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Isomers in the chemistry of mercury coordination compounds

Invited Review

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Abstract: The coordination chemistry of mercury is an extremelybroad field, as shown by a survey covering the crystallographic and structural data of over 550 examples. About 12% of those complexes exist as isomers and are summarised and classified in this review. Included are distortion (73%), polymerisation (20.6%), coordination number (3.2%) and ligand (3.2%) isomerism. These are discussed in terms of the coordination around the mercury atoms, and correlations are drawn between donor atoms, bond distances and bond angles. Distortion isomers, differing only by the degree of distortion in the Hg – L and L – Hg – L angles, are the most common. These isomers are discussed and compared with those found in the chemistry of zinc and cadmium.

Keywords: • *Mercury complexes* • *Distortion* • *Polymerisation* • *Coordination number* • *Ligand isomerism*

1.Introduction

Although mercury belongs to the IIB group of elements, it shows such unique behavior that it cannot be considered a homologue of zinc and cadmium. All are remarkably volatile for heavy metals, particularly mercury. Mercury becomes extremely hazardous in the biosphere because there are bacteria that can convert it to the exceedingly toxic soft acid CH_3Hg^+. The latter is highly persistent in biological systems and becomes concentrated in the food chain. It is well known that Hg(II) has a special affinity for sulfur and thus tends to form extremely stable complexes with thioamino acids such as cysteine, and methionine. This affinity between sulfur and mercury is responsible for many of the toxic effects of mercury in biological systems.

Systematic studies in the field of stereoselectivity of coordination compounds over the last 50 years have become of increasing interest. Stereoselectivity in coordination compounds is very often related to important stereospecifity in biological systems, catalysis and stereochemical effects in industrial processes. Isomers can be broadly classified into two major categories: structural and stereoisomers. The former can be divided into ionization, hydration, coordination, linkage and polymerisation sub-categories, and the latter can be divided into geometric (cis-trans, fac-mer), optical, distortion and ligand isomerism.

Mercury exist in the following oxidation states: Hg(1) (Hg_2(2+)), Hg(0.33) Hg(1.33) and Hg(2). Of these, +2 is the most common. Crystallographic and structural data for over 550 mercury coordination compounds has been surveyed [1] with 65 isomeric examples noted. In this review, we analyze and classify these examples.

Analysis of zinc(II) coordination compounds [2] reveals two isomeric types: distortion (96%) and ligand (4%) isomerism. Analysis of cadmium(II) compounds [3] reveals several isomeric types: distortion (91.5%), ligand (6.5%), cis-trans (1%) and polymerization (1%) isomerism.

The aim of this work is to discuss the factors which could lead to a better understanding of stereochemical interactions within the coordination sphere. The systems discussed have been sorted by nuclearity and subdivided according to the coordination number of the mercury atom. Within each coordination number, the

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compounds are listed in order of increasing covalent radius of the principal coordination ligand atom and increasing complexity of the coordination sphere. A comprehensive discussion of isomers of complexes of group IIB metals is also presented.

2. Distortion Isomerism

The coexistence of two or more species, even within the same crystal, differing only by the degree of distortion, is typical of the general class of distortion isomerism [4]. There are 46 such examples.

2.1.Monomeric mercury compounds

The crystallographic and structural data for monomeric mercury compounds which exist in two isomeric forms are summarized in Table 1. There are 12 such examples with chromophores: HgS_2 [5,6], HgS_4 [7-13] and $HgCl_2P_2$ [14,15]. In two colorless,monoclinic isomers, α-$Hg(SCN)_2(PPh_3)$ [5] and β-$Hg(SCN)_2(PPh_3)$ [6], the three coordination sites around each Hg(II) atom are occupied by the two unidentate S-donor atoms of the two SCN groups and the P donor atom of the PPh_3 ligand (HgS_2P). While the Hg – S bond distances of the α- and β- isomers differ from each other with values of 2.469(4) and 2.539(4) Å for the α-isomer *vs.* 2.491(4) and 2.519(4) Å for the β- isomer, the Hg – P bond distance is equal in both isomers (2.461(4) Å). The S – Hg – S and S – Hg – P (av) bond angles are 118.3(5) and 123.1(1)° for the α-isomer, and 106.4(2) and 126.8(2)° for the β- isomer. This indicates that the β-isomer is somewhat more distorted than the α-isomer.

In two colorless triclinic isomers of composition (bed-ttf)$_2$[KHg(SCN)$_4$] [7], each mercury atom is tetrahedrally coordinated. Four SCN groups are located around each Hg(II) atom in a tetrahedral arrangement (HgS_4). These isomers differ from one other by their degree of distortion.

In two monoclinic colorless isomers, α-[Hg(tu)$_4$]Cl_2 [8] and β-[Hg(tu)$_4$]Cl_2 [9], four unidentate thiourea ligands form a tetrahedral arrangement around each Hg(II) atom (HgS_4). The mean Hg – S bond distances are 2.536 Å in the α-isomer and 2,549 Å in the β-isomer. The six “tetrahedral angles” fall in the narrow range 94.0(1) – 124.2(1)° in the α-isomer and 102.1(1) – 116.9(1)° in the β-isomer. This indicates that the α-isomer is somewhat more crowded and has a higher degree of distortion than the β-isomer.

Two homobidentate $Pr^i_2NCS_2$ ligands in two yellow monoclinic isomers, α-Hg(η^2- $Pr^i_2NCS_2$)$_2$ [10] and β-(η^2-$Pr^i_2NCS_2$) [11] create a tetrahedral arrangement around each Hg(II) atom (HgS_4). The sum of all Hg – S bond distances is 10.18 Å in the case of the α-isomer and 10.21 Å in the case of the β-isomer. Unfortunately, the value of the S – Hg – S bond angle is known only for the α-isomer. Five of the six “tetrahedral angles” fall in the narrow range 117.5(2) – 149.7(3)°, while the angle which is part of the four-membered metallocycle (S – Hg – S) is significantly smaller (70.7(2)°).

Another two colorless monoclinic isomers, α-[Hg(η^4-$C_{12}H_{24}S_4$)](ClO_4)$_2$ [12] and β-[Hg(η^4-$C_{12}H_{24}S_4$)](ClO_4)$_2$ [13] are the only examples in which each Hg(II) atom has a square planar arrangement created by a homo-tetradentate ligand (HgS_4). The mean Hg – S bond distances are 2.597 Å (α-) and 2.616 Å (β-), while the S –Hg – S bond angles in the α- isomer are deviated by 2.4° from the ideal square planar angle (90.0°) and by 1.7° in the β- isomer. This indicates that the β-isomer is somewhat less crowded but somewhat less distorted than the α-isomer.

The remaining two colorless isomers, α-($HgPPh_3$)$_2Cl_2$ [14] and β-($HgPPh_3$)$_2Cl_2$ [15], differ not only by degree of distortion but also by crystal class: α- is orthorhombic and β- is monoclinic. Each Hg(II) atom is tetrahedrally coordinated ($HgCl_2P_2$). The mean Hg – Cl and Hg – P bond distances (α- *vs.* β-) are 2.498 and 2.518 Å *vs.* 2.552 and 2.470 Å, respectively. The Cl – Hg – Cl, P – Hg – P and Cl – Hg – P (av) bond angles are: 106.6(2), 113.5(1) and 109.0(2)° for the α-isomer and 110.7, 134.1(1) and 102.8(1)° for the β-isomer. The β- isomer is somewhat more distorted than the α-isomer.

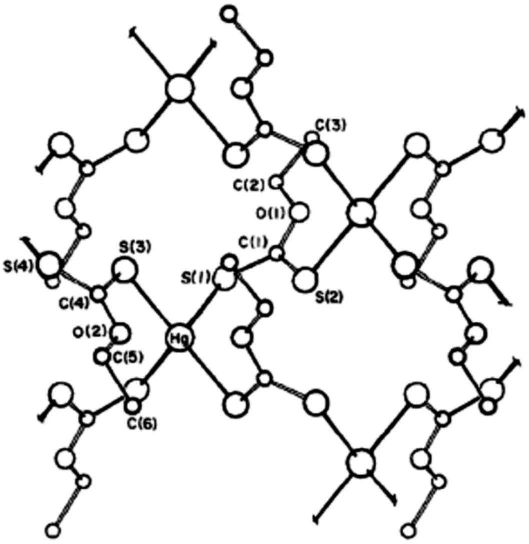

Figure 1. Structure of Hg(Etxan)$_2$ [20]

Table 1. Crystallographic and Structural Data for Monomeric Mercury Complexes – Pairs of Distortion Isomers[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Hg-L [Å]	L-Hg-L [°]	Ref
α-$Hg(SCN)_2(PPh_3)$ (colourless)	m $P2_1/c$ 4	10.75(6) 21.136(11) 10.745(4)	112.37(4)	HgS_2P	S[b] 2.504(4,35) P 2.461(4)	S,S[b] 118.3(5) S,P 117.1(1) 129.2(1)	5
β-$Hg(SCN)_2(PPh_3)$ (colourless)	m $P2_1/c$ 4	21.071(5) 17.716(5) 11.285(3)	101.66(5)	HgS_2P	S 2.505(5,14) P 2.461(4)	S,S 106.4(2) S,P 121.1(2) 132.5(2)	6
$(bed\text{-}ttf)_2[KHg(SCN)_4]$ (colourless)	tr P-1 2	10.082(10) 20.082(4) 9.933(2)	103.70(2) 90.91(4) 93.06(4)	HgS_4	S 2.560(4,11)	S,S 109.5(1,2.5)	7
$(bed\text{-}ttf)_2[KHg(SCN)_4]$ (colourless)	tr P-1 2	9.948(2) 20.505(11) 9.833(4)	103.34(4) 90.53(3) 92.80(3)	HgS_4	S 2.559(2,8)	S,S 109.5(1,2.4)	7
α-$[Hg(tu)_4]Cl_2$ (colourless)	m $P2_1/c$ 4	16.580(8) 10.032(4) 10.754(6)	90.2(1)	HgS_4	S 2.536(3,64)	S,S 109.1(1,15.1)	8
β-$[Hg(tu)_4]Cl_2$ (colourless)	m $P2_1/a$ 4	33.45(3) 8.47(2) 6.09(1)	92.2(3)	HgS_4	S 2.549(8,68)	S,S 109.5(3,7.4)	8
α-$Hg(\eta^2\text{-}Pr^i_2NCS_2)_2$ (yellow)	m C_2/c 4	19.468(1) 8.017(1) 14.832(1)	119.18(3)	HgS_4	S 2.445(4,0) 2.645(4,0)	S,S 70.7(2)[c] 122.3(2,4.8) 149.7(3)	10
β-$Hg(\eta^2\text{-}Pr^i_2NCS_2)_2$ (yellow)	m A2/a 4	35.06(2) 9.806(3) 19.78(2)	115.7(1)	HgS_4	S 2.455(-,10) 2.649(-,10)	S,S not given	11
α-$[Hg(\eta^4\text{-}C_{12}H_{24}S_4)]\ (ClO_4)_2$ (colourless)	m C2/c 4	10.033(3) 13.421(4) 15.960(4)	96.48(2)	HgS_4	S 2.597(4,10)	S,S 90.0(2,2.4)	12
β-$[Hg(\eta^4\text{-}C_{12}H_{24}S_4)]\ (ClO_4)_2$ (colourless)	m $P2_1$ 2	13.448(5) 9.538(4) 8.680(2)	95.10(3)	HgS_4	S 2.616(6,53)	S,S 90.0(-,1.7)	13
α-$Hg(PPh_3)_2Cl_2$ (colourless)	or $Pna2_1$ 4	17.782(8) 9.9678(9) 18.283(7)		$HgCl_2P_2$	Cl 2.498(6,7) P 2.518(5,15)	Cl,Cl 106.6(2) P,P 113.5(1) Cl,P 109.0(2,3.9)	14
β-$Hg(PPh_3)_2Cl_2$ (colourless)	m $P2_1/n$ 4	9.907(5) 17.525(9) 19.664(12)	90.12(6)	$HgCl_2P_2$	Cl 2.552(3,7) P 2.470(2,8)	Cl,Cl 110.7(1) P,P 134.1(1) Cl,P 102.8(1,4.2	15

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and thesecond is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Four-membered metallocyclic ring.

2.2. Di- and polymeric mercury compounds

Crystallographic and structural data for di- and polymeric isomers are summarized in Table 2. There are two pairs of dimeric isomers, both of which are monoclinic. In red α-$[Hg(Ph_2Se)_2]_2(ClO_4)_2$ [16] and β-$[Hg(Ph_2Se)_2]_2(ClO_4)_2$ [17], two equivalent $(Ph_2Se)_2Hg$ moieties are held together by a direct Hg(I) – Hg(I) bond, with a length of 2.553(1) Å in the α-isomer and 2.557(8) Å in the β-isomer. Each Hg(I) atom has a trigonal planar arrangement ($HgSe_2Hg'$). The mean Hg – Se bond distances are 2.786 for the α-isomer and 2.752 Å for the β-isomer. The Se – Hg – Se and Se – Hg – Hg' (x2) bond angles are 102.7(1), 104 and 152° in the α-isomer *vs*.. 100.56(5), 116.39(5) and 141.05(5)° in the β- isomer. The α-isomer is somewhat more distorted than the β- isomer.

In α- and β-$(Me_4ttf)_2[Hg(\mu\text{-}Cl)Cl_2]_2$ [18], a pair of chlorine atoms which serve as a bridge between two $HgCl_2$ units form a tetrahedral arrangement around each mercury atom ($HgCl_4$). The α-isomer contains two crystallographically independent molecules. The mean Hg – Cl (terminal) and Hg – Cl (bridge) bond distances (α- *vs*.. β-) are 2.36 and 2.72 Å (molecule 1), 2.40 and 2.63 Å (molecule 2) *vs*.. 2.398 and 2.618 Å, respectively.

The structure of two colorless monoclinic isomers, α-$Hg(Etxan)_2$ [19] and β-$Hg(Etxan)_2$ [20] consists of two-dimensional sheets formed by the mutual bridging of mercury(II) and ethylxanthate anions. Every Hg(II) atom is coordinated to four S atom, each from a separate xanthate moiety (Fig. 1). The coordination geometry around the Hg(II) atom is a very distorted tetrahedron. The $S(2)^1$- Hg - S(3) angle, between the two Hg – S bonds (average lengths of 2.419(4) Å in β- and 2.409(9) Å in α-) is the largest of the six tetrahedral angles: 147.7(1)° (in β-) and 148.8(3)° (in α-). The S(1)

Table 2. Crystallographic and Structural Data for Di- and Polymeric Mercury Complexes – Pairs of Distortion Isomers[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Hg-L [Å]	Hg-Hg [°] Hg-L-Hg [°] μ'L-Hg-μL [°]	L-Hg-L [°]	Ref
α-$[Hg(Ph_2Se)_2]_2(ClO_4)_2$ (red)	m $P2_1/n$ 2	11.609 14.462 14.391	98.2	$HgSe_2Hg'$	Se[b] 2.653(2) 2.919(2)	2.533(1)	Se,Se[b] 102.7(1) Se,Hg 104 152	16
β-$[Hg(Ph_2Se)_2]_2(ClO_4)_2$ (red)	m $P2_1/n$ 2	13.910(8) 14.575(9) 12.109(6)	92.6	$HgSe_2Hg'$	Se 2.701(1) 2./802(1)	2.5579(8)	Se,Se 100.56(5) Se,Hg 116.39(5) 141.05(5)	17
α-$(Me_4ttf)_2[Hg(\mu\text{-}Cl)Cl_2]_2$ (not given)	m $P2_1/b$ 8	12.518(5) 20.298(7) 14.125(6)	112.18(3)	$HgCl_4$	Cl 2.36(-,0) μCl 2.72(-,5)	not given 90 90	Cl,Cl not given Cl,μCl 101(-,2)	18
β-$(Me_4ttf)_2[Hg(\mu\text{-}Cl)Cl_2]_2$ (not given)	m $P2_1/n$ 4	15.298(5) 13.776(9) 6.881(3)	89.95(3)	$HgCl_4$	Cl 2.398(5,11) μCl 2.618(4,21)	not given 91.3(2) 88.7(2)	Cl,Cl 123.6(2) Cl,μCl 108.4(2,4.6)	18
α-$Hg(Etxan)_2$ (colourless)	m $P2_1$ 2	9.904(2) 6.903(7) 9.104(8)	100.21(3)	HgS_4	S 2.409(9,96) 2.846(9,97)		S,S 97.6(3,15.8) 148.8(3)	19
β-$Hg(Etxan)_2$ (colourless)	m $P2_1/c$ 4	9.300(2) 6.693(2) 19.585(9)	100.94(3)	HgS_4	S 2.419(4,2) 2.822(4,33)		S,S 98.5(1,14.2) 147.7(1)	20

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

[b] The chemical identity of the coordinated atom or ligand is specified in these columns.

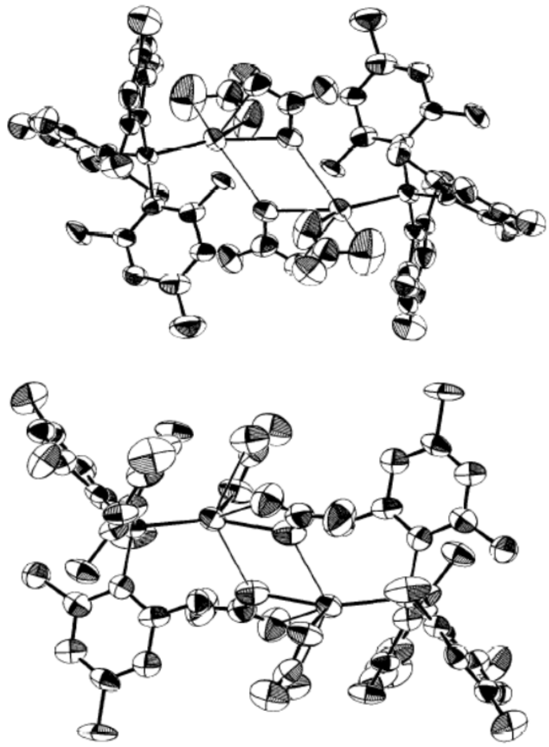

Figure 2. Structure of two $[Hg(Pmes_3)(NO_3)_2]_2$ [40]

– Hg -S(4)' angle formed by two long Hg – S bonds (lengths of 2.822(4) Å in β- and 2.846(9) Å in α-) is the smallest: 84.3(1)° in β- and 81.8(3)° in α-. The tetrahedrons in the α- isomer are somewhat less squeezed than those in the β- isomer.

2.2.1. Monomeric mercury compounds

There are nineteen derivatives, three [21-23] of which contain four crystallographicaly independent molecules, one [24] which contains three such molecules, and the remainder [23,25-38] contain two such molecules. The crystallographic and structural data are gathered in Table 3. In all three derivatives which contain four crystallographically independent molecules, each Hg(II) atom is doubly coordinated. In two yellow compounds, $[Hg\{Me_2N(CH_2)_3S\}_2](PF_6)_2$ [21] and $Hg(C_{11}H_{14}OS)_2$ [22], two coordination sites are occupied by unidentate ligands, which permits a linear arrangement to be adapted. The S – Hg – S angles are 176.1(3)° (av.) [21] and 178.2(2)° (av.) [22]. The mean Hg – S bond distance of 2.336 Å for all four molecules in the former [21] is somewhat smaller than that found in the latter (2.345 Å). In colourless $Hg\{(EtO)_2PO\}Cl$ [23] two unidentate ligands create a linear arrangement around each Hg(II) atom (HgClP). Noticeably, the mean Cl - Hg – P bond angles are 169.1(6)° (molecule 1), 177.1(6)° (molecule 2), 172.3(6)° (molecule 3) and 174.7(9)° (molecule 4).

In yellow $[Cr(en)_3]_2[HgCl_4]_3$ [24], which contains three crystallographically independent molecules, each Hg(II) atom is tetrahedrally coordinated ($HgCl_4$) with different degrees of distortion. The mean Hg – Cl bond distances and the deviation of the Cl – Hg – Cl bond angles from the ideal (109.5°) are: 2.472 Å and 1.1° (molecule 1), 2.513 Ǻ and 2.7° (molecule 2) and 2.515 Å and 2.9° (molecule 3).

The remaining derivatives contain two crystallographically independent molecules. In five derivatives, $Hg(sac)_2$ [25], $[HgCl_2]•C_9H_{16}O$ [26], $(NHMe_3[HgCl_2]Cl$ [27], $(bzNH_3)[HgCl_2]Cl$ [28] and $Hg(Ph_3Ge)_2$ [29], two coordination sites are occupied by unidentate ligands, which permits the linear arrangement to be adopted: HgN_2 [25], $HgCl_2$ [26-28] and $HgGe_2$ [29]. The twins of independent molecules differ from each other by their degrees of distortion (Table 3). The mean Hg – L bond distance increases with the covalent radius of the donor atom in the following order: 2.05 Å (N, covalent radius of 0.75 Å) < 2.305 Å (Cl, 0.99 Å) < 2.528 Å (Ge, 1.22 Å).

There are another four colorless derivatives, which contain two crystallographically independent $[HgX_3]^-$ anions (X = Cl [30, 31] or Br [31, 32]). From a geometrical perspective, these are examples which contain Hg(II) atoms in a trigonal – planar (Y – shaped) form with different degrees of distortion (Table 3). The mean Hg – Cl bond distances and deviation of the Cl – Hg – Cl bond angles from the ideal angle of 120° (molecule 1 *vs.* molecule 2) are: 2.410 Å and 2.0° *vs.* 2.390 Å and 6.0° [30]; 2.409 Å and 0.9° *vs.* 2.412 Å and 4.5° [31]. For $\{HgBr_3\}$ derivatives, the values are 2.544 Å and 3.5° *vs.* 2.544 Å and 5.2° [31], 2.52 Å and 4.0° *vs.* 2.52 Å and 6.8° [32].

The structure of orange $(C_{15}H_{11}S_2)_2[HgCl_4]$ [33] contains well separated $C_{15}H_{11}S_2^+$ cations and $[HgCl_4]^{2-}$ anions. Each Hg(II) atom has a tetrahedral environment, with mean Hg – Cl bond distances of 2.476 Å (molecule 1) and 2.418 Å (molecule 2). The deviations of the Cl – Hg – Cl bond angles from the ideal (109.5°) are 12.5° and 7.0°, respectively.

In colorless $Hg(\eta^2\text{-}dmv)_2$ [34], two heterobidentate donor atoms, O and N, belonging to the dmv ligands create a tetrahedral geometry about each Hg(II) atom (HgO_2N_2) with different degrees of distortion (Table 3). Six "tetrahedral angles" can be divided into two groups: three (N – Hg – N (x1) and O – Hg – N (x2)) angles, with values (molecule 1 *vs.* molecule 2) of 148(1) and 136(1)° (av) *vs.* 147(1) and 130(1)° (av), and the remaining three (O – Hg –O (x1) and O – Hg – N (x2)) angles with values of 88(1) and 72(1)° (av) *vs.* 88(1) and 73(1)° (av). The latter (O – Hg – N) angles, which are part of the four-membered metallocycles are the closest to each other, as expected.

In another colourless derivative, $Hg(\eta^2\text{-}C_{11}H_{16}N_4)(CN)_2$ [35], a tetrahedral arrangement around each Hg(II) atom is formed by one homo-bidentate (N,N') ligand and two unidentate CN groups (HgN_2C_2). The mean Hg –N and Hg – C bond distances (molecule 1 *vs.* molecule 2) are 2.63(1) Å and 2.06(2) Å *vs.* 2.46(1) Å and 2.10(2) Å . Five of the six "tetrahedral angles" fall in the range 95.5 – 163.1° and 100.9 -148.2°, while the angle which is part of the five-membered metallocycles (N – Hg – N) is significantly smaller (71.7(4) *vs.* 79.0(5)°).

Two heterobidentate (N,S) 2-methyl ligands in yellow $Hg(\eta^2\text{-}Mequs)_2$ [36] create a very distorted tetrahedral arrangement around each Hg(II) atom (HgN_2S_2). The mean Hg – N and Hg – S bond distances (molecule 1 *vs.* molecule 2) are: 2.586 and 2.349 Å *vs.* 2.543 and 2.371 Å . Two of the six "tetrahedral angles", which are part of the five-membered metallocycles (N – Hg – S) are 79.5(1) *vs.* 79.1(1)°. The remaining four angles (N – Hg – N, S – Hg – S and N – Hg – S (x2)) fall in a wide range of 88.8(3) – 161.44(5)° *vs.* 98.5(3) – 156.4(2)°.

Two pairs of unidentate ligands in colorless $Hg\{P(CH_2CH_2CN)_3\}_2Cl_2$ [37] create a tetrahedral arrangement ($HgCl_2P_2$). The mean Hg – Cl and Hg – P bond distances (molecule 1 *vs.* molecule 2) are 2.615 and 2.451 Å *vs.* 2.636 and 2.431 Å . The L – P – L bond angles increase with larger covalent radii of the coordinated atoms in the sequence: 95.0(3)° (Cl – Hg – Cl) < 101.2(4)°(av) (Cl – Hg – P) < 146.9(3)° (P – Hg – P) (in molecule 1) and 98.1(3)° < 98.1(3)° < 153.9(3)° (in molecule 2).

In colorless $Hg(\eta^2\text{-}phen)(CCl_3)(Cl)$ [38], a tetrahedral arrangement around Hg(II) is formed with the chromophore, HgN_2CCl. The mean Hg – L bond distance (molecule 1 *vs.* molecule 2) takes on the following values, in increasing order: 2.12 Å (C) < 2.30 Å (Cl) < 2.65 Å (av) (N) *vs.* 2.07 Å < 2.32 Å < 2.57 Å . The former molecule is less crowded than the latter,with the sum of all four Hg – L bond distances measuring 9.72 *vs.* 9.53 Å .

2.2.2 Di- and polymeric mercury compounds

There are six dimers [39-44] and three polymers of mercury compounds [45-47] that contain two crystallographically independent molecules within the same crystal. Their crystallographic and structural parameters are listed in Table 4.

In colorless triclinic $[Hg(\mu\text{-}urea)Cl_2]_2$ [39], a pair of two oxygen ligands (urea) serve as bridges between two equivalent $HgCl_2$ units. Each Hg(II) atom has a tetrahedral arrangement (HgO_2Cl_2). The mean Hg – O

Table 3. Crystallographic and Structural Data for Monomeric Mercury Complexes – Independent molecules (Distortion Isomers)[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Hg-L [Å]	L-Hg-L [°]	Ref
A: Four Independent Molecules							
$[Hg\{Me_3N(CH_2)_3S\}_2]. (PF_6)_2$	tr	15.097(4)	71.74(1)	HgS_2	S^b 2.340(11,11)	S,S^b 178.9(3)	21
(yellow)	P-1	18.968(5)	68.50(1)	HgS_2	S 2.352(11,19)	S,S 175.4(3)	
	2	20.365(6)	75.46(2)	HgS_2	S 2.325(9,4)	S,S 175.6(3)	
				HgS_2	S 2.327(9,0)	S,S 174.8(4)	
$Hg(C_{11}H_{19}OS)_2$	m	27.699(9)		HgS_2	S 2.344(6,7)	S,S 178.4(2)	22
(yellow)	$P2_1/c$	15.404(4)	114.67(2)	HgS_2	S 2.366(7,13)	S,S 177.9(2)	
	16	28.082(7)		HgS_2	S 2.337(6,8)	S,S not given	
				HgS_2	S 2.333(6,7)	S,S not given	
$Hg\{(EtO)_2PO\}Cl$	m	17.43		HgClP	Cl 2.37(2)	Cl,P 169.1(6)	23
(colourless)	Cc	17.47	90.15		P 2.40(2)		
	16	12.59		HgClP	Cl 2.37(2)	Cl,P 177.1(6)	
					P 2.31(2)		
				HgClP	Cl 2.38(2)	Cl,P 172.3(6)	
					P 2.38(2)		
				HgClP	Cl 2.31(3)	Cl,P 174.7(9)	
					P 2.36(2)		
B: Three Independent Molecules							
$[Cr(en)_3]_2[HgCl_4]_3$	tr	11.250(2)	81.86(1)	$HgCl_4$	Cl 2.472(4,6)	Cl,Cl 109.5(1,1.1)	24
(yellow)	P-1	11.245(1)	72.25(1)	$HgCl_4$	Cl 2.513(4,9)	Cl,Cl 109.8(1,2.7)	
	2	17.421(4)	90.01(1)	$HgCl_4$	Cl 2.515(4,9)	Cl,Cl 109.7(1,2.9)	
C: Two Independent Molecules							
$Hg(sac)_2$	tr	14.460(9)	106.56(2)	HgN_2	N 2.05(2,1)	N,N 167(1)	25
(colourless)	P-1	13.054(10)	94.96(3)				
	4	10.471(10)	111.09(2)	HgN_2	N 2.05(1,2)	N,N 175(1)	
$[HgCl_2]C_9H_{16}O$	m	7.588(2)		$HgCl_2$	Cl 2.28(1,0)	Cl,Cl 177.2(5)	26
(colourless)	$P2_1/c$	12.214(3)	96.26(2)				
	8	25.148(6)		$HgCl_2$	Cl 2.27(1,1)	Cl,Cl 177.5(5)	
$(NHMe_3)[HgCl_2]Cl$	m	14.296(1)		$HgCl_2$	Cl 2.312(2,0)	Cl,Cl 180.0	27
(colourless)	I2/c	8.835(2)	97.31(2)				
	8	14.622(5)		$HgCl_2$	Cl 2.389(2,0)	Cl,Cl 180.0	
$(bzNH_3)[HgCl_2]Cl$	m	17.370(5)		$HgCl_2$	Cl 2.282(4,7)	Cl,Cl 166.6(2)	28
(colourless)	C2/c	6.891(2)	104.06(2)				
	8	24.735(7)		$HgCl_2$	Cl 2.300(4,2)	Cl,Cl 169.9(1)	
$Hg(Ph_3Ge)_2$	tr	7.660(2)	79.04(1)	$HgGe_2$	Ge 2.514(2,0)	Ge,Ge 178.65(5)	29
(not given)	P1	16.562(3)	81.65(2)				
	4	19.220(4)	81.68(2)	$HgGe_2$	Ge 2.543(1,0)	Ge,Ge not given	
$(NMe_4)[HgCl_3]$	m	8.70(1)		$HgCl_3$	Cl 2.410(3,40)	Cl,Cl 119.9(9,2.0)	30
(colourless)	$P2_1$	16.02(2)	93.5(5)				
	4	7.47(2)		$HgCl_3$	Cl 2.390(2,20)	Cl,Cl 119.9(9,6.0)	
$(NMe_4)[HgCl_3]$	m	8.848(4)		$HgCl_3$	Cl 2.409(8,22)	Cl,Cl 119.8(3,9)	31
(colourless)	P1	15.650(8)	93.58(4)				
	4	7.559(5)		$HgCl_3$	Cl 2.412(9,20)	Cl,Cl 119.9(3,4.5)	
$(NMe_4)[HgBr_3]$	m	9.104(5)		$HgBr_3$	Br 2.544(3,35)	Br,Br 119.1(1,3.5)	31
(colourless)	P1	15.976(10)	93.54(6)				
	4	7.912(6)		$HgBr_3$	Br 2.540(4,32)	Br,Br 119.2(1,5.2)	
$(NMe_4)[HgBr_3]$	m	9.05(2)		$HgBr_3$	Br 2.52(2,4)	Br,Br 118.4(8,4.0)	32
(colourless)	$P2_1$	15.90(5)	93.6(2)				
	4	7.94(2)		$HgBr_3$	Br 2.52(2,3)	Br,Br 118.5(8,6.8)	
$(C_{15}H_{11}S_2)[HgCl_4]$	tr	16.26(1)	94.5(1)	$HgCl_4$	Cl 2.476(4,47)	Cl,Cl 109.6(2,12.5)	33
(orange)	P-1	22.31(1)	82.8(1)				
	4	17.12(1)	99.8(1)	$HgCl_4$	Cl 2.481(4,54)	Cl,Cl 109.5(1,7.0)	
$Hg(\eta^2\text{-dmv})_2$	tr	16.635(2)	98.74(2)	HgO_2N_2	O 2.45(1,2)	O,O 88(1)	34
(colourless)	P-1	11.765(2)	102.99(2)		N 2.13(1,1)	N,N 148(1)	
	4	9.288(2)	108.13(1)			O,N 72(1,2)[c]	
						136(1,3)	
				HgO_2N_2	O 2.45(1,3)	O,O 88(1)	
					N 2.14(1,1)	N,N 147(1)	
						O,N 73(1,0)[c]	
						130(1,11)	

Continued **Table 3.** Crystallographic and Structural Data for Monomeric Mercury Complexes – Independent molecules (Distortion Isomers)[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Hg-L [Å]	L-Hg-L [°]	Ref
$Hg(\eta^2\text{-}C_{11}H_{16}N_4)(CN)_2$ (colourless)	or $Pb2_1/a$ 8	22.224(7) 17.746(7) 8.243(5)		HgN_2C_2	η^2N 2.63(1,8) NC 2.06(2,3)	N,N 71.7(4)^c C,C 163.1(9) N,C 96.8(7,1.3)	35
				HgN_2C_2	η^2N 2.46(1,6) NC 2.10(2,4)	N,N 79.0(5)^c C,C 148.2(8) N,C 102.2(7,1.3)	
$Hg(\eta^2\text{-}2\text{-}Mequs)_2$ (yellow)	m $P2_1/b$ 8	22.978(3) 19.427(6) 8.444(4)	 91.80(4)	HgN_2S_2	N 2.586(11,22) S 2.349(7,15)	N,N 88.8(3) S,S 161.44(5) N,S 79.5(1,6)^c 117.8(4,3.2)	36
				HgN_2S_2	N 2.543(19,45) S 2.371(7,3)	N,N 98.5(3) S,S 156.4(2) N,S 79.1(5,2.2)^c 116.8(5,1.4)	
$Hg\{P(CH_2CH_2CN)_3\}_2Cl_2$ (colourless)	m $P2_1/c$ 8	25.728(8) 8.627(2) 24.482(8)	 115.14(1)	$HgCl_2P_2$	Cl 2.615(1,7) P 2,451(12,1)	Cl,Cl 95.0(3) P,P 146.9(3) Cl,P 101.2(4,8.9)	37
				$HgCl_2P_2$	Cl 2.636(11,33) P 2.431(7,20)	Cl,Cl 98.1(3) P,P 153.9(3) Cl,P 98.1(3,8.5)	
$Hg(\eta^2\text{-}phen)(CCl_3)Cl$ (colourless)	tr P-1 4	14.05(2) 8.44(1) 15.53(2)	119.8(2) 85.2(2) 107.7(2)	HgN_2CCl	η^2N 2.65(-,3) C 2.12 Cl 2.30	C,Cl 155	38
				HgN_2CCl	η^2N 2.57(-,4) C 2.07 Cl 2.32	C,Cl 145	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

[b] The chemical identity of the coordinated atom or ligand is specified in these columns.

[c] Four-membered metallocyclic ring.

Table 4. Crystallographic and Structural Data for Di- and Polymeric Mercury Complexes – Independent molecules (Distortion Isomers)[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Hg-L [Å]	Hg-Hg [°] Hg-L-Hg [°] μ'L-Hg-μL [°]	L-Hg-L [°]	Ref
A : Dimers								
$[Hg(\mu\text{-}urea)Cl_2]_2$	tr P-1 2	8.56(1) 11.335(5) 6.758(3)	103.4(1) 97.4(1) 75.5(1)	HgO_2Cl_2	μO^b 2.647(6,32) Cl 2.308(3,7)	not given 101.5(5) 77.5(4)	Cl,Cl^b 168.0(1) Cl,O 94.5(4,2.9)	39
				HgO_2Cl_2	μO 2.679(6,13) Cl 2.305(3,6)	not given 99.1(5) 80.9(1)	Cl,Cl 171.3(1) Cl,O 93.3(4,2.8	
$[Hg(NO_3)_2(Pmes_3)]_2$ (colourless)	m $P2_1/c$ 4	19.940(3) 17.588(2) 16.403(2)	 100.3(2)	HgO_5P	O 2.180(12) O 2.736(11,161) μO 2.639(9,216) P 2.395(3)	not given 118.6(2) 60.4(4)	O,O 44.7^c-120.8(4) O,P 103.0-146.3(3)	40
				HgO_5P	O 2.342(9) O 2.654(11,17) μO 2.535(8,278) P 2.418(3)	not given 119.1(2) 60.9(4)	O,O 50.3^c-116.0(3) O,P 108.1-148.7(2)	
$[Hg(NO_3)_2(SAsmes_3)]_2$ (white)	m $P2_1/c$ 4	20.001(2) 17.591(5) 16.553(2)	 99.991(6)	HgO_5As	O 2.20(2) O 2.73(2,18) μO 2.60(2,19) As 2.476(3)	not given 120(1) 60.1(6)	O,O 45.3^c-125.0(7) O,As 107.3(6,6.4) 138.2(5,3.9)	41
				HgO_5As	O 2.39(2) O 2.64(2,2) μO 2.50(2,22) As 2.482(3)	not given 115(1) 63.8(6)	O,O 50.5^c-118.9(7) O,As 114.1(4,7.9) 137.8(4,10.8)	
$[Hg(\mu\text{-}Cl)Cl(Pcy_3)]_2$ (white)	tr P-1 4	10.843(2) 14.118(2) 14.792(3)	94.76(1) 80.38(1) 110.62(2)	$HgCl_3P$	Cl 2.391(5) μCl 2.653(4,12) P 2.416(3)	3.773(1) 90.6(1) 89.4(1)	Cl,μCl 98.0(2,2.8) Cl,P 139.6(2) μCl,P 110.3(1,1.6)	42
				$HgCl_3P$	Cl 2.413(3) μCl 2.691(4,89) P 2.412(3)	3.937(1) 94 86.0(1)	Cl,μCl 103.8(1,2.3) Cl,P 132.0(1) μCl,P 116.1(1,10.3)	

Continued **Table 4.** Crystallographic and Structural Data for Di- and Polymeric Mercury Complexes – Independent molecules (Distortion Isomers)[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Hg-L [Å]	Hg-Hg [°] Hg-L-Hg [°] μ'L-Hg-μL [°]	L-Hg-L [°]	Ref
[Hg(μ-Cl)Cl(dchptc)]$_2$. CH$_2$Cl$_2$ (colourless)	tr P-1 2	10.668(4) 14.978(3) 16.834(4)	111.80(2) 101.03(2) 91.06(2)	HgCl$_3$P	Cl 2.348(8) μCl 2.705(7,15) P 2.393(7)	3.850(2) 90.8(2) 89.2(2)	Cl,μCl 101.0(3,1) Cl,P 142.9(3) μCl,P 105.1(2.2.0)	43
				HgCl$_3$P	Cl 2.352(8) μCl 2.732(7,17) P 2.400(7)	4.043(2) 95.9(2) 84.5(2)	Cl,μCl 98.9(3,4) Cl,P 144.8(3) μCl,P 106.9(2,1.1)	
(bitt){Hg$_2$I$_6$] (yellow)	m P2$_1$/c 4	12.574(3) 15.717(4) 14.560(4)	90.83(4)	HgI$_4$	I 2.692(4,10) μI 2.924(4,27)	not given 86.4(2) 93.6(2)	I,I 118.5(2,0) I,μI 110.5(2,4.4)	44
				HgI$_4$	I 2.683(4,14) μI 2.962(4,82)	not given 86.4(2) 93.6(2)	I,I 126.7(2,0) I,μI 107.6(2,5.8)	
B : Polymers								
[Hg(μ-SMe)(4-Mepy)(η^2-MeCOO)]$_n$ (yellow)	m P2$_1$/a 4	16.617(9) 7.271(3) 20.476(2)	16.617(9) 7.271(3) 20.476(2)	HgO$_2$S$_2$N	O 2.55(2,11) μS 2.443(7,29) N 2.49(2)	not given 108.6(3) 141.3(2)	O,O 51.7(6)[c] O,S 101.0(5,12.8) O,N 83.2; 128.1(6) S,N 100.6(5,14.3)	45
				HgO$_2$S$_2$N	O 2.59(2,22) μS 2.466(7,7) N 2.41(2)	not given 106.8(2) 136.1(2)	O,O 149.9(6)[c] O,S 100.3(4,13.2) O,N 85.8; 135.3(6)	
(C$_5$H$_6$N$_5$)[HgCl$_3$].1.5H$_2$O (colourless)	m P2$_1$/c 8	23.99(1) 4.245(2) 25.98(1)	117.58(7)	HgCl$_6$	Cl 2.357(5,21) μCl 2.78895,27) μ$_3$Cl 3.252(5,6)		Cl,Cl 90.0(1,9.2)	46
				HgCl$_6$	Cl 2.348(5,4) μCl 2.815(5,30) μ$_3$Cl 3.201(5,16)		Cl,Cl 90.0(1,7.9)	
Hg(Pr^{i}OCS$_2$)$_2$ (yellow)	m P2$_1$/c 8	14.226(8) 9.806(8) 21.410(10)	100.13(10)	HgS$_4$	S 2.462(10,20) 2.752(10,132)		S,S 66.8(3)[c] 109.6(3,8.3) 143.2(3)	47
				HgS$_4$	S 2.490(9,13) 2.679(10,62)		S,S 67.1(3)[c] 108.6(3,17.6)	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

[b] The chemical identity of the coordinated atom or ligand is specified in these columns.

[c] Four-membered metallocyclic ring.

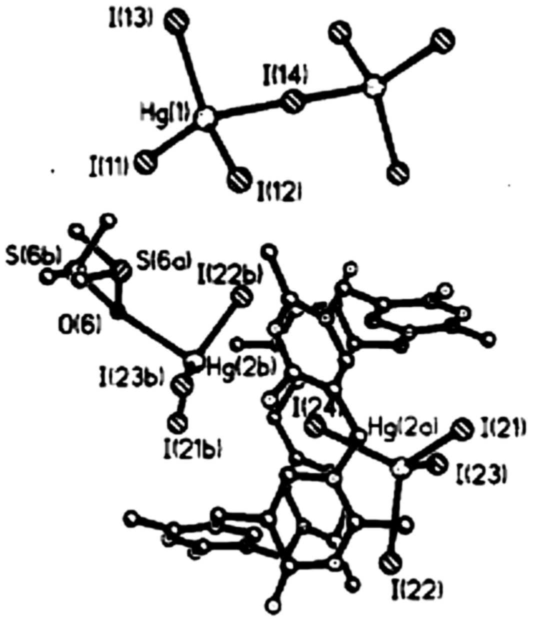

Figure 3. Structure of [24 - pyridinium - crown - 6]$^{6+}$, [HgI$_4$]$^{2-}$, HgI$_3$(dmso)]- and [Hg$_2$(μ-I)I$_6$]$^{3-}$ [52]

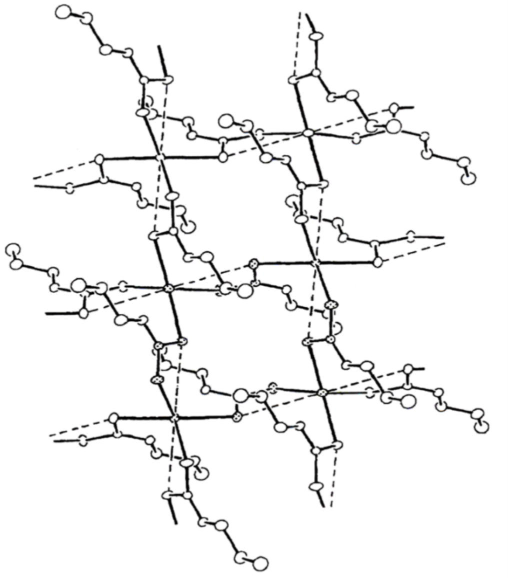

Figure 4. Structure of [Hg(η^2-Pr$_2$OCS$_2$)$_2$]$_n$ [61]

(bridge) and Hg – C (terminal) bond distances (dimer 1 *vs.* dimer 2) are 2.647 and 2.308 Å *vs.* 2.679 and 2.305 Å. The L – Hg – L bond angles have values in the following order: 77.5(4)° (O – Hg – O) < 94.5(4)° (av) (O – Hg – Cl) < 168.0(1) (Cl – Hg – Cl) (in dimer 1) and 80.9(1)° < 93.3(4)° (av) < 171.3(1)° (in dimer 2).

The mean Hg – O – Hg bond angles are 101.5(3)° and 99.1(5)° for dimer 1 and dimer 2, respectively.

There are two isostructural derivatives $[Hg(NO_3)_2(Emes_3)]_2$ (E = P [40] or As [41]) which contain pairs of dimers. Each Hg(II) atom has a coordination number of six (HgO_5E). The structure of both $[Hg(NO_3)_2(Pmes_3)]_2$ dimers is shown in Fig. 2. In both dimers, two $Hg(\eta^2\text{-}O_2NO)(Pmes_3)$ moieties are bridged by two $\mu\text{-}ONO_2$ groups and form a central Hg_2O_2 ring, with the mean Hg – O (bridge) distances of 2.639(9) Å for dimer 1 and 2.535(8) Å for dimer 2. Each bidentate ($\eta^2\text{-}O_2NO$) group is asymmetrically coordinated around every Hg(II) atom with the following mean values (dimer 1 *vs.* dimer 2): 2.180 and 2.736 Å *vs.* 2.342 and 2.645 Å. The six-fold coordination at each Hg(II) is completed by the $Pmes_3$ ligand (Hg– P = 2.395(3) and 2.418(3) Å) (HgO_5P) (Table 4).

In $[Hg(NO_3)_2(Asmes_3)]_2$ [41], the mean Hg – O (bridge), Hg – O (short and longer) and Hg – As bond distances (dimer 1 *vs.* dimer 2) are: 2.60(2), 2.20(2), 2.73(2) and 2.476(3) Å *vs.* 2.50(2), 2.39(2),2.64(2) and 2.482(3) Å.

Another two isostructural, triclinic derivatives are $[Hg(\mu\text{-}Cl)(Cl)(PL)]_2$ (PL = Pcy_3 [42] or dchptc [43]). Each of them contains two crystallographically independent dimers. In each of the dimers, two Hg(Cl)(PL) moieties are held together by a pair of chlorine atoms. Each Hg(II) atom is tetrahedrally coordinated ($HgCl_3P$). The mean Hg – L bond distance takes the following values, sorted in increasing order (dimer 1 *vs.* dimer 2): 2.391(5) Å (Cl) < 2.416(3) Å (P) < 2.653(4) Å (μ-Cl) *vs.* 2.412(3) Å (P) < 2.413(3) Å (Cl) < 2.691(4) Å (μ-Cl). The Hg-Hg separations of 3.773(1) *vs.* 3.973(1) Å rule out a direct metal-metal bond.

The structure of the yellow monoclinic derivative [44] contains well-separated $[bitt]^+$ cations and $[Hg_2I_6]^{2-}$ anions. In the anions, two equivalent HgI_2 units are bridged by a pair of iodine atoms. Each Hg(II) atom has a tetrahedral arrangement (HgI_4). The mean Hg – I (terminal) and Hg – I (bridge) bond distances are 2.692(4) and 2.924(4) Å *vs.* 2.683(4) and 2.962(4) Å. The six "tetrahedral angles" fall in the range of 93.6(2) – 118.5(2) ° *vs.* 93.6(2) – 126.7(2)°.

In yellow monoclinic $[Hg(\mu\text{-}SMe)(\eta^2\text{-}MeCOO)(4\text{-}Mepy)]$ [45], the $Hg(\eta^2\text{-}MeCOO)(4\text{-}Mepy)$ moieties are connected by μ-SMe ligands and form a polymeric chain, as follows :$\{\text{-}S(Me)\text{-}Hg(\eta^2\text{-}MeCOO)(4\text{-}Mepy)\text{-}_n.S(Me)\text{-}\}$Each Hg(II) atom has a square-pyramidal geometry (HgO_2S_2N) with the N atom in the apical position. The mean Hg – L bond distance (molecule 1 *vs.* molecule 2) are ordered as follows: 2.443(7) Å (μ-S) < 2.49(2) Å (N) < 2.55(2) Å (O) *vs.* 2.41(2) Å (N) < 2.466(7) Å (μ-S) < 2.59(2) Å (O). The Hg – S – Hg and μS – Hg -μS angles are 108.6(3) and 141.3(2)° *vs.* 106.8(2) and 136.1(2) (Table 4).

The structure of the colorless monoclinic derivative [46] consists of well separated $[C_5H_6N_5]^+$ cations and $[HgCl_3]^-$ anions. Two crystallographically independent molecules are present. In the anions, chlorine atoms serve as bridges between $\{HgCl_2\}$ units and form a polymeric chain. Each Hg(II) atom is pseudo-octahedrally coordinated ($HgCl_6$). The mean Hg–Cl bond distances (molecule 1 *vs.* molecule 2) are ordered as follows: 2.357(5) Å (Cl) < 2.788(5) Å (μ-Cl) < 3.252(5) Å (μ_3-Cl) *vs.* 2.348(5) Å (Cl) < 2.815(5) Å (μ-Cl) < 3.201(5) Å (μ_3-Cl).

In yellow monoclinic $Hg(Pr^iOCS_2)_2$ [47], a bidentate Pr^iOCS_2 serves as diatomic bridge between Hg(II) atoms a form a polymeric chain. Each Hg(II) atom has a tetrahedral geometry (HgS_4). The mean Hg – S bond distances are 2.607 Å (molecule 1) and 2.585 Å (molecule 2).

Inspection of the data in the series of distortion isomers (Tables 1 – 4) reveals that 16 exist in two isomeric forms, 12 in monomeric forms [5-15] (Table 1), 4 in dimeric forms [16-18] and 2 in polymeric forms [19,20] (Table 2). There are three examples [21-23] that contain four crystallographically independent molecules, one derivative [24] that contains three such molecules and the remainder [25-47] contain two such molecules (Tables 3 and 4). They belong to three crystal classes: orthorhombic (x2) < triclinic (x12) < monoclinic (x32). In these isomers, mercury exists in its +1 oxidation state [16,17]; in the remaining derivatives, mercury exists in its +2 oxidation state.

In α- and β-$[Hg(Ph_2Se)_2]_2$, each Hg(I) atom has a trigonal planar arrangement ($HgSe_2Hg'$) with a direct Hg(I) – Hg(I) bond length of 2.553(1) Å (α-) [16] and 2.5579(8) Å (β-) [17]. The sum of Hg(I) – Se (x2) and Hg – Hg bond distances in α- is 8.061 Å and 8.125 Å in the β- isomer.

Coordination numbers around Hg(II) atoms range from two to six. In general, the sum of Hg(II) – L bond distances increases with the sum of the covalent radii of the coordinated atoms. In the series of two coordinated species (HgX_2) the sum of Hg – X(x2) bond distances increases with the covalent radius of X (isomer 1 *vs.* isomer 2), as follows: 4.09 *vs.* 4.10 Å (N_2

1.50 Å) < 4.58 *vs.* 4.70 Å (Cl_2, 1.98 Å) < 4.658 *vs.* 4.698 Å (S_2, 2.04 Å) < 4.66 *vs.* 4.77 Å (ClP, 2.05 Å) < 5.028 *vs.* 5.086 Å (Ge_2, 2.44 Å). In the series of three coordinated species (HgX_3), the order is: 7.199 *vs.* 7.233 Å (Cl_3, 2.97 Å) < 7.469 *vs.* 7.471 Å (S_2P, 3.10 Å) < 7.590 *vs.* 7.569 Å (Br_3, 3.42 Å). In the series of four coordinated species the order is: 9.16 *vs.* 9.18 (O_2N_2, 2.96 Å) < 9.120 *vs.* 9.380 Å (N_2C_2, 3.04 Å) < 9.530 *vs.* 9.992 Å (Cl_4, 3.96 Å) < 9.882 *vs.* 10.088 Å (Cl_2P_2, 4.10 Å) < 10.237 *vs.* 10.277 Å (S_4, 4.08 Å) (monomeric); and 9.910 *vs.* 9.968 Å (O_2Cl_2, 3.44 Å) < 10.045 *vs.* 10.163 Å (Cl_4, 8.96 Å) < 10.132 *vs.* 10.241 Å (Cl_3P, 4.03 Å) < 10.410 *vs.* 10.470 Å (S_4, 4.08 Å) < 11.232 *vs.* 11.290 Å (I_4, 5.32 Å) (di- and polymeric). In the series of five coordinated species, the values are: 12.476 *vs.* 12.500 Å (O_2S_2N 4.25 Å). In the series of six coordinated species, the order is: 15.138 *vs.* 15.336 Å (O_5As, 4.95 Å) < 16.728 *vs.* 16.794 Å (Cl_6, 5.94 Å).

The mean value of the Hg(II) – L bond distance increases with the covalent radius of the coordinated atom as well as with the coordination number around mercury(II) as expected, in the following order:

2-coordinate: 2.05 Å (N, 0.75 Å) < 2.326 Å (Cl, 0.99 Å) < 2.340 Å (S, 1.02 Å) < 2.363 Å (P, 1.06 Å) (monomers)

3-coordinate: 2.405 Å (Cl, 0.99 Å) < 2.461 Å (PL, 1.06 Å) < 2.505 Å (SL, 1.02 Å < 2.530 Å (Br, 1.14 Å) (monomers);

4-coordinate: 2.065 Å (CL, 0.77 Å) < 2.467 Å (PL, 1.06 Å) < 2.522 Å (Cl, 0.99 Å) < 2.564 Å (SL, 1.02 Å) (monomers);

2.364 Å (Cl) < 2.450 Å (PL) < 2.609 Å (SL) < 2.663 Å (μ-OL) < 2.678 Å (μ-Cl) < 2.687 Å (I, 1.33 Å) < 2.943 Å (μ-I) (dimers, polymers)

5-coordinate: 2.45 Å (NL) < 2.455 Å (μ-SL) < 2.55 Å (O^2L)

6-coordinate: 2.278 Å (O^2L) < 2.351 Å (Cl) < 2.406 Å (PL) < 2.480 Å (AsL) < 2.568 Å (μ-OL) < 2.800 Å (μ-Cl) < 3.226 Å (μ_3-Cl)

As can be seen, homo- as well as heterobidentate ligands form metallocyclic rings, with varying atoms and numbers of atoms in the ring. The mean chelating L – Hg – L bond angles take on the following values, in increasing order (less squeezed isomer *vs.* more squeezed isomer) : 46.6° *vs.* 50.8° (-OCO-) < 66.8° *vs.* 70.7° (-SCS-) < 72° *vs.* 73° (-OC$_2$N-) < 79.1° *vs.* 79.5° (-NC$_2$S-) < 89.3° *vs.* 91.2° (-SC$_3$S-).

3. Polymerisation Isomerism

There are thirteen derivatives [23,48-58] which belong to the class of polymerization isomers. Their crystallographic and structural parameters are gathered in Table 5. Eight derivatives contain monomers and dimers within the same crystal. Three of them, $[HgCl_2][Hg(\mu\text{-dmso})Cl_2]_2$ [48], $[HgCl_2]_2[Hg(\mu\text{-bet})Cl_2]_2$ [49] and $[HgCl_2]_2[Hg(\mu\text{-pyac})Cl_2]_2$ [49], contain $\{HgCl_2\}$ monomers and $[Hg(\mu\text{-OL})Cl_2]_2$ dimers. In the monomers, each Hg(II) atom is linearly coordinated with Cl – Hg - Cl bond angles of 180° [48,49] and 174.0(2)° [49]. The mean Hg-Cl bond distances are 2.306(6) Å [48], 2.294(5) Å and 2.295(5) Å [49]. In dimers, two $\{HgCl_2\}$ moieties are held together by a pair of oxygen ligands, dmso [48], bet [49] and pyac [49]. Each Hg(II) atom has a very distorted tetrahedral arrangement (HgO_2Cl_2). The mean Hg – O bridge and Hg - Cl bond distances are 2.54(1) Å (μ-dmso) and 2.315(6) Å ; 2.54(2) Å (μ-bet) and 2.347(5) Å; and 2.63(1) Å (μ-pyac) and 2.315(6) Å, respectively. The mean Hg – O – Hg and μO –Hg - μO bond angles are 104.7(4) and 75.3(4)° [48], 109.2(2) and 70.89(8)° [49] and 102.9(2) and 71.1(5)° [49], respectively. Noticeably, while the mean Cl – Hg – Cl bond angle decreases, the mean O –Hg – Cl bond angle increases in the following order: 166.2(2) and 95.4(3)° [48], 157.9(2) and 96.1(4)° [49], and 156.2(2) and 98.2(3)° [49].

Yellow derivative [50] contains the $[Hg(PMe_3)_2]^{2+}$ monomer and the $[Hg(\mu\text{-}I)I_2]_2^{2-}$ dimer. In the monomer, the Hg(II) atom has a linear P – Hg – P structure (180°) with a mean Hg – P bond distance of 2.413(6)°. In the dimer, two HgI_2 units are bridged by a pair of iodine atoms. Each Hg(II) atom has a tetrahedral geometry (HgI_4). The mean Hg – I bond distance is 2.708(2) Å. The Hg – I (bridge) distances are 2.774(2) and 3.113(2) Å. The Hg...Hg separation of 4.134(1) Å excludes a direct metal-metal bond, while the mean Hg – I – Hg bond angle is 89.0(1)°. The six “tetrahedral angles” fall in the range of 91.0(1) to 117.1(1)°.

The structure of another yellow derivative [51] contains well-separated $[NEt_4]^+$ cations, the $[HgI_2]$ monomer and the $[Hg(\mu\text{-}I)I_2]_2^-$ dimer. Two iodine atoms in the monomer create a linear structure around the Hg(II) atom (I – Hg – I = 180.00(0)°) with two equal Hg – I bond distances (2.574(1) Å). In the dimer, two iodine atoms serve as bridges between two HgI_2 units. The central Hg_2I_2 ring has mean Hg – I – Hg and μI – Hg - μI bond angles of 83.81(4) and 96.19(4)°, with an Hg...Hg separation of 3.912(2) Å, once again ruling out a direct bond.

Table 5. Crystallographic and Structural Data for Di- and Polymeric Mercury Complexes – Polymerisation Isomers[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Hg-L [Å]	Hg-Hg [°] Hg-L-Hg [°] μ'L-Hg-μL [°]	L-Hg-L [°]	Ref
[HgCl$_2$][HgCl$_2$(μ-dmso)]$_2$ (colourless)	tr P-1 1	6.672(7) 9.286(8) 8.764(8)	60.0(1) 95.5(1) 90.1(2)	HgCl$_2$ (monomer) HgO$_2$Cl$_2$ (dimer)	Cl[b] 2.306(6,0) μO 2.54(1,2) Cl 2.315(6,6)	not given 104.7(4) 75.3(4)	Cl,Cl[b] 180 Cl,Cl 166.2(2) Cl,O 95.4(3,2.3)	48
[HgCl$_2$][Hg(μ-bet)Cl$_2$]$_2$ (colourless)	tr P-1 1	7.302(2) 9.364(3) 10.559(12)	103.48(2) 104.45(2) 97.63(3)	HgCl$_2$ (monomer) HgO$_2$Cl$_2$ (dimer)	Cl 2.294(5,18) μO 2.54(2,9) Cl 2.347(5,1)	not given 109.2 70.89(8)	Cl,Cl 174.0(2) Cl,Cl 157.9(2) Cl,O 96.1(4,4.3)	49
[HgCl$_2$][Hg(μ-pyac)Cl$_2$]$_2$ (colourless)	tr P-1 1	7.247(5) 9.093(3) 9.626(5)	107.93(4) 99.41(5) 92.97(4)	HgCl$_2$ (monomer) HgO$_2$Cl$_2$ (dimer)	Cl 2.295(5,0) μO 2.63(1,4) Cl 2.315(6,4)	not given 102.9 71.1(5)	Cl,Cl 180 Cl,Cl 156.2(2) Cl,O 98.2(3,15.6)	49
[Hg(PMe$_3$)$_2$][Hg(μ-I)I$_2$]$_2$ (yellow)	tr P-1 1	9.439(2) 8.101(6) 8.352(1)	105.74(8) 88.48(3) 103.64(3)	HgP$_2$ (monomer) HgI$_4$ (dimer)	P 2.413(6,0) I 2.708(2,2) μI 2.774(2) 3.113(2)	4.134(1) 89.0(1) 91.0(1)	P,P 180 I,I 117.1(1) I,μI 110.5(1,9.3)	50
(NEt$_4$)$_2$][Hg(μ-I)I$_2$]$_2$ (yellow)	trg P4$_2$/m 2	10.391(1) 17.051(1)		HgI$_2$ (monomer) HgI$_4$ (dimer)	I 2.574(1,0) I 2.690(2) μI 2.934(1,0)	3.919(2) 83.81(4) 96.19(4)	I,I 180.00(0) I,I 129.63(7) μI,I 106.5(1,3.0)	51
[C$_{36}$H$_{48}$N$_{18}$][HgI$_4$]. [HgI$_3$(dmso)]. [Hg$_2$(μ-I)I$_6$].11dmso.2H$_2$O (bright yellow)	tr P-1 1	13.308(4) 15.693(5) 16.618(9)	68.86(3) 80.39(4) 89.63(3)	HgI$_4$ (monomer) HgI$_3$O (monomer) HgI$_4$ (dimer)	I 2.833(4,99) I 2.664(1,101) O 2.75(3) I 2.743(3,9) μI 2.903(2)		I,I 109.5(1,2.8) I,I 119.1(1,5.6) I,O 96(1,9) I,I 114.0(1,3.4) I,μI 104.5(1,1.7)	52
[Hg(η^5-dapmp)Cl][Hg(μ-Cl)$_2$Cl$_4$]$_{0.5}$ (yellow)	m P2$_1$/c 4	12.081(2) 10.295(2) 21.480(2)	93.00(1)	HgN$_5$Cl (monomer) HgCl$_4$ (dimer)	N$_{eq}$ 2.385(7,69) Cl$_{ap}$ 2.505(3) Cl 2.365(4,5) μCl 2.584(4,0)		N,N 66.3(2,1.7) 128.2(2,33.0) N,Cl 102.1(2,19.0) Cl,Cl 131.7(1) Cl,μCl 108.6(2,2.2)	53
[Hg(η^5-C$_{17}$H$_{27}$N$_5$)Br]. [Hg$_2$(μ-Br)$_2$Br$_4$] (yellow)	tr P-1 1	12.577(10) 10.485(9) 10.098(12)	89.49(12) 100.98(12) 106.15(14)	HgN$_5$Br (monomer) HgBr$_4$ (dimer)	N$_{eq}$ 2.39(4,14) Br$_{ap}$ 2.565(5) Br 2.501(6,10) μBr 2.649(6) 2.856(5)		N,N 70(1,8) 125(1,13) N,Br 110(1,28) not given	54
(bedt-ttf)$_3$[HgCl$_2$]. [Hg(μ-Cl)Cl$_2$]$_2$ (colourless)	m I2/c 2	11.082 8.754 35.92	91.01	HgCl$_2$ (monomer) HgCl$_4$ (dimer)				55
[Cr(dien)$_2$][HgCl$_7$ (yellow)	or Pbca 8	8.521(2) 16.175(5) 31.914(9)		HgCl$_4$ (monomer) HgCl$_4$ (trimer)	Cl 2.497(8,66) Cl 2.710(7,74)	3.880 not given 104.0(1)	Cl,Cl 109.5(3,12.6) Cl,Cl 154.6(3) Cl,μCl 97.3(3,5.5)	24
[HgCl$_4$]{Hg(η^2-C$_{12}$H$_{28}$N$_2$)(μ-Cl)]$_2$ (colourless)	tg P4/nmm 2	13.426(1) 10.973(3)		HgCl$_4$ (monomer) HgN$_4$Cl$_2$ (polymer)	Cl 2.503(9,0) N$_{eq}$ 2.38(3,1) μCl$_{ap}$ 2.74(2,10)		Cl,Cl 108.8(2) N,N not given Cl,Cl 18-0.0 N,Cl 94.6(7,1.3)	56
Hg(tu)$_{2/3}$Cl$_2$ (colourless)	m P2$_1$/c 6	8.00(1) 14.99(2) 7.21(2)	93.5(5)	HgCl$_2$ (monomer) HgCl$_3$S (polymer)	Cl 2.32(2) Cl 2.39(2) μCl 2.89(2,5) S 2.40(2)		Cl,Cl 180.0 Cl,Cl 91.6(6,4.4) Cl,S 155.0(7) 104.9(6,3.9)	57
(ttf)[HgCl$_3$] (colourless)	tr P-1 4	12.661(3) 15.969(4) 7.416(2)	98.69(2) 95.73(2) 120.01(2)	HgCl$_4$ (dimer) HgCl$_5$ (polymer)	Cl 2.375(5,7) μCl 2.648(5,48) Cl 2.374(5) μCl 2.470(5,75) 3.047(5,65)		Cl,Cl 132.2(2) Cl,μCl 106.4(2,7.5) Cl,Cl 94.7(2,17.2) 141.0(2) 163.4(2)	58

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

[b] The chemical identity of the coordinated atom or ligand is specified in these columns.

[c] Four-membered metallocyclic ring.

Table 6. Crystallographic and Structural Data for Monomeric Mercury Compounds – Coordination number Isomers and Ligand Isomers[a]

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Hg-L [Å]	L-Hg-L [°]	Ref
A : Coordination number Isomers							
$[HgI_3][Hg(\eta^2\text{-en})I]$. $[Hg(\eta^2\text{-en})I_2]$ (yellow)	tr P-1 2	15.170(6) 8.999(3) 8.561(4)	83.52(5) 84.12(5) 78.69(4)	HgI_3	I[b] 2.673(3) 2.752(4,24)	I,I[b] 120.0(1,6.7)	59
				HgN_2I	N 2.27(3,5) I 2.571(3)	N,N 77.1(11)[c] N,I 141.3(8,2.2)	
				HgN_2I_2	N 2.35(3,3) I 2.688(3,15)	N,N 78.9(10)[c] I,I 113.8(1) N,I 115.0(7,8.5)	
$[HgCl_4][Hg(C_{10}H_{20}N_4Cl]_2$ (colourless)	m C2/c 4	15.686(9) 15.058(8) 14.979(8)	103.03(4)	$HgCl_4$ HgN_4Cl	Cl 2.50(3,0) N_{eq} 2.37(4,9) Cl_{ap} 2.46(5)	Cl,Cl 109.5(2,6.5) N,N 83.2(8,7)[c] 86.4(7)[d] 140.8(4,9.8) N,Cl 104.1(5,7.3) 124.6(3)	60
B : Ligand isomers							
$Hg(\eta^2\text{-}Pr_2OCS_2)_2$ (pale yellow)	or $P2_12_12_1$ 2	7.371(3) 8.534(4) 11.618(4)		HgS_4	S 2.418(3,0) 2.835(4,0)	S,S 82.0(3) 101.9(3,10.3) 148.9(3)	61
$Hg(\eta^2\text{-}Pr^i_2OCS_2)_2$ (yellow)	m $P2_1/c$ 8	14.226(8) 9.806(8) 21.410(10)	100.13(10)	HgS_4	S 2.462(10,20) 2.752(10,132)	S,S 66.8(3) 109.6(3,8.3) 143.2(3)	47
				HgS_4	S 2.490(9,13) 2.679(10,62)	S,S 108.6(3,17.6)	

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Four-membered metallocyclic ring.
d. Six-membered metallocyclic ring

The structure of bright yellow derivative [52] is complex, contains well-separated [24-pyrimidium-crown-6]$^{6+}$ cations, $[HgI_4]^{2-}$ monomers and $[HgI_3(dmso)]^-$ anions, a $[Hg_2(\mu\text{-}I)I_6]^{3-}$ anion dimer, eleven dmso molecules and two water molecules. The structure of the monomers and the dimer are shown in Fig. 3. In the monomer $[HgI_4]^{2-}$, four iodine atoms form a tetrahedral geometry with a mean Hg – I bond distance of 2.833 Å.

The six "tetrahedral angles" fall in the range of 106.7(1) – 112.3(1)°. In another monomer, $[HgI_3(dmso)]^-$, three iodine atoms along with the oxygen atom of the dmso ligand form a distorted tetrahedral arrangement around the Hg(II) atom in (HgI_3O). The mean Hg – I bond distance of 2.664(1) Å is much shorter than that found in $[HgI_4]^{2-}$. The Hg – O bond distance is about 0.09 Å longer than the mean Hg – I bond distance. The six "tetrahedral angles" fall in the range of 87(1) – 124.7(1)°. In the dimer, two HgI_3 units are connected by a single iodine atom and form a tetrahedral geometry around each Hg(II) atom (HgI_4). The mean Hg – I (terminal) and Hg – I (bridge) bond distances are 2.743(3) and 2.903(2) Å, respectively.

Yellow derivative [53] contains the $[Hg(\eta^5\text{-dapmp})Cl]^+$ monomer and the $[Hg_2(\mu\text{-}Cl)_2Cl_4]^-_{0.5}$ anionic dimer. In the monomer, the Hg(II) atom has a pentagonal pyramidal arrangement (HgN_5Cl). The plane is formed by nitrogen atoms (Hg – N = 2.385(7) Å (av)) and the chlorine atom occupies an apical position (Hg – Cl = 2.505(2) Å). In the dimer, two equivalent $HgCl_2$ units are connected by a pair of chlorine atoms and form a central Hg_2Cl_2 ring. Each Hg(II) atom is tetrahedrally coordinated ($HgCl_4$). The mean Hg – Cl (terminal) and Hg – Cl (bridge) bond distances are 2.365(4) and 2.584(4) Å, respectively. The mean Cl – Hg - μCl bond angle of 108.6(2)° is about 23.1° smaller than that of Cl – Hg – Cl (131.7(1)°).

Another yellow derivative [54] contains the $[Hg(\eta^5\text{-}C_{17}H_{27}N_5)Br]^{3+}$ monomer and the $[Hg(\mu\text{-}Br)Br_2]^{2-}_2$ dimer. The structure of the monomer is similar to that of $[Hg(\eta^5\text{-dapmp})Cl]^-$ [53]. A pentagonal pyramid around the Hg(II) atom is formed by the five N atoms of the $C_{17}H_{27}N_5$ moiety which are in a plane, while the bromine atom occupies an apical position. The Hg – N and Hg –Br bond distances are 2.39(4) Å (av) and 2.565(5) Å. The dimer is classical, meaning that two $HgBr_2$ units are double bridged by a pair of bromine atoms. Each Hg(II) atom has a tetrahedral arrangement ($HgBr_4$). The mean Hg – Br (terminal) bond distance is 2.501(6) Å. Each of three bridged bromine atoms are coordinated asymmetrically, with Hg –Br (bridge) bond distances of 2.649(6) and 2.8567(5) Å.

Unfortunately, for the colourless monoclinic (bedt-ttf)$_3$[HgCl$_2$][Hg(μ-Cl)Cl$_2$]$_2$ [55] which contains the [HgCl$_2$] monomer and the [Hg(μ-Cl)Cl$_2$]$^-_2$ dimer, only crystallographic data are known.

Yellow orthorhombic [Cr(η^3-dien)$_2$][Hg$_2$Cl$_7$] [24] is the only example that contains three monomeric [HgCl$_4$]$^{2-}$ units and trimeric [Hg$_3$Cl$_{10}$]$^{4-}$. In the trimer, the tetrahedrally coordinated Hg(II) atoms are singly bridged by chlorine atoms (HgCl$_4$). The Hg...Hg distance of 3.880 Å indicates the absence of a bond. The Hg – Cl (bridge) bond distances range from 2.636(7) to 2.784(7) Å. The mean Hg – Cl (terminal) bond distance of 2.368(7) Å is about 0.129 Å shorter than the mean Hg – Cl bond distance found in the monomers (2.497(8) Å). There are two colourless derivatives [56,57] that consist of monomeric and polymeric units. Tetragonal derivative [56] contains the monomeric [HgCl$_4$]$^{2-}$ anion and the polymeric [Hg(η^2-C$_{12}$H$_{28}$N$_2$)$_2$(μ-Cl)]$^{2+}_2$ cation. In the monomer, four chlorine atoms create a tetrahedral arrangement around the Hg(II) atom , with a mean Hg – Cl bond distance of 2.503(9) Å. In the complex cation {Hg(η^2-C$_{12}$H$_{28}$N$_2$)}, units are connected by chlorine atoms and form a polymeric chain in the manner, -Cl – Hg(L$_2$) – Cl – Hg(L$_2$) -. Each Hg(II) has a coordination number of six. Two homobidentate C$_{12}$H$_{18}$N$_2$ ligands form a plane with a mean Hg – N bond distance of 2.38(3) Å.

Chlorine atoms which serve as bridges are bound in axial positions (Hg – Cl = 2.70(2) Å (av)) and complete a tetragonal bipyramidal arrangement around each Hg(II) atom (HgN$_4$Cl$_2$).

X-ray analysis of colourless monoclinic Hg(tu)$_{2/3}$Cl$_2$ [57] shows the presence of monomeric {HgCl$_2$} and polymeric {HgCl$_3$(tu)} units. In the monomer, the Hg(II) atom has a linear coordination (Cl – Hg – Cl = 180.0°), with an Hg – Cl bond distance of 2.32(2) Å. In the polymer, Hg(tu)Cl moieties are connected by chlorine atoms to form a polymeric chain. Each Hg(II) atom has a distorted tetrahedral geometry (HgCl$_3$S). The mean Hg – L bond distance increases in the following order: 2.39(2) Å (L=Cl) < 2.40(2) Å (S) < 2.89(2) Å (μ-Cl). The L – Hg – L bond angles range form 87.2(6)° to 155.0(7)°.

Colourless triclinic (ttf)[HgCl$_3$] [58] is the only example that contains a dimer {HgCl$_4$} and a polymer {HgCl$_5$}. In the dimer, two HgCl$_2$ units are bridged by a pair of chlorine atoms. The mean Hg –Cl (terminal) and Hg – Cl (bridge) bond distances are 2.375(5) and 2.648(5) Å, respectively. The Hg...Hg separation of 3.43 Å excludes the presence of a direct bond. The mean Hg – Cl – Hg and μCl – Hg - μCl bond angles are 89.9(2) and 90.1(2)°, respectively, while the mean Cl – Hg – Cl and Cl – Hg – μCl bond angles are 132.2(2) and 106.4(2)°, respectively. In the polymer, two chlorine atoms serve as bridges between HgCl$_3$ units to form a polymeric chain. Each Hg(II) atom has a coordination number of five (HgCl$_5$) (Table 5).

Inspection of the data in Table 5 reveals that in the series of polymerization isomers there exist derivatives which contain within the same crystal a monomer plus a dimer [48-51,53,54], two monomers plus a dimer [52], three monomers plus a trimer [24], and a monomer plus a polymer [56-58]. The isomers are found in the following crystal classes: triclinic (x7), monoclinic (x3), trigonal, orthorhombic and tetragonal (x1). Mercury atoms exist only in the +2 oxidation state. In the monomers, the mercury(II) atoms have a coordination number of two in the chromophores HgCl$_2$ [48,49,55,57], HgP$_2$ [50] and HgI$_2$ [51]; a coordination number of four in HgCl$_4$ [24,56], HgI$_4$ and HgI$_3$O [52]; and a coordination number of six in HgN$_5$X (X=Cl [53] or Br [54]). The mean Hg – L bond distances increase in the following order: 2.298 Å (Cl) < 2.413 Å (PL) < 2.547 Å (OL) < 2.770 Å (I) (coordination number of four); and 2.39 Å (N^{2}L) < 2.505 Å (Cl) < 2.565 Å (Br) (coordination number of six). In the dimers, each Hg(II) atom is a tetrahedrally coordinated (HgO$_2$Cl$_2$ [48,49], HgI$_4$ [50,52], HgCl$_4$ [53,55] and HgBr$_4$ [55]). The mean Hg – L bond distances increase as follows: 2.336 Å (Cl) < 2.500 Å (Br) < 2.714 Å (I); and 2.57 Å (μ-OL) < 2.584 Å (μ-Cl) < 2.725 Å (μ-Br) < 2.930 Å (μ-I). In the trimer (HgCl$_4$), the mean Hg - Cl bond distances are 2.368 Å (terminal) and 2.710 Å (bridged). In the polymers, the Hg(II) atoms have a coordination number of four for (HgCl$_3$S) [57], five for (HgCl$_5$) [58] and six for (HgN$_4$Cl$_2$) [56].

In general, the mean Hg – L (terminal) bond distances are shorter than the Hg – L (bridge) bond distances, and all of them increase with the covalent radius of the coordinated atom/ligand, as expected.

4. Coordination Number Isomerism

There are two derivatives [59,60] which belong to this class of isomerism and their crystallographic and structural parameters are given in Table 6A. Crystals of yellow triclinic derivative [59] contain three monomers [HgI$_3$], [Hg(η^2-en)I] and [Hg(η^2-en)I$_2$]. The Hg(II) atoms in [HgI$_3$]$^-$ and [Hg(η^2-en)I]$^+$ are triply coordinated. In the former, three iodine atoms with Hg – I bond distances of 2.673(3), 2.728(4) and 2.776(4) Å form a trigonal planar arrangement (Y –shape) around the Hg(II) atom. The I – Hg – I bond angles are deviated from the ideal bond angles (120°) by 6.7°. In $[Hg(\eta^2\text{-}en)I]^+$, a bidentate ethylenediamine ligand with an iodine atom form a very distorted trigonal planar arrangement (HgN_2I)around the Hg(II) atom. The mean Hg – N bond distance of 2.27(3) Å is much shorter than that of Hg – I with a length of 2.571(3) Å . The five – membered metallocyclic ring (N – Hg – N) with a value of 77.1(11)° is much smaller than the mean I – Hg – N bond angle (141.3(8)°). In the third monomer $[Hg(\eta^2\text{-}en)I_2]$, the Hg(II) atom has a distorted tetrahedral arrangement (HgN_2I_2). The mean Hg – N and Hg – I bond distances are 2.35(3) and 2.688(3) Å , respectively. The N – Hg – N, I – Hg – I and N – Hg – I bond angles are 78.9(10), 113.8(1) and 115.0(7)° (av.).

The crystal of colourless monoclinic $[HgCl_4][Hg(\eta^4\text{-}C_{10}H_{20}N_4)Cl]_2$ [60] contains two different monomers. The first of these is $[HgCl_4]^{2-}$, in which four chlorine atoms create a tetrahedral geometry around the Hg(II) atom with equal Hg – Cl bond distances of 2.50(3) Å . The six “tetrahedral angles” fall in the narrow range of 103.0 -116.0°. In the other monomer, $[Hg(\eta^4\text{-}C_{10}H_{20}N_4)Cl]^+$, the Hg(II) atom has a square-pyramidal geometry, with the four N atoms of $C_{10}H_{20}N_4$ ligand in the plane (mean Hg – N = 2.37(4) Å) and a chlorine atom in the apical position (Hg – Cl = 2.46(5) Å). The tetradentate $C_{10}H_{20}N_4$ ligand creates a pair of five- and six- membered metallocyclic rings (N – Hg – N) with mean values of 83.2(8) and 86.4(7)° around the Hg(II) atom. The N – Hg – Cl bond angles range from 97.0 to 124.6(3)°.

5. Ligand Isomerism

Two classic examples of ligand isomerism are yellow, orthorhombic $Hg(\eta^2\text{-}Pr_2OCS_2)_2$ [61] and monoclinic $Hg(\eta^2\text{-}Pr^i{}_2OCS_2)_2$ [47]. Their crystallographic and structural data are gathered in Table 6B. These compounds adopt two-dimensional structures comprised of connected 16-membered rings which arise as a result of bridging propylxantate ligands. The structure of $Hg(\eta^2\text{-}Pr_2OCS_2)_2$ [61] is shown in Fig. 4. Each mercury(II) atom lies on a crystallographic twofold axis of symmetry and is coordinated in a distorted tetrahedral geometry (HgS_4). The mean Hg – S bond distances are 2.626 Å and 2.596 Å in the orthorhombic and monoclinic derivatives, respectively.

6. Conclusions

This review summarizes the crystallographic and structural data for over fifty isomers of mercury coordination compounds. These isomers are classified into five categories, as follows: distortion, polymerization, coordination number and ligand isomers. The distortion isomers by far prevail (73%). The distortion isomers can be divided into several additional subgroups. Eighteen examples (Tables 1 and 2) exist in two isomeric forms. In sixteen cases, both isomers belong to the homo-monoclinic [5,6,8-13,16-20] and triclinic [7] classes. The remaining examples differ form each other not only by the degree of distortion but also by the crystal class: one isomer is orthorhombic [14] and the other monoclinic [15].

The remaining derivatives (Tables 3 and 4) contain crystallographically independent molecules within the same crystal and differ mostly by the degree of distortion. Three examples [21-23] contain four crystallographically independent molecules; in [24], there are three such molecules; the remaining examples [25-47] contain two independent molecules. These examples exist in three crystal classes: monoclinic (x18), triclinic (x10) and orthorhombic (x1). In two isomeric forms, $\alpha\text{-}[Hg(Ph_2Se)_2]_2(ClO_4)_2$ [16] and $\beta\text{-}[Hg(Ph_2Se)_2]_2(ClO_4)_2$ [17], mercury atoms are in the +1 oxidation state ($Hg_2(+2)$). All of the remaining mercury atoms are found only in the +2 oxidation state (Hg(II)).

Typical examples of polymeric isomerism, the second type of isomerism (20.6%), include those which contain both monomers and dimers [48-55], monomers and trimers [24], monomers and polymers [24,56,57] and dimers and polymers [58]. Coordination number isomerism, the third type of isomerism (3.2%) has been found in only two cases [50,60]. Ligand isomerism, the fourth type of isomerism (3.2%), has also only been found in two cases [47,61].

This review, together with its precursors [2,3], represents the first overall survey of the structural data of isomers for this non-transition metal subgroup. In the chemistry of this subgroup of non-transition elements, the following types of isomerism exist:
zinc: distortion (96%) and ligand (4%) [2] cadmium: distortion(91.5%), ligand (6.5%), cis-, trans- (1%) and polymerization (1%) [3] mercury: distortion (73%), polymerisation (20.6%), coordination number (3.2%) and ligand (3.2%). All three metal atoms are in the +2 oxidation state for all of the isomers, with two exceptions [16,17], in which mercury atoms are in the +1 oxidation state ($Hg_2(+2)$). The isomers exist in the following crystal classes:

zinc: monoclinic (x29) > orthorhombic (x12) > triclinic (x10); cadmium: monoclinic (x18) > triclinic (x10) > orthorhombic (x8) > tetragonal (x3) > hexagonal (x2) > trigonal (x1); mercury: monoclinic (x32) > triclinic (x12) > orthorhombic (x2).

As can be see, the monoclinic crystal is by far the most common.

In the chemistry of “borderline” Zn(II) and “soft” Cd(II) and Hg(II), a wide variety of ligands are found that form the following inner coordination spheres about the metal atoms, with varying degrees of distortion and of inner coordination spheres:

Zinc: ZnX_4 (X = O, Cl, S, Se or I), ZnO_2X_2 (X = C, Cl or Br), ZnN_2X_2 (x = Cl or S), ZnN_3O, $ZnCl_2CS$; ZnN_5, ZnN_4O, ZnN_3I_2, ZnN_3OS; ZnN_6, ZnO_3N_3.

Cadmium: CdS_3; CdX_4 (X = S, Se or I), CdN_2I_2; CdI_4O, $CdCl_3NP$; CdX_6 (X = O or S), CdS_5O, CdO_4N_2, CdN_4X_6 (X = O or S), CdS_4N_2, CdN_4OS, $CdO_2N_2S_2$; CdO_7, CdO_5N_2; $CdeO_6I_2$.

Mercury: HgX_2 (X = N, Cl, S, I or Ge), HgClP; HgX_3 (X = Cl, Br or I), HgS_2P; HgX_4 (X = S, Br or I), $HgCl_3X$ (X = S or P), HgI_3O, HgO_2X_2 (X = N or Cl), HgN_2X_2 (X = C, S or I), $HgCl_2P_2$, HgN_2CCl; $HgCl_5$, HgN_4X (X = Cl or I), HgO_2S_2N; $HgCl_6$, HgO_5X (X = P or As), HgN_5Br, HgN_4X_2 (X = Cl or I).

As can be seen, a variety of inner coordination spheres around the metals become increasingly larger: 4–6 (Zn) < 2-6 (Hg) < 3-8 (Cd). A tetrahedral arrangement with a different degree of distortion is by far the most prevalent form for all three metals, as expected.

Although Zn(II) should preferentially bind to ”borderline” donor ligands, there is no known example of such a ligand, but there are examples with pure “hard” and “soft” donor atom ligands. A combination of “hard” with “soft” donor atom ligands by far prevails.

Likewise, in the series of Cd(II) and Hg(II) isomers, the combination of “hard” and “soft” donor atom ligands are most suitable for the formation of the respective isomers.

We believe that a systematic overall review is necessary, and that such reviews serve the useful purpose of delineating areas of both interest and weakness.

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Abbreviations

$Asmes_3$	trimethylarsine
bedt-thf	bis(ethylenedithiolo)tetrathiofulvalene
bz	benzyl
$C_5H_6N_5$	adeninium
$C_{10}H_{20}N_4$	1,4,8,11-tetra-azacyclotetradecane
$C_{11}H_{16}N_4$	bis(3,5-dimethyl-pyrazol-1-yl) methane
$C_{12}H_{24}S_4$	1,5,9,13-tetrathiacyclohexadecane
$C_{12}H_{28}N_4$	1,5,9,13-tetra-azacyclohexadecane
$C_{15}H_{11}S_2$	bis-(3,5-diphenyl-1,2-dithiolium)
$C_{36}H_{48}N_{18}$	24-pyridinium-crown-6
$C_{17}H_{27}N_5$	2,15-dimethyl-3,7,10,14,20,-pentaazabicyclo[14.3.1]eicosa-1(20)-2,14,16,18- pentane
damp	2,6-diacetylpyridine bis[N-methyl-N-(2′-pyridyl)hydrazone]
dchptc	dicyclohexylphosphino-N-phenylthioformamide
dien	diethylenetriamine
dmso	dimethylsulphoxide
dmv	1,3-dimethyl-violurate
en	ethylenediamine
Et	ethyl
Etxan	ethylxanthate
m	monoclinic
Me	methyl
MeCOO	acetate
4-Mepy	4-methylpyridine
2-Mequs	2-methyl-8-mercaptoquinolinate
Me_4ttf	tetramethyltetrathiofulvalene
or	orthorhombic
$P(CH_2CH_2CN)_3$	tris(ethylenecyanide)phosphine
Ph	phenyl
Phen	1,10-phenantroline
Ph_2Se	diphenylselenide
PMe_3	trimethylphosphine
$Pmes_3$	trimesitylphosphine
PPh_3	triphenylphosphine
Pr	propyl
Pr^i	iso-propyl
$Pr^i_2NCS_2$	diisopropyldithiocarbamate
$Pr^i_2OCS_2$	isopropylxanthate
pyac	pyridineacetate
sac	sacharine
tg	tetragonal
tr	triclinic
trg	trigonal
ttf	tetrathiofulvalene
tu	thiourea

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