chelating group and two nitrate anions act as both a chelating and a bridging group (totally quadridentate) and thus honeycomb-like chain structure of nitrate moieties is generated that is held together by Hg(II) ions positioned inside the combs (Fig. 26). The mercury(II) has a distorted hexagonal bipyramidal geometry. The water of crystallization present in the structure bridges neighbouring nitrate ions within a nitrate chain.

2.6. More than one mercury center with different coordination number

The complex $[Hg_3(4,4'\text{-}bipy)_2(OAc)_2(SCN)_4]_n$ **(213)** [22,152], is a 1D helical-chain polymer in which there are two types of Hg-atoms, two in a four- and one in a six-coordinate $HgOS_2N$ and HgO_4N_2 units, in a distorted tetrahedral and distorted octahedral geometry, respectively (Fig. 27). The structure of complex $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n\{(ClO_4)_4\}_n$ **(214)** [153] consists of discrete $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n{}^{4+}$ and $ClO_4{}^-$ cations and anions, respectively, the former making up a zigzag chain of Hg atoms, involving interactions with both OAc^- and neighbouring Hg atoms. In this structure, there are two Hg(II) atoms, Hg(1) and Hg(2) are six(HgN_2O_4) and seven (HgN_2O_4Hg) coordinated, respectively (Fig. 28).

In the polymeric complex $\{[HgCl_2{\cdot}1,9\text{-}DiMeG]_2HgCl_2\}_n$ **(215)** [154] Hg(II) binds through N(7) of the purine and its coordination sphere is completed by three Cl ligands. One of these, is terminal and others are bridged between Hg(II) centers. The $HgCl_2$ molecule is linear and Hg(2) forms four long contacts with Cl atoms, thereby linking the polymeric chains. The structure of $\{[HgCl(\mu\text{-}Cl)(toacpd)][Hg(\mu\text{-}Cl)_2]\}_n$ **(216)** [155] consists of two chloride bridged mercury atoms. Hg(1) associated with the macrocyclic ligand and one bridging chloride, and Hg(2) with five bridging chlorides. Hg(1) is seven-coordinate and located above the plane of the macrocyclic ring. Hg(2) is five-coordinate with approximately square-pyramidal coordination. Complex $\{Hg(amoimy)_2{\cdot}[HgCl_4]\}_n$ **(217)** contains one-dimensional polymeric chains formed by $Hg(amoimy)_2$ and $[HgCl_4]^{2-}$ through weak Hg···Cl bonds. Hg(1) is six-coordinate and Hg(2) is four-coordinate [156]. This complex has fluorescent emission. In compound $[Hg_3Cl_5(SCH_2CH_2NH_3)_3Cl]_n$ **(218)** [89] the repeating unit is $[Hg_3Cl_5(SCH_2CH_2NH_3)]^+$ with highly distorted coordination around the Hg atoms. Three independent types of Hg atoms are observed, namely HgS_2Cl, HgS_3Cl and $HgSCl_3$. The geometry around Hg(2) and Hg(3) can be best described as distorted tetrahedral and around Hg(1) as slightly distorted 'T' shape. A 3D structure is constructed by intermolecular hydrogen bonding between Cl atoms and amine protons of a second chain.

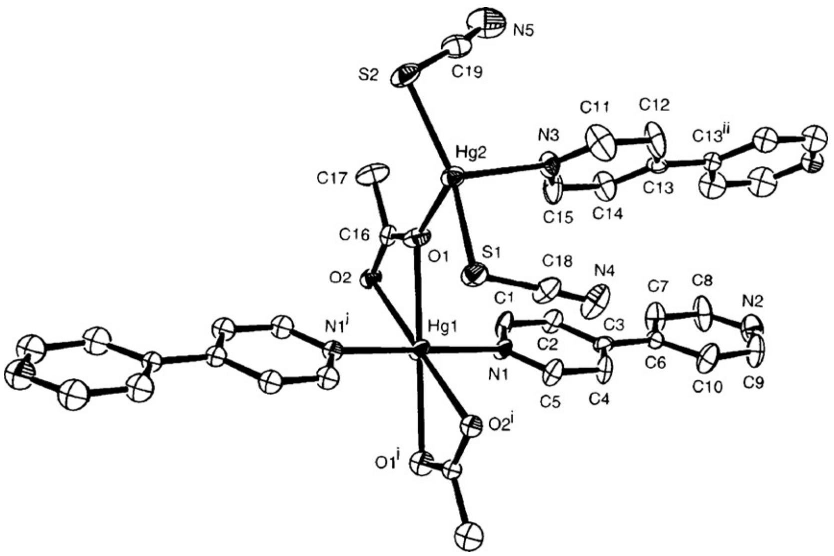


Fig. 27. ORTEP view of compound $[Hg_3(4,4'\text{-}bipy)_2(OAc)_2(SCN)_4]_n$ **(213)** [22]. Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

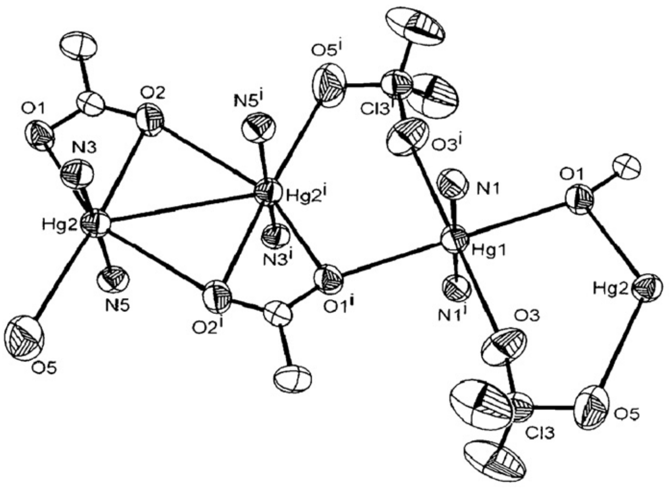


Fig. 28. Bonding interactions made visible for a fragment of the polymeric complex $[Hg_3(dmap)_6(\mu\text{-}OAc)_2]_n\{(ClO_4)_4\}_n$ **(214)** [153]. Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

The structure of complex $[(HgBr)_3(3\text{-tmpio})]$ **(219)** [157] consists of two crystallographically independent units, $HgBr_2$ and $[(HgBr_2)_2(3\text{-tmpio})_2]$. Each Hg(2) atom is coordinated by two bromide atoms and N atom of a pyridyl and O of the nitroxide group, forming a zigzag polymeric chain. Complex $[(HgBr_2)_3(2\text{-tmmpio})_2]_n$ **(220)** [157] has two coordination types of Hg(II), in which the Hg(2) atom has a distorted tetrahedral coordination, consisting of chelating O and N atoms of ligand 2-tmmpio and two terminal Br atoms. Atom Hg(1), originally coordinated by two bromides, has a linear coordination, and additional weak bonds to four bromide atoms, from neighbouring $Hg(2)Br_2$ moieties; thus, there is six-coordination about Hg(1), leading to a chain-like motif in the structure.

In complex $[Hg_2(pipdtc)_3]ClO_4$ **(221)** [158] the environments of mercury atoms Hg(l) and Hg(2) are very similar, apart from the weak coordination of the perchlorate ion to Hg(2). Both are coordinated by five S atoms in a distorted trigonal-bipyramidal geometry. The weak interaction of the perchlorate ion with Hg(2) causes only very slight distortion. Hg(l) is linked to Hg(2) via a μ-bridging dithiocarbamate and by two long mercury-sulfur contacts. Compound $[ClHg(S\text{-neo-Pent})\cdot 0.5py]_n$ **(222)** [105,106] forms a zigzag polymer $[(neo\text{-PentS})_2Hg(py)\cdot HgCl_2]_n$ in which the environment of mercury atoms Hg(1) and Hg(3) is distorted trigonal bipyramidal. Atom Hg(2) possesses a coordination number of four, with a tetrahedral array of two S and two Cl atoms. There are two different Hg(II) atoms in complex $\{(cryptand\ 5)_2[Hg(SCN)_2]_4\}_n$ **(223)** [117], both are bound *via* sulfur atoms to two SCN^- groups, one being a terminal SCN^- group, the other acting as a bridge to the Hg atom of a neighbouring complex unit. The first Hg atom is connected to a chinolyl N atom and two oxygen atoms, the second to a chinolyl N atom and three oxygen atoms. There are two independent complex units per asymmetric unit which are related by a non-crystallographic twofold axis, and which are connected *via* two SCN bridges. These “double molecules” are also interconnected by thiocyanate bridges, thus forming a chain structure. The molecular structure of $[Hg_4Cl_8(NO_3)_2(MB)_2]_n$ **(224)** [159] is a coordination polymer whose asymmetric unit consists of MB cations and a $Hg_4Cl_8)NO_3)_2{}^{2-}$ anion (Fig. 29). The anionic polymeric layer consists of two chains; one comprised of four-coordinated mercury atoms Hg(2) and Hg(4) which are alternatively bridged by chlorine and nitrate oxygen atoms. The other chain consists of tri- and five-coordinated mercury Hg(3) and Hg(1), again alternatively bridged by chlorine and nitrate oxygen atoms. The crystal structure is stabilized by C–H···Cl and C–H···O hydrogen bonding interactions. The cationic columns are interposed between the anionic layers, leading to the formation of a supramolecular 3D array.

3. Two-dimensional coordination polymers

Two-dimensional compounds are obtained with three or four ligand molecules coordinating around the metal ion and the elementary motif expands now in two directions; the most important motifs among two-dimensional coordination polymers are square grids, rhombic and rectangular grids based on square grids, 2D-motifs with T-shape nodes like brick wall or other parquet floor, honeycomb and pseudo-honeycomb grid, herringbone and bilayer.

3.1. Coordination number 4

Combination of tecton **VII** (Fig. 3) with $HgCl_2$ leads to the formation of a 2D coordination polymer (compound **225**) resulting from the mutual bridging between tecton **VII** and $HgCl_2$ [16]. The Hg(II) centers are in a distorted tetrahedral geometry. The 2D net-

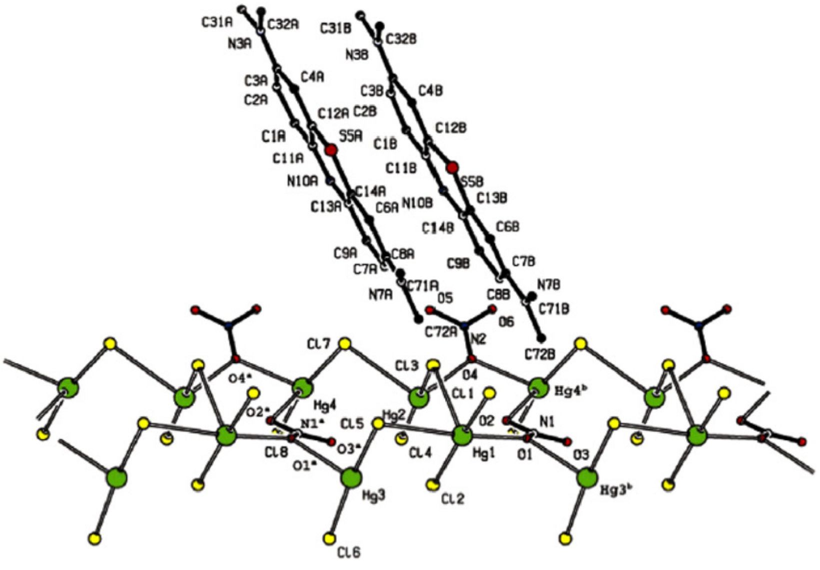


Fig. 29. Molecular structure of $[Hg_4Cl_8(NO_3)_2(MB)_2]_n$ **(224)** [159]. Reproduced with permission of Elsevier.

works are packed parallel to each other generating channels which are occupied by solvent molecules. Also the 2D network of compound **226** is formed by the bridging of consecutive tectons **VIII** (Fig. 3) by $HgCl_2$ units [160]. Because of the size of tecton **VIII** and the divergent orientation of the pyridine groups, their interconnection by mercury centers leads to the formation of large cavities. As a result, a double interpenetration is observed for packing reasons. Complex $\{[Hg(4\text{-bpmpd})I_2](Hg(4\text{-bpmpd})_{1/2}I_2)\}_n$ **(227)** [161] has two crystallographically independent Hg(II) ions in the asymmetric unit: Hg(1) was coordinated by two N atoms from two individual 4-bpmpd and two I^- anions, giving a distorted tetrahedral geometry, while tetrahedral geometry of Hg(2) was completed by three I^- anions and one N atom from an individual 4-bpmpd ligand. One I^- anion connects Hg(1) and Hg(2) to offer an unsymmetrical 'T-shaped' building block responsible for the overall 2D brick-wall network topology. The brick-wall networks in this compound, although each is crystallographically independent, interlock in a specific way to fill in the voids mutually, thus resulting in a threefold parallel entanglement (Fig. 30).

In compound $[Hg_2(H_4bpb)I_4]_n$ **(228)** [162] each H_4bpb ligand links to four Hg(II) atoms through its four N atoms and each Hg(II) connects two H_4bpb ligands to generate a 38-membered ring. Therefore undulant 2D rhombohedral grid network was achieved. The Hg(II) center is four-coordinated with a distorted tetrahedral geometry. The 2D networks are further connected by inter-layer N–H···I hydrogen bonds to form 3D network. In complex $(HgCl_2)_2$(hmt) **(229)** [163] a two-dimensional polymer is formed with all four nitrogen donor atoms equally bonding to Hg(II) atom (Fig. 39).

In the compound $[Hg_2(\mu\text{-2,5-dmpyr})(\mu\text{-SCN})_2(SCN)_2]_n$ **(230)** [54] the geometry of the Hg(II) is trigonal bipyramidal with the two S and the N atom of the SCN^- anions forming a trigonal planar HgS_2N_1 unit that is augmented on one side by the N atom of the bridging 2,5-dmpyr ligand and on the other side by a vacant space at the mercury ion. Of the SCN^- anions one acts as a monodentate ligand, whereas the other forms a bridge to a mercury atom of an adjacent moiety. $[MeHg(3\text{-}SC_6H_4NH_2)_2]_n$ **(231)** [91] has two crystallographically independent molecules in an asymmetric unit. Each Hg(II) atom is bonded linearly to C and S atoms and form a centrosymmetric dimer through Hg···S bonds. Further bonding, between amino groups and mercury, links the dimers into sheet networks. The geometry around Hg(II) is pseudo-octahedral with two *cis*-positions vacant.

In compound, $[Hg(dmdp)_2]_n$ **(232)** [164] the Hg atom is coordinated by four S atoms in a distorted tetrahedral arrangement. The S–P–S parts of the two ligands bridge adjacent Hg atoms, forming one half of a 16-membered ring, the other half being generated by a center of symmetry at the center of the ring. In complex $[Hg_2(dedtp)_3I]_n$ **(233)** [165], dedtp ligands act as bridges between the Hg atoms. One of the two unique Hg atoms coordinates three S and one I atoms in a tetrahedral geometry, while the other Hg also coordinates three S and one I atoms but has an almost planar coordination to the three S atoms. Complex $[Hg_2(bptb)Cl_4]_n$ **(234)** [166] is a two-dimensional coordination polymer, constructed by chloro-bridged $HgCl_2$ units that are linked by the bptb ligand. The geometry around each mercury atom is distorted tetrahedral. The coordination sphere is constructed by a terminal chloro ligand, two μ-chloro ligands and an S atom from bptb ligand. The complex $[Hg_2(bptb)Br_4]_n$ **(235)** [166] is isomorphous with **234** and substitution of the chloro ligands by two bromo ligands does not affect its structural features in a significant manner.

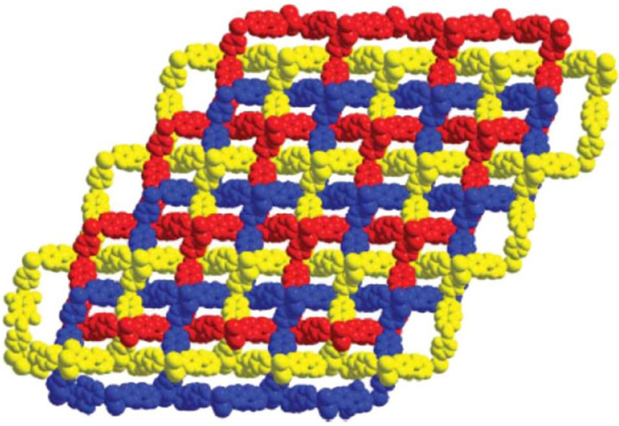


Fig. 30. Three fold parallel Borromean interpenetration in complex **227** [161]. Reproduced by permission of The Royal Society of Chemistry.

3.2. Coordination number 5

In compound $[Hg_2(2\text{-bpdb})I_4]_n$ **(236)** [37,167], ligand 2-bpdb is chelating with each one nitrogen atom of the pyridyl and diaza groups on one side of the molecule coordinating to a mercury(II) ion. Of the I^- anions one acts as a monodentate ligand, whereas the other forms a full halogen bridge to a mercury atom of an adjacent I_2Hg(2-bpdb) moiety. The geometry around Hg(II) is distorted tetragonal pyramid. The compound $[Hg_3(3\text{-bpdh})_{1.5}(SCN)_6]_n$ **(237)** [168] has a polymeric structure and contain two parts, 2D (part A) and 1D (part B) coordination polymers. Part **A** consists of mercury(II) ions bridged by both 3-bpdh and thiocyanate ligands and the environment of each Hg(II) is a distorted square pyramidal. Part **B** consists of linear double chains formed by bridging 3-bpdh ligands. The two individual adjacent 1D (part **B**) and 2D (part **A**) in this compound are almost parallel to each other and further linked by weak Hg···S and this interaction extends the structure into a three-dimensional coordination polymer. The 2D net (part **A**) is polycatenated by the 1D double chain (part **B**) (Fig. 31) which is a very rare case of 2D + 1D = 2D polycatenation [169]. If the weak S···Hg interaction is taken into account the "ladders" connect every other two layers with the result of a twofold interpenetrated nets with complex topology (Fig. 32).

In compounds $[Hg_4(\mathbf{L6})Cl_8]_n$ **(238)** and $[Hg_4(\mathbf{L7})Cl_8]_n$ **(239)** [143] columns of HgCl, bridged by carboxy oxygen atoms, are cross-linked by the double-betaine skeleton to generate a two-dimensional polymeric network. There are two crystallographically independent mercury(II) atoms with nearly square coordination geometry of Hg(1), if the two chelating oxygen atoms of the carboxylate group of the flexible double-betaine ligand are regarded as occupying one corner, and square pyramidal Hg(2). In the polymeric complex, $[Hg(nic)Br]_n$ **(240)** [170], the Hg atom is bonded by two carboxylic acid O atoms, two symmetry-related bridging Br atoms and the pyridine N atom.

The molecular structure of complex $[Hg_2(4,4'\text{-bipy})_2(OAc)_2]_n(ClO_4)_{2n}$ **(241)** [22] consists of a $[Hg(4,4'\text{-bipy})(OAc)]^+$ cation and a $ClO_4{}^-$ anion. The cationic complex is polynuclear, with each 4,4′-bipy ligand bridging two different Hg atoms thus creating a chain structure. The acetato ligand is in a bidentate chelating fashion but one of the chelating O atoms of the acetato ligand is linked to two different Hg atoms of adjacent chains yielding 1D infinite chains, and thus a two-dimensional brick-wall coordination polymer is formed. Complex $[Hg(\mu_3\text{-trz})(SCN)]_n$ **(242)** [171] is a two-dimensional coordination polymer consisting of linear chains formed by bridging trz ligands. The geometry around Hg(II) is a distorted trigonal bipyramid. The trz anion acts as a three fold donor ligand and connects to three different Hg(II) ions. This complex is stable up to 400 °C. The complex $[Hg(besb)Br_2]$ **(243)** [172] has a dinuclear structure formed by one besb ligand linking two $HgBr_2$ units in which Hg(II) ion is coordinated by two Br atoms and one

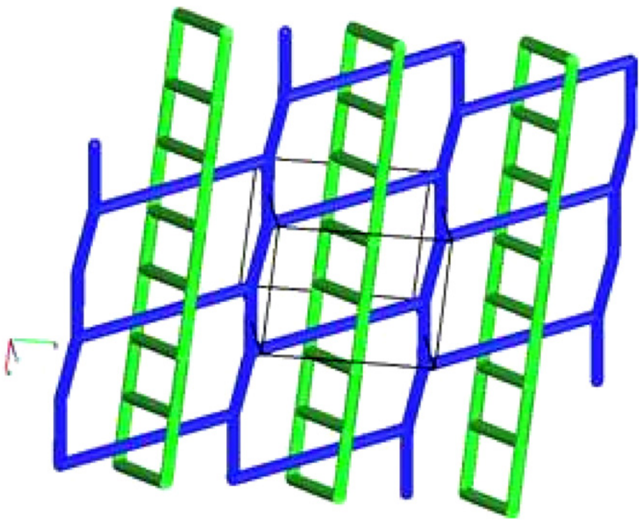


Fig. 31. Representation of 2D + 1D = 2D polycatenation in compound $[Hg_3(3\text{-}bpdh)_{1.5}(SCN)_6]_n$ **(237)** [168]. Reproduced by permission of The Royal Society of Chemistry.

S atom from the besb ligand and is weakly coordinated by two Br^- anions of adjacent molecules to form a two-dimensional layer containing $(HgBr_2)_n$ chains. Thus, the Hg(II) center has a trigonal-bipyramidal coordination geometry and each Br^- anion has a μ_2 bridging coordination mode.

3.3. *Coordination number 6*

Connection between tecton **IX** (Fig. 3) and $HgCl_2$ leads to the formation of a 2D coordination polymer (compound **244** [20]) in which the coordination sphere around Hg(II) is composed of two chloride anions, two nitrogen and two oxygen atoms. In complex $[(HgCl_2)(\mu\text{-}\mathbf{L8})_2]_n$ **(245)** [67], each bis(amidopyridine) ligand, **L8**, bridges two mercury(II) centers to generate sheet structures. These sheets contain 68-membered macrocyclic $(HgCl_2)_4(\mu\text{-}\mathbf{L8})_4$ units. The neighbouring sheets have ligands in opposite conformations in sequences ***A***..***B***..***A***..***B***. The ***A*** and ***B*** sheets are connected via intersheet hydrogen bonds to generate a 3D network, comprised of chiral sheets of interconnected macrocycles.

In complexes $[Hg(\mu\text{-}pyr)(\mu\text{-}Cl)_2]_n$ **(246)** [173], $[Hg(\mu\text{-}pyr)(\mu\text{-}Br)_2]_n$ **(247)**, $[Hg(\mu\text{-}pyr)(\mu\text{-}SCN)_2]_n$ **(248)** [54], $[Hg(\mu\text{-}4,4'\text{-}bipy)(\mu\text{-}Cl)_2]_n$ **(249)** [174], $[Hg(\mu\text{-}4,4'\text{-}bipy)(\mu\text{-}Br)_2]_n$ **(250)** [175], $[Hg(Pym)]Cl_2$ **(251)** and $[Hg(Pym)]Br_2$ **(252)** [163] mercury(II) ions are bridged by both N-donor ligands and anionic ligands, thus forming a two-dimensional, infinite framework (Fig. 33). Compound **249** displays a strong emission in the green region. The crystal structure of $[Hg_2(\mu\text{-}bpe)(\mu\text{-}OAc)_2(\mu\text{-}SCN)_2]_n$ **(253)** [176] and $[Hg_2(\mu\text{-}bpa)(\mu\text{-}OAc)_2(\mu\text{-}SCN)_2]_n$ **(254)** [132] may be considered as a coordination polymer of mercury(II) with linear chains formed by bridging SCN^- and OAc^- ligands. These linear chains are further bridged by neutral bpe and bpa ligands in a two-dimensional polymeric array. The two OAc^- anions simultaneously adopt bidentate chelating and bridging coordination modes. Noncovalent π–π interactions and weak hydrogen bonds help to form a 3D network. In the structure of $[Hg(\mu\text{-}4\text{-}bpo)_2(N_3)_2]$ **(255)** [177], 4-bpo ligand acts as a bridging group (totally bidentate) where one nitrogen atom of pyridyl group and one nitrogen atom of oxadiazole group coordinate to mercury(II) ions, resulting in a two-dimensional framework. Two $N_3{}^-$ anions link to mercury(II) ions via one nitrogen atom and act as a terminal ligand. The geometry of mercury(II) is a distorted octahedron.

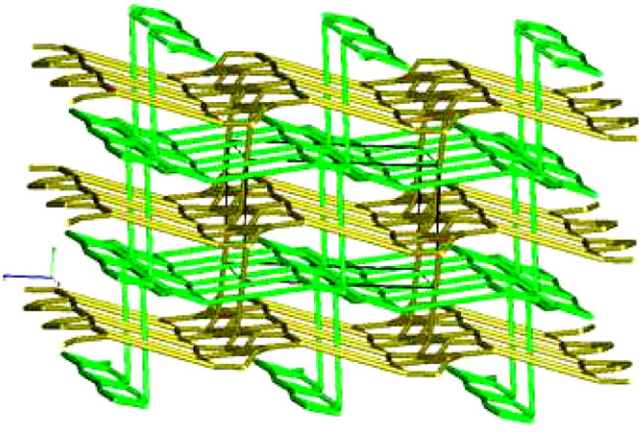


Fig. 32. Representation of a twofold interpenetrated nets generated by weak S···Hg interaction in compound **237** [168]. Reproduced by permission of The Royal Society of Chemistry.

In complex $[Hg(\mu\text{-}Cl)_2(3,5\text{-}Me_2py)_2(\mu\text{-}HgCl_2)_3]_n$ **(256)** [109] which is a 2D layer structure, $(HgCl_2)_3$ oligomers are coordinated by the metal-bridging chloro ligands and link neighbouring strands where coordination number of Hg(1), Hg(2) and Hg(3) atoms are 6, 2 + 3 + 1 and 2 + 4, respectively. In compound $\{[Hg(\mu\text{-}Pym)_2](ClO_4)_2\}_n$ **(257)** four N-donor ligands bridge Hg(II) centers forming a 2D structure. The coordination sphere of Hg(II) completed by two O atoms of two perchlorate anions [163].

The structure of complex $[Hg(pom)Br_2)]_n$ **(258)** [178] is polymeric through six bridging atoms. The very distorted octahedral mercury(II) is bonded to two O atoms from two pom ligands and four Br atoms. In polymeric complex $[Hg(picOH)Cl]_n$ **(259)** [115] both carboxylate oxygen atoms of the deprotonated picolinic acid are involved in coordination with two neighbouring mercury atoms to bridge them and form infinite zigzag chains. Mercury(II) also binds to N and Cl atoms and forms infinite two-dimensional layers with two more long Hg···O contacts.

In compound $[Hg_3(SHCH_2CH_2NH_2)_2Cl_6]\cdot 2H_2O$ **(260)** [88] the ligand is present as the zwitterionic cysteamine instead of anionic cysteaminate and subsequently coordinates with its S atom only to the Hg(II) (Fig. 34). This complex contains two differently coordinate Hg atoms. Hg(1) exhibits a slightly distorted octahedral geometry with a $Hg(Cl_4S_2)$ coordination mode. Hg(2) displays a “5 + 1” coordination, with a $Hg(Cl_4S)$ coordination mode and a long Hg···Cl contact, the geometry being strongly distorted octahedral. All Cl atoms in this compound act either as μ_2 or even μ_3 bridges. Thus, parallel chains of Cl and S bridged Hg atoms are formed which are held together by long Hg···Cl contacts and N–H···Cl hydrogen bonds [88].

3.4. *Coordination number 8*

In compounds $\{[Hg(\mu\text{-}Pym)_2](NO_3)_2\}_n$ **(261)** and $\{[Hg(\mu\text{-}pyr)_2](ClO_4)_2\}_n$ **(262)** [163] four N-donor ligands are bridged between Hg(II) centers forming two-dimensional coordination polymers in which the nitrate and perchlorate ions attach bidentatively to mercury(II) centers.

3.5. *More than one mercury center with different coordination number*

In $[2Hg_3(mbtma)C1_6\cdot Hg_2(mbtma)Cl_4]_n$ **(263)** [179] two asymmetric molecules and one symmetric molecule are arranged alternatively, and belts of $HgCl_2$ bridged by carboxyl oxygen or chlorine atoms are formed. The skeleton of the double betaines

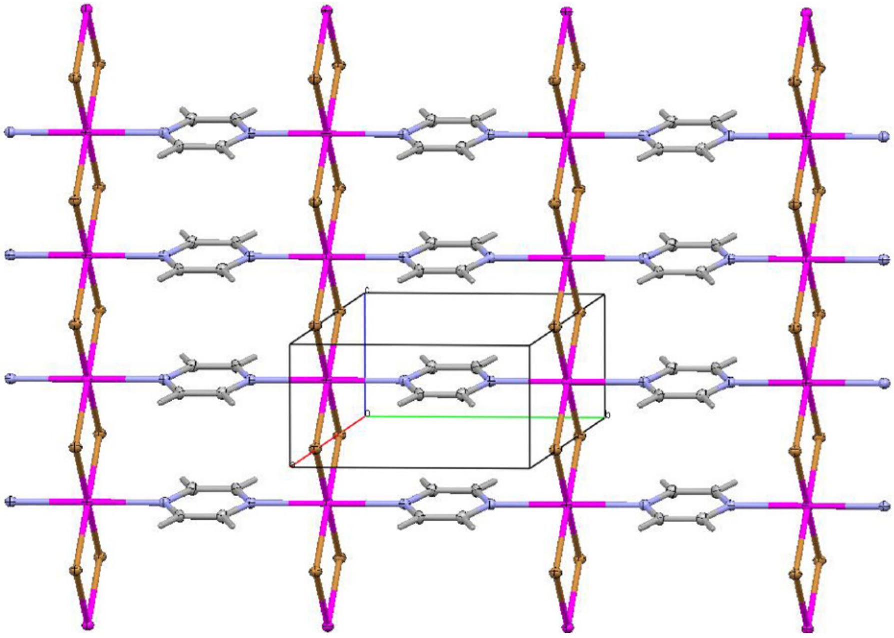


Fig. 33. Representation of 2D coordination polymer in $[Hg(\mu\text{-pyr})(\mu\text{-Br})_2]_n$ **(247)** [54].

cross-link these belts to generate a two-dimensional polymeric network. In this complex Hg(1), Hg(3) and Hg(4) are irregular five-coordinate and Hg(2) is six-coordinate. In complex $[Hg_3(mbpa)Cl_6]_n$ **(264)** [179], mercury atoms in the zigzag chains are linked by the weak Hg···C1 bonds to form a two-dimensional polymeric structure. This complex has two crystallographically independent mercury(II) atoms which exhibit different coordination geometries.

Complex $[Hg_2(tmaa)_2C1_4\cdot 2HgC1_2]_n$ **(265)** [180] consists of centrosymmetrical $Hg_2(tmaa)_2C1_4$ dimeric units and virtually linear $HgCl_2$ units in which secondary bonding links the dimeric and $HgCl_2$ units into a two-dimensional polymeric network. Hg(1) is in a highly distorted tetrahedral geometry and Hg(2) is a compressed octahedron. Complex $[Hg_2(pyia)_2Cl_4\cdot HgC1_2]_n$ **(266)** [180] is also composed of centrosymmetrical $Hg_2(pyia)_2C1_4$ dimers and linear $HgCl_2$ units in which again secondary bonding links the dimeric and $HgCl_2$ units into a two-dimensional polymeric network. Hg(1) is in a highly irregular five-coordinate arrangement.

In compound $\{[Hg(S\text{-iso-Pr})_2]\cdot HgCl_2\}_n$ **(267)** [105,106], atom Hg(1) has a coordination number of six comprised of two S atoms and four Cl atoms. Hg(2) is in a distorted tetrahedral environment and interacts with two S atoms and two Cl atoms. In complex $[Hg_2(PEDT)I_4]_n$ **(268)** [181] the inorganic (HgI_2) and organic (PEDT) components are coordinated via Hg–S bonds. Two kinds of mercury centers are found within the inorganic layer. Hg(1) is coordinated tetrahedrally by three I atoms and thiocarbonyl S atom of the ligand and Hg(2) has a highly distorted five coordinate environment composed of five I atoms and is considered as square pyramidal [181].

The structure of complex $[(Me_3P)_2(HgI_2)_3]_n$ **(269)** [182], comprises $Hg(PMe_3)^{2+}$ cations linked via weak Hg–I interactions to four HgI_3^- anions to give chains. The HgI_3^- units are grouped in pairs and further weak Hg···I interactions give rise to $Hg_2I_6^{2-}$ dimers, thereby linking the chains together. Hg(1) is six-coordinate by four I atoms and two P atoms and the coordination sphere around Hg(2) is comprised of four I atoms. In complex $\{[Hg_2(ampa)_2](H_2O)_2(NO_3)\}_n$ **(270)** [183] one ampa molecule bridges two mercury centers in which one mercury atom is coordinated by the amine group, while a second mercury center is coordinated by the phosphonate oxygen atoms. Hg(1) is five-coordinate and comprised of N atom from an amine group and $\mu 2$ oxygen atoms from the ampa. The coordination sphere around Hg(2) consists of a nitrogen atom and two bridging oxygen atoms from the phosphonate group.

In complex $[Hg_2(\mu\text{-4-bpdb})_{1.5}(\mu\text{-OAc})(\mu_{1,1}\text{-SCN})(\mu_{1,3}\text{-SCN})(SCN)]_n\cdot CH_3CN$ **(271)** [132] linear chains formed by bridging SCN^- and OAc^- ligands. These linear chains are further bridged by neutral ligands 4-bpdb resulting in a two-dimensional polymeric array. This complex has two different mercury atoms, one seven-

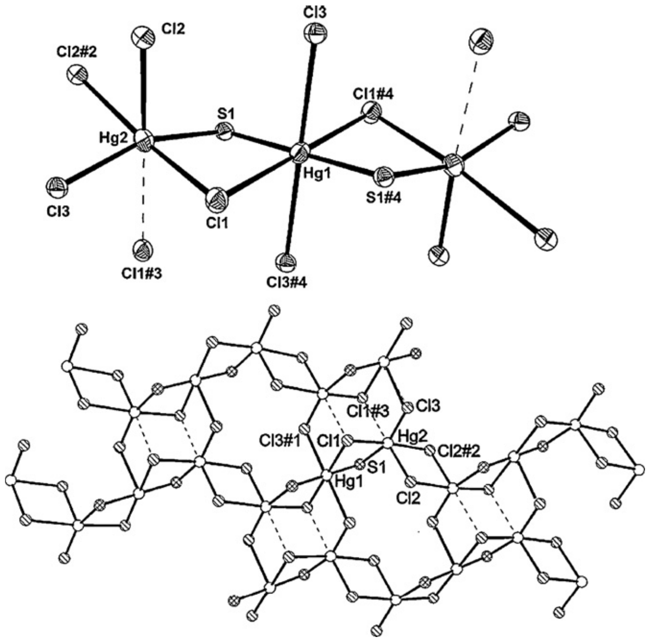


Fig. 34. (a) ORTEP diagram of $[Hg_3(SHCH_2CH_2NH_2)_2Cl_6]\cdot 2H_2O$ **(260)**, showing the coordination mode of the two crystallographically different Hg atoms (b) packing diagram of compound **(260)** [88]. Reproduced with permission of American Chemical Society.

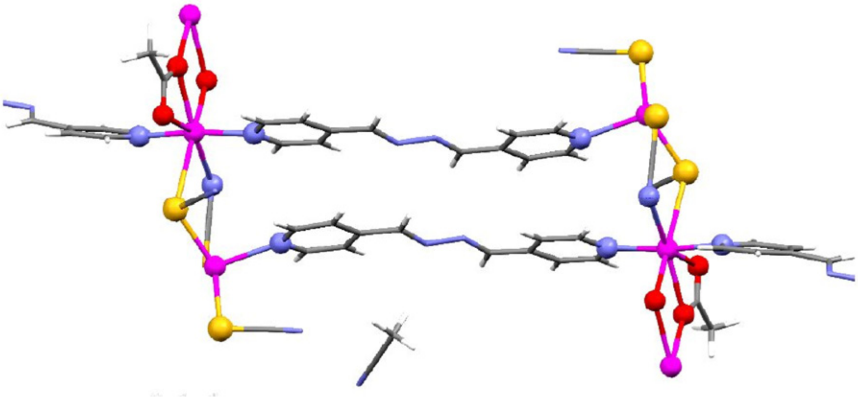


Fig. 35. Schematic representation of Hg(II) environment of the $[Hg_2(\mu\text{-}4\text{-bpdb})_{1.5}(\mu\text{-OAc})(\mu_{1,1}\text{-SCN})(\mu_{1,3}\text{-SCN})(SCN)]_n\cdot CH_3CN$ **(271)** [132]. Reproduced with permission of Elsevier.

coordinate, distorted pentagonal bipyramidal, mercury atom with a O_3N_3S donor array while the other is four-coordinate with S_3N donor atoms array in a distorted tetrahedral environment (Fig. 35). The carboxylate moiety of acetate ligand acts as both a chelating and a bridging group and SCN^- anions act in different coordination modes, one terminal fashion, one $\mu_{1,1}$-bridge fashion bridged from sulfur atom and one $\mu_{1,3}$-bridge fashion bridged from sulfur and nitrogen atoms.

4. Three-dimensional coordination polymers

Three-dimensional structures can be built with metal ions of higher coordination number (tetrahedral or octahedral nodes); the most important motifs among three-dimensional coordination polymers are Diamondoid net, Octahedral net, NbO-, ThSi2-, PtS-, SrSi2- and CdSO4-like motifs. [5].

4.1. Coordination number 4

In complex $[Hg_8(\mu\text{-}n\text{-}C_3H_7Te)_{12}(\mu_2\text{-Br})Br_3]$ **(272)** [184] closely packed subunits of $[Hg_8(\mu\text{-}n\text{-}C_3H_7Te)_{12}(\mu_2\text{-Br})]^{3+}$ are linked with a centered Br^- to form a three-dimensional network through six bromo-bridges (Fig. 36). This finally enables a three-dimensional linking of the cluster units and a close packing in the solid state. The eight mercury atoms of the cluster units are in a distorted cubic arrangement with the μ_2-Br atom in its center. The coordination environment of Hg(2) is a distorted trigonal pyramid, whereas that of Hg(1) is intermediate between a trigonal pyramid and a tetrahedron [184].

4.2. Coordination number 5

In compound **273** connection between the organic tecton **X** (Fig. 3) and $HgCl_2$ leads to the formation of a 1D coordination polymer with helical geometry [185]. The Hg(II) ion adopts a distorted square planar geometry with two Cl and two N atoms in trans configuration. Interstrand interactions between pyridine units of different strands lead to the formation of a triple stranded helical arrangement (Fig. 37b). Furthermore, the triple stranded helical units are further interconnected through coordination bonding between the O atoms of the carbonyl group of ester groups belonging to a triple stranded helices and Hg centers of the adjacent triple helices. When taking into account the lateral interconnection between triple helices, the coordination geometry around Hg(II) ion is a distorted square based pyramid and the overall structure as a three-dimensional coordination polymer [185]. In complex $[Hg(hmt)_{1/2}Br_2]_n$ **(274)** [186] the central mercury ion adopts a distorted trigonal bipyramid geometry. The axial Hg–Br bonds connect the $Hg(hmt)Br_2$ units, forming an extended three-dimensional network.

4.3. Coordination number 6

The structure of $Hg(tcm)_2$ **(275)** consists of two interpenetrating rutile-related networks. Each of the two identical networks consists of six-connecting centers (octahedral metal ions) and

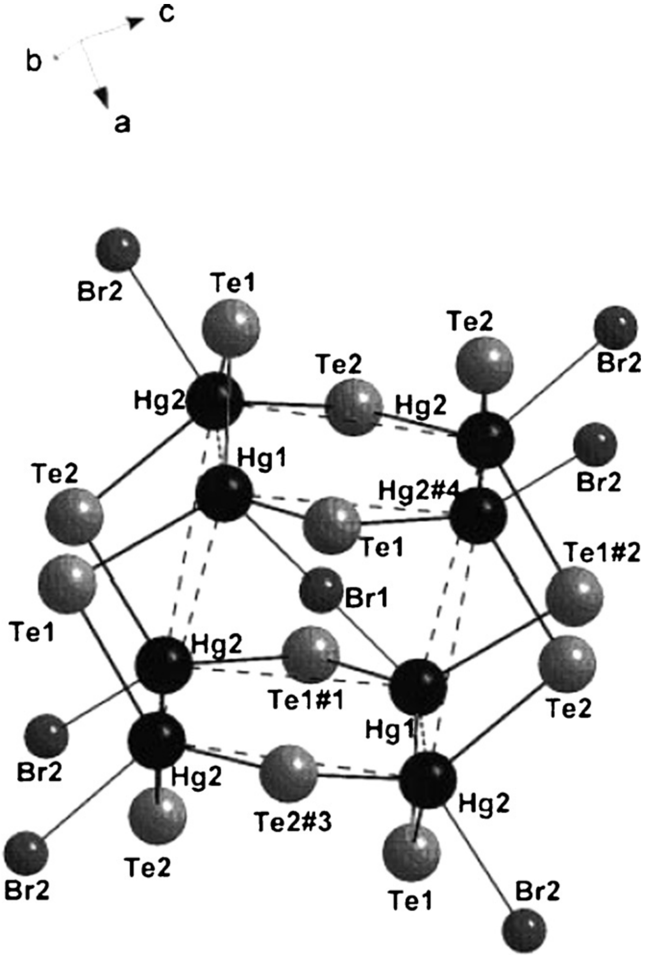


Fig. 36. Representation of the cluster units of $[Hg_8(\mu\text{-}n\text{-}C_3H_7Te)_{12}(\mu_2\text{-Br})Br_3]$ **(272)** [184]. Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

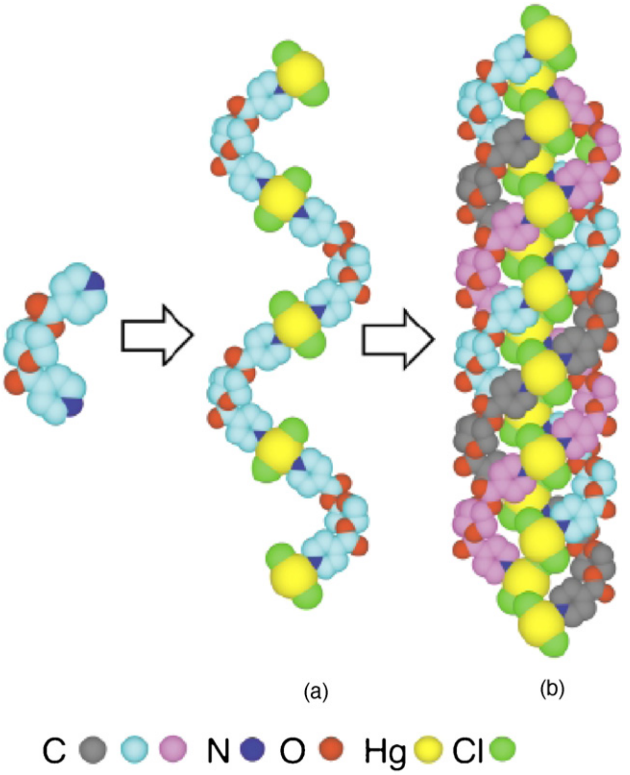


Fig. 37. A perpendicular view of a portion of the enantiomerically pure infinite helical 1D coordination network (P helicity) formed upon bridging of consecutive tectons **X** by $HgCl_2$ (a) and a portion of the triple stranded helix formed between three single stranded helices through aromatic/aromatic interactions (b) [185]. Reproduced by permission of The Royal Society of Chemistry.

three-connecting centers (tcm^- ligands) in the ratio 1:2, with a topology identical to that of rutile [187].

In the complex $[Hg(tpt)_2](ClO_4)_2{\cdot}6C_2H_2Cl_4$ **(276)** [188] Hg centers and tpt units form an infinite (6,3)-connected 3D network; the spacious intraframework regions are occupied by well-ordered $C_2H_2Cl_4$ molecules and $ClO_4{}^-$ ions. In complex $[Hg(pya)Cl]_n$ **(277)** [189] the Hg(II) center is in a highly distorted octahedral coordination environment. The carboxylate group binds to the Hg(II) ions as a μ_3-bridge and takes the unusual μ-*O*, *O*-η-*O*, *O*′-μ-*O*′, *O*′ mode. As a result, a dimeric boxlike unit, consisting of two Hg(II) centers that are connected by a pair of pya ligands, with the dimensions of 6.83(2) Å × 4.48(1) Å is formed. Through a pair of Hg–O coordinative interactions, these boxlike units are bridged to form 1D chain arrays. Self-assembled by further Hg–O bonds, A and A′ chains are alternatively arranged to generate a 2D layered structure (Fig. 38) and additional Hg–O interactions lead to the formation of a 3D coordination polymer.

Complex $[Hg(\mu\text{-}2,6\text{-dmpyr})(\mu\text{-SCN})_2]_n$ **(278)** [54] consists of one-dimensional linear chains, with $[Hg(\mu\text{-}2,6\text{-dmpyr})]$ building blocks. The individual parallel polymeric chains are further bridged by the bidentate thiocyanate anions, resulting in a three-dimensional framework. The coordination geometry around the mercury(II) ion is irregular and is distorted octahedral. As already pointed out in $(HgCl_2)_2(hmt)$ **(229)** hmt ligands connect to four $HgCl_2$, generating 2D (4,4) sheets (Fig. 39). But these sheets stack so that the $HgCl_2$ molecules of adjoining sheets associate to form chains through long Hg···Cl interactions (3.105 Å) (Fig. 40). When taking into account the lateral interconnections, a three-dimensional coordination polymer of compound **279** is achieved and these interactions complete the pseudo-octahedral geometry of the mercury(II) [190].

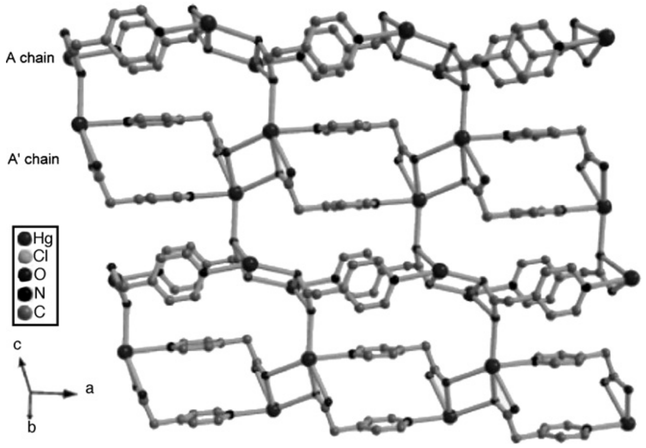


Fig. 38. 2D coordination network of **(277)** with boxlike dimeric subunits [189]. Reproduced with permission of American Chemical Society.

4.4. More than one mercury center with different coordination number

In the crystal structure of $[Hg_2(Mmt)(Dmt)_2](NO_3)(H_2O)$ **(280)** [191] there are three crystallographically independent Hg(II) central ions surrounded in different ways by Dmt^- and Mmt^- ligands. The coordination polyhedra $[Hg(1)N_2ON_2]$ and $[Hg(2)N_2O_2N_2]$ are attached to each other to form corrugated layers. These layers are connected via $[Hg(3)N_4]$ tetrahedra to a three-dimensional structure.

The complexes $[Hg_2(tpmb)Cl_4]_n$ **(281)** and $[Hg_2(tpmb)Br_4)]_n$ **(282)** [69] have the same framework structure. In complex **281** each tpmb ligand acts as a three-connecting linker to link two Hg(1) and one Hg(2) atoms, while the Hg(1) center servers as two-connecting node. Therefore, a 2D network structure is achieved. Six tpmb ligands are linked together by eight Hg(II) atoms to form a M_8L_6 macrocycle. The 2D networks are further held together by the $Hg(2)(\mu\text{-}Cl)_2Hg(2)$ 1D chain linkage to give a 3D coordination framework. The coordination geometry of Hg(1) and Hg(2) is a distorted tetrahedron and a distorted trigonal bipyramid, respectively. As a result of large 1D channels in each individual 3D framework, fourfold interpenetration with formation of C–H···Cl and C–H···O hydrogen bonds is observed.

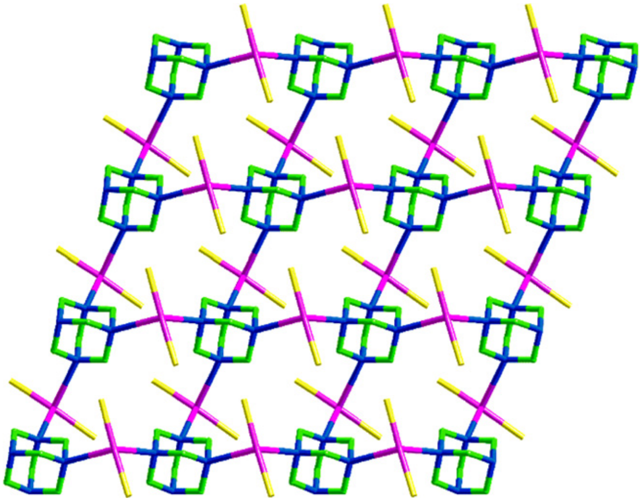


Fig. 39. 2D (4,4) sheet in the structure of $(HgCl_2)_2(hmt)$ **(279)** [190]. Reproduced with permission of American Chemical Society.

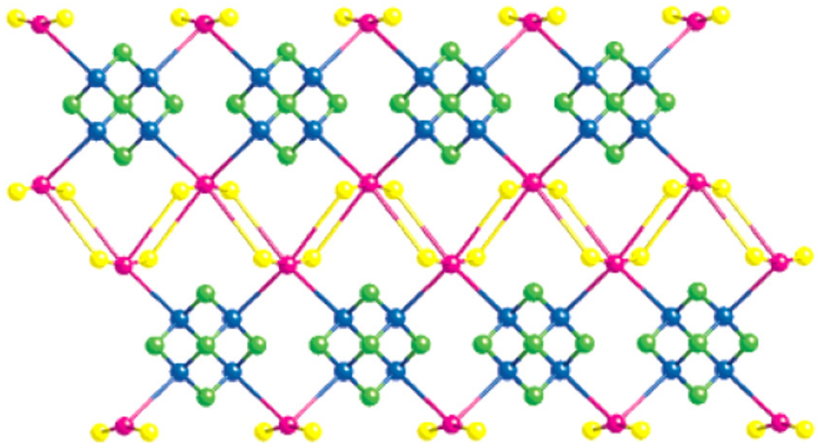


Fig. 40. Adjacent sheets in the structure of **279**, viewed side-on, linked by 1D chains of weak Hg–Cl interactions running across the page [190]. Reproduced with permission of American Chemical Society.

5. Conclusions

Considering the structures discussed in this paper, one-dimensional polymers constitute a great portion of coordination polymers of mercury(II), among which zigzag structure with counter ion iodide is drastically dominant. This dominance of zigzag structures may be due to the steric effect of the counter ion, in particular iodide group, the rigidity of the ligands, and the preference of Hg(II) for tetrahedral coordination geometry [28,52,55]. Mercury(II) exhibits greater tendency to forming one-dimensional coordination polymers and three-dimensional polymers are less common. This may be related to mercury's greater radii, mercury's tendency for having a smaller coordination number and taking a tetrahedral coordination geometry by mercury(II). Moreover, the effects related to structure, size and rigidity of ligands as well as number and size of anions, are important in explaining the greater number of one-dimensional coordination polymers.

Acknowledgement

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