THE STRUCTURAL CHEMISTRY OF MERCURY

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1. Introduction

IN recent years knowledge of the structures of mercury compounds has been greatly expanded, mainly by *X*-ray work. Wells[1] has provided a good general summary, and there have been recent reviews of mercury–nitrogen,[2] halogenomercurate(II),[3] and mercurous compounds.[4] This review deals with the structural chemistry of mercury in both molecular and macromolecular compounds. The applications of ligand field theory[5–7] to d^{10}-metal ions,[8,9] though promising, are not yet numerous, and it is hoped that the present survey will stimulate further work in this field.

2. Radii of Mercury

The nearest neighbours of mercury in a crystal structure are those in "contact" with it. In a free molecule (*e.g.* in the vapour state) these contacts are chemical bonds and their number is defined by valency or co-ordination 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 co-ordination sphere) of mercury to those within a defined distance. This is difficult for mercury, as frequently the distances between the surrounding atoms and mercury do not follow the additivity rule of the atomic radii currently accepted, yet are less than the sum of the van der Waals radii. Even when only atoms of one element surround mercury, markedly different distances may be found. Consequently, the adoption of a suitable set of atomic radii should precede any discussion of the structural chemistry of mercury.

(a) *The Metallic Radius.*—The parameters of the crystal structure of solid mercury[10] at low temperature have recently been determined very accurately.[11] The structure differs from the common metallic close packed

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[1] Wells, "Structural Inorganic Chemistry," 3rd edn., Clarendon Press, Oxford, 1962, pp. 890—900.

[2] Lipscomb, *Annals New York Acad. Sci.*, 1957, 427—435.

[3] Deacon, *Rev. Pure and Appl. Chem.*, 1963, **13**, 189; see also Bergerhoff, *Angew. Chem. Internat. Edn.*, 1964, **3**, 686.

[4] Tarayan, *Uspekhi Khim.*, 1953, **22**, 1002.

[5] Nyholm, "Report of the 10th Solvay Conference in Chemistry," Brussels, 1956, p. 225.

[6] Gillespie and Nyholm, *Progr. Stereochem.*, 1958, **2**, 261.

[7] Orgel, "An Introduction to Transition-Metal Chemistry—Ligand Field Theory," Methuen and Co. Ltd., London, 1960.

[8] Orgel, *J.*, 1958, 4186.

[9] Dunitz and Orgel, *Adv. Inorg. Chem. Radiochem.*, 1960, **2**, 34.

[10] McKeehan and Cioffi, *Phys. Rev.*, 1922, **19**, 444.

[11] Barrett, *Acta Cryst.*, 1957, **10**, 58.

structure, and may be interpreted as a packing of flattened rotational ellipsoids instead of spheres. There are two groups of six equal interatomic distances, 3·000 and 3·466 Å.[12] Each mercury atom is surrounded by six closer mercury atoms in an octahedron drawn along one of its triad axes and six equatorial, more distant mercury atoms in a hexagon (Figure 1). This gives mercury twelve-co-ordination in a flat cuboctahedron.

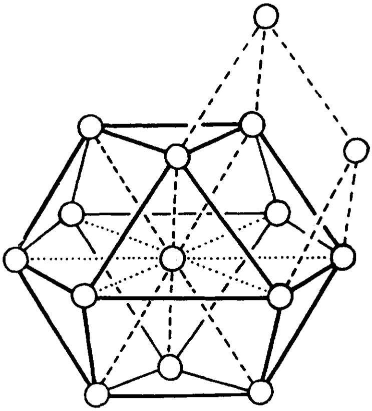

FIG. 1. *The environment of mercury atoms in the crystal of metallic mercury: each mercury atom has six closer neighbours at* 3·000 Å *(dashed lines) in a distorted octahedron and six more at* 3·466 Å *(dotted lines) in a hexagon. The resulting co-ordination polyhedron is a flattened cuboctahedron which relation to the rhombohedral crystal lattice* (a = 3·000 Å, α = 70° 32′) *is shown.*

As a single Hg–Hg distance cannot be given for the metal, both values have to be used in defining the metallic radius, ρ (Hg), so that 1·50 Å $\leqslant \rho$ (Hg) $\leqslant$ 1·73 Å. In amalgams, this means that Hg–Hg distances of 2·90—3·24 Å represent true contacts between mercury atoms, while those longer than 3·466 Å do not.

(b) *The van der Waals Radius.*—In a discussion of the stereochemistry of mercury, the distinction between bonded and non-bonded atoms surrounding mercury is very important. The van der Waals radius of mercury, R(Hg), is expected to be nearly equal to its metallic radius. The experimental results are rather unsatisfactory, because there are very few contacts between mercury and non-bonded atoms in crystal structures. The lowest value of R(Hg) (1·58 Å, from the Hg . . . . C contact[13]) is only slightly larger than the lower metallic radius of mercury. Thus the value R(Hg) = 1·50 Å will henceforth be used for the van der Waals radius. Provided R(Hg) < 1·73 Å, some form of bonding is considered to occur.

(c) *The Ionic Radius.*—Anhydrous mercuric fluoride is the only mercury

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[12] Pauling, "The Nature of the Chemical Bond", 3rd edn., Cornell University Press, Ithaca, 1960.

[13] Kitaigorodskii, Khotsyanova, and Struchkhov, *Zhur. fiz. Khim.*, 1953, **27**, 780.

compound which is purely ionic. It crystallises in a fluorite type structure[14] with $a = 5{\cdot}54$ Å, and Hg–F = 2·40 Å. Thus $R(Hg^{2+}) = 1{\cdot}04$ Å {using Pauling's value[12] for $R(F^{-})$.} [The value $R(Hg^{2+}) = 1{\cdot}10$ Å, which is usually quoted in tables was probably obtained by using Goldschmidt's value for $R(F^{-})$.]

(d) *The Covalent Radii.*—As stated in section (*b*), each Hg–L (L is any atom, ion, etc., in a mercury compound) approach of $R(Hg) < 1{\cdot}73$ Å can be considered as bonding. The larger Hg–L distances, indicative of weak interactions, are not observed in the vapour or in apolar solvents, but only in crystal structures, melts, and polar solvents. This review is concerned with the environment of mercury in free molecules or crystal structures.

Digonal covalent radius. The most familiar mercury compounds are those of the type L–Hg–L (*e.g.* mercuric chloride) and L–Hg–L′ (*e.g.* methylmercuric chloride). In addition there are also many polymeric mercury compounds with linear L–Hg–L bonding (*e.g.* amidomercuric chloride, which contains the polymeric ion $^{+}NH_2{\cdot}Hg{\cdot}NH_2{}^{+}{\cdot}Hg$). The differing values of $r(Hg)$ derived from Hg–L distances in these compounds are usually explained by the postulation of double bonding or partial ionic bonding for relatively short or long bonds respectively.

Because the influence of surrounding atoms on L–Hg–L bonds is significant (see section 5), the most reliable digonal covalent radius of mercury, r[Hg(2)], should be one derived from data obtained for free L–Hg–L molecules in the vapour. The Hg–L bond lengths obtained by electron diffraction or microwave spectroscopy are given in Table 1.

TABLE 1. Hg–L *bond lengths* (*in* Å) *observed in the vapour phase by electron diffraction* (*e*) *or microwave* (*mw*) *spectroscopy*

Hg–Cl. Mercuric chloride: 2·20 (e)[a]; 2·34 (e)[b]; 2·27 (e)[c]. Methylmercuric chloride: 2·282 (mw)[d].

Hg–Br. Mercuric bromide: 2·40 (e)[a]; 2·44 (e)[b]; Methylmercuric bromide: 2·406 (mw)[d].

Hg–I. Mercuric iodide: 2·55 (e)[a]; 2·61 (e)[b].

Hg–C. Dimethylmercury: 2·20 (e)[e]; 2·23 (e)[b]. Methylmercuric chloride: 2·061 (mw)[d]. Methylmercuric bromide: 2·074 (mw)[d].

[a] Braune and Knocke, *Z. phys. Chem.*, 1933, *B*23, 163. [b] Gregg *et al.*, *Trans. Faraday Soc.*, 1937, **33**, 852. [c] Maxwell and Mosley, *Phys. Rev.*, 1940, **57**, 21. [d] Gordy and Sheridan, *J. Chem. Phys.*, 1954, **22**, 92. [e] Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036.

To derive the bicovalent radius of mercury it is preferable to use data from compounds in which the electronegativity difference $x(Hg) - x(L)$ is as low as possible, *i.e.* in Hg–C and Hg–I derivatives.* Thus from Hg–I (2·61 Å)*r[Hg(2)] = 1·28 Å, which is close to the values of 1·29 and 1·30 Å derived from C–Hg data for methylmercuric chloride and

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* Using electronegativities and radii given by Pauling.[12]

[14] Ebert and Woitinek, *Z. anorg. Chem.*, 1933, **210**, 269.

bromide. The corresponding Hg–Cl and Hg–Br data give values of 1·29 and 1·27 Å, respectively. However the value obtained from the Hg–C distance of dimethylmercury (2·23 Å) is significantly higher $\{r[\mathrm{Hg}(2)] = 1{\cdot}46\ \text{Å}\}$. Although the Hg–C bond in methylmercuric chloride or bromide must be influenced by the halogen, the extent of bond shortening from $\mathrm{Me_2Hg}$ to MeHgX seems surprising, and a re-investigation of the structure of $\mathrm{Me_2Hg}$ is desirable.

Theoretically $r[\mathrm{Hg}(2)]$ could be defined as half the observed Hg–Hg distance in mercurous compounds. However, this distance varies with change of L in L·Hg·Hg·L derivatives. For example, in mercurous halides[15] the Hg–Hg distance increases from 2·43 Å in the fluoride to 2·69 Å in iodide. The crystal structure[16] of mercurous dihydrate contains $[\mathrm{H_2O{\cdot}Hg{\cdot}Hg{\cdot}OH_2}]^{2+}$ ions with an Hg–Hg distance of 2·54 Å, which gives $r[\mathrm{Hg}(2)] = 1{\cdot}27$ Å. As this agrees well with the above $r[\mathrm{Hg}(2)]$ values, the condition of minimum electronegativity difference $x(\mathrm{Hg})–x(\mathrm{L})$ must be fulfilled.

By taking into account the influence of the electronegativity difference[12] (Schomaker–Stevenson coefficient = 0·03), the mean value for the digonal covalent radius is 1·30 Å. This obeys the additivity rule satisfactorily for the free $\mathrm{L_2Hg}$ or LHgL′ molecules. In crystal structures additivity is not preserved because of the close approach of neighbouring groups to mercury. Support for the value of $r[\mathrm{Hg}(2)]$ comes from the fact that it is less than the metallic radius of mercury. The bicovalent radius for *sp* (or *ds*—see section 6) hybridisation should be much shorter than the corresponding metallic radius, especially as metallic bonding is relatively weak with mercury.

In the literature the bicovalent and tetrahedral covalent radii of mercury have often been confused.

TABLE 2. *Bond lengths (in Å) in crystal structures having tetrahedrally co-ordinated mercury*

Hg–I. Mercuric iodide (red): 2·78[a]; 2·80[b]; 2·77[c]; 2·80[d]. Silver(I) tetraiodomercurate: 2·74[d]; Copper(I) tetraidomercurate: 2·64[d].

Hg–S. Mercuric sulphide (black, metacinnabarite): 2·53[e,f]; 2·54[g]; 2·525[h]; Cobalt(II) tetrathiocyanatomercurate: 2·50[i]; Bisethylenediaminecopper(II) tetrathiocyanatomercurate: 2·56[j]; Nickel(II) tetrathiocyanatomercurate dihydrate: 2·50[k]; Potassium tetrathiocyanatomercurate: 2·54[l].

Hg–Se. Mercuric selenide: 2·62.

Hg–Te. Mercuric telluride: 2·78.

[a] Havighurst, *Amer. J. Sci.*, 1925, **10**, 556. [b] Bijvoet, Classen, and Karssen, *Proc. k. ned. Akad. Wetenschap.*, 1926, **29**, 529. [c] Huggins and Magill, *J. Amer. Chem. Soc.*, 1927, **49**, 2357. [d] Ketelaar, *Z. Krist.*, 1931, **80**, 190. [e] Lehmann, *Z. Krist.*, 1924, 60, 379. [f] Kolkmeijer and Bijvoet, *Proc. k. ned. Akad. Wetenschap.*, 1924, **27**, 390, 847. [g] Buckley and Vernon, *Mineralog. Mag.*, 1925, **20**, 382. [h] Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, *Skrifter Norske Videnskaps Akad.*, vol. 8, 1926. [i] Jeffery, *Nature*, 1947, **159**, 6106. [j] Scouloudi, *Acta Cryst.*, 1953, **6**, 1953. [k] K'uo-Hsiang Chou and Porai-Koshits, *Kristallografiya*, 1960, **5**, 462. [l] Zvonkova, *Zhur. fiz. Khim.*, 1952, **26**, 1952.

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[15] Grdenić and Djordjević, *J.*, 1956, 1319.

[16] Grdenić, *J.*, 1956, 1312.

The tetrahedral covalent radius. Interatomic Hg–L distances, determined by *X*-ray or neutron-diffraction methods, for crystals in which mercury has regular tetrahedral stereochemistry are recorded in Table 2. The HgL_4 group is either a complex ion [as in $K_2Hg(SCN)_4$] or the structural element of a layer (as in red mercuric iodide) or of a three-dimensional framework of the zinc blende type (as in metacinnabarite).

From the Hg–L distances and the covalent radii[12] of sulphur (1·04 Å), selenium (1·14 Å), tellurium (1·32) Å, and iodine (1·28 Å), the tetrahedral covalent radius of mercury is found to be 1·48 Å. This radius is not of general use, as those structures in which mercury has distorted tetrahedral stereochemistry are actually derived from bicovalently or tricovalently bonded mercury, with additional close approaches of other, usually more electronegative, atoms or ions. To summarise, the following mercury radii are adopted and used in this review.

Metallic radius, ρ(Hg): $1{\cdot}50 \leqslant \rho(\mathrm{Hg}) \leqslant 1{\cdot}73$ Å
van der Waals radius: $R(\mathrm{Hg}) = 1{\cdot}50$ Å
Ionic radius: $R(\mathrm{Hg}^{2+}) = 1{\cdot}04$ Å
Digonal covalent radius: $r[\mathrm{Hg}(2)] = 1{\cdot}30$ Å
Tetrahedral covalent radius: $r[\mathrm{Hg}(4)] = 1{\cdot}48$ Å

3. Valency Bond Angle of Mercury

The only compounds of mercury that exist as discrete molecules or give them in vapour or solution are of the type LHgL (*e.g.* mercuric chloride) and LHg·HgL (*e.g.* mercurous trichloroacetate). They are not very numerous, especially the latter. The presence of linear bonds has been confirmed in free molecules (vapour phase) by electron diffraction and microwave spectroscopy, and in some crystalline compounds by *X*-ray diffraction. A slight departure from linearity has been found for the C–Hg–C bonds in mercury diethylene oxide[17] (bond angle 176°) and in mercuric cyanide[18] (bond angle 171°), but in all other crystal structures of organomercurials the C–Hg–C or C–Hg–X bond angles are close to 180°. However, the dipole moments of various diarylmercurials in benzene and decalin solution are unexpectedly not zero,[19–21] suggesting either a bent C–Hg–C skeleton or at least significant oscillation of the molecules away from linearity in solution. Further investigations as to the configurations of free molecules of the diaryl mercurials seem desirable. In the crystal structures of these compounds, because of a combination of inter- and intra-molecular factors, linearity of C–Hg–C bonds seems a requirement for minimum energy, but this is not necessarily true for free molecules.

In other crystalline mercury compounds, particularly those with halogen, oxygen, or sulphur atoms, nonlinear L–Hg–L skeletons are frequently

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[17] Grdenić, *Acta Cryst.*, 1942, **5**, 367.
[18] Hvoslef, *Acta Chem. Scand.*, 1958, **12**, 1568.
[19] Hampson, *Trans. Faraday Soc.*, 1934, **30**, 877.
[20] de Laszlo, *Trans. Faraday Soc.*, 1934, **30**, 884.
[21] Horning, Lautenschlaeger, and Wright, *Canad. J. Chem.*, 1963, **41**, 1441.

found, due to the electronegativity of the ligands or the packing conditions in the crystal structure.

4. Co-ordination Chemistry of Mercury

All atoms surrounding mercury at a distance of less than the sum of the van der Waals radii [$D(\text{Hg-L}) < R(\text{Hg}) + R(\text{L})$] are considered to belong to the mercury co-ordination sphere. (The values used for R(L) are those given by Pauling.[12]) The following classification of the co-ordination behaviour of mercury is suggested.

(a) *Characteristic Co-ordination.*—The mercury atom is considered to have the characteristic co-ordination number (m) in the system HgL_m when all m Hg–L bonds are of the same length. In free molecules or complex ions characteristic co-ordination numbers of two, three, and four for covalent bonding and eight for ionic bonding are known. Examples are given in Table 3 and are illustrated in Figure 2. Regular octahedral stereochemistry for mercury has not been authenticated by full structure determinations, but in the recently prepared $HgL_6(ClO_4)_2$ (L is pyridine 1-oxide, dimethylsulphoxide etc.) complexes,[22] this stereochemistry is probably realised.

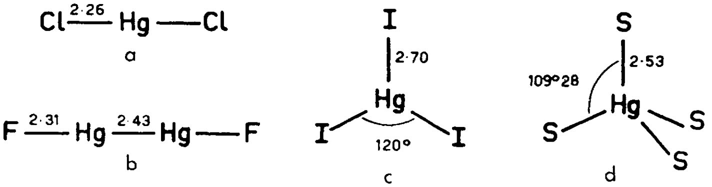

FIG. 2. *Examples of characteristic co-ordination of mercury:* (a), (b) *digonal as in mercuric and mercurous halides,*[1] (*c*) *trigonal as in* $(Me_3S)HgI_3$,[33] *and* (d) *tetrahedral as in tetrathiocyanatomercurates* (*for references see Table* 2).

Only one characteristic ionic co-ordination number is known ($m = 8$). The co-ordination polyhedron is a cube in crystalline mercuric fluoride, but other possible polyhedra are not excluded for eight co-ordination. The structure[23] of potassium tetranitritomercurate(II) nitrate has been described as containing the tetrahedral complex ion, $Hg(NO_2)_4^{2-}$. However, eight oxygens are equidistant from mercury and the Hg–O distance (2·4 Å) indicates almost pure ionic bonds. Thus the co-ordination polyhedron may be a distorted trigonal dodecahedron. Ionic structures with $m = 6$ have not yet been established (see, however, Table 3). Such an arrangement requires $R(\text{Hg}^{2+})/R(\text{L}^-)$ to be less than 0·73 .These conditions apply when L = Cl, but the structures of mercury–chlorine derivatives show a departure from octahedral symmetry, two Hg–Cl distances being markedly less than the other four.

(b) *Effective or Actual Co-ordination.*—The effective co-ordination

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[22] Carlin, Roitman, Dankleff, and Edwards, *Inorg. Chem.*, 1962, **1**, 182.
[23] Hall and Holland, *Proc. Chem. Soc.*, 1963, 204.

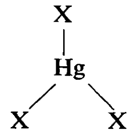
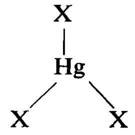
number n is an extension of the characteristic co-ordination number to include all ligands fulfilling the condition D(Hg-L) < R(Hg) + R(L). This arises from the close approach of adjacent molecules, etc., in a crystal structure. Thus HgL_m becomes HgL_n where $n>m$. The value $n = 6$ is the highest known (Table 4). Only when $m = 2$ or 3 can additional ligands be accommodated. With $m = 4$, $n = 4$, digonal characteristic co-ordination leads to distorted trigonal, square planar, tetrahedral, pyramidal, or octahedral stereochemistry, while trigonal co-ordination gives elongated trigonal bipyramidal, or very distorted tetrahedral effective co-ordination. Linear bonds in digonal characteristic co-ordination become bent when the molecule acquires distorted trigonal or tetrahedral effective co-ordination. The new ligands lengthen the Hg–L bonds of the characteristically co-ordinated ligands. To summarise, in effective co-ordination two groups of D(Hg-L) distances are observed: (1) shorter ones, which represent characteristic co-ordination and (2) longer ones, due to close approaches in crystal structures. This criterion is also applicable to systems involving different ligands. Examples of all known effective co-ordination arrangements are given in Figures 3—5, the most common being distorted octahedral, based on digonal characteristic co-ordination.

TABLE 3. *Characteristic co-ordination* (m) *of mercury in molecules, complex ions, and crystal structures in relation to the electronegativity* (x_L) *of the ligands*

Covalent

m	species	x_L	D(Hg–L)
4	$PbHgP_{14}$, HgTe, HgSe, HgS (cubic) $Hg(SCN)_4^{2-}$, HgI_2(red)	2·1 ↓ 2·5	D(Hg–L) = r[Hg(4)] + r(L)
3	HgI_3^-, $HgBr_3^-$, $HgCl_3^-$	2·5 ↓ 3·0	D(Hg–L) < r[Hg(4)] + r(L)
2	HgF_2, $HgCl_2$, $HgBr_2$, and HgI_2 in vapour or dissolved in apolar solvents; Me_2Hg, MeHgCl; molecules with –O–Hg–O, –N–Hg–N–. Mercurous compounds with –O–Hg–Hg–O– as in $Hg_2(OH_2)_2^{++}$ or $Hg_2(OCOCCl_3)_2$	2·5 | ↓ 3·5	D(Hg–L) = r[Hg(2)] + r(L)
	Ionic		
6	Probable but not established yet. Partly realised in $Hg(OHgCl)_2$	3·0 ↓ 3·5	D(Hg–L) = $R(Hg^{2+})$ + $R(L^-)$
8	HgF_2, $K_3[Hg(NO_2)_4]NO_3$	3·5 ↓ 4·0	

TABLE 4. *Effective co-ordination* (n) *of mercury in crystal structures in relation to the characteristic co-ordination* (m) *and bond distances* D(Hg–L)

		Characteristic bonds		
n	Species	$m = 2$	$m = 3$	D(Hg–L)
6	HgO $Hg(NH_3)_2Cl_2$ $Hg(CN)_2$ $HgPy_2Cl_2$ NH_4HgCl_3 $K_2HgCl_4 \cdot H_2O$ $HgBr_2$ HgI_2(yellow) HgS(cinnabar) Hg_2X_2	O–Hg–O N–Hg–N Cl–Hg–Cl Br–Hg–Br C–Hg–C I–Hg–I S–Hg–S and mixed	—	
5 Distorted square pyramid	$(MeS)_2Hg$			*m* distances with $D(Hg–L \geqslant r[Hg(2)] + r(L)$ and $n - m$ distances with D(Hg–L) $< R(Hg) + R(L)$
5 Elongated trigonal bipyramid	Me_3SHgI_3 Hg_2NHBr_2	Probable but not observed yet	 X = Br or I	
4	$(Me_4N)HgBr_3$ $(Me_4N)HgCl_3$ $(Me_4N)HgI_3$		 X = Cl, Br, or I	
	$HgSO_4$ $(NCHg)_2O$ $HgCl_2,2HgO$ $Hg(SCN)_2,KSCN$	O–Hg–O C–Hg–O O–Hg–Cl S–Hg–S	—	
3 Planar or nearly planar	Mercury diethylene oxide	C–Hg–C	—	

(c) *Factors Influencing Co-ordination.*—The following are the main features of the crystal chemistry of mercury. (1) Linear covalent bond formation. (2) Tetrahedral co-ordination in zinc blende type structures. (3) Metal–metal bond formation. (4) The formation of ionic structures. All rules valid in crystal chemistry can be applied to any groups of mercury

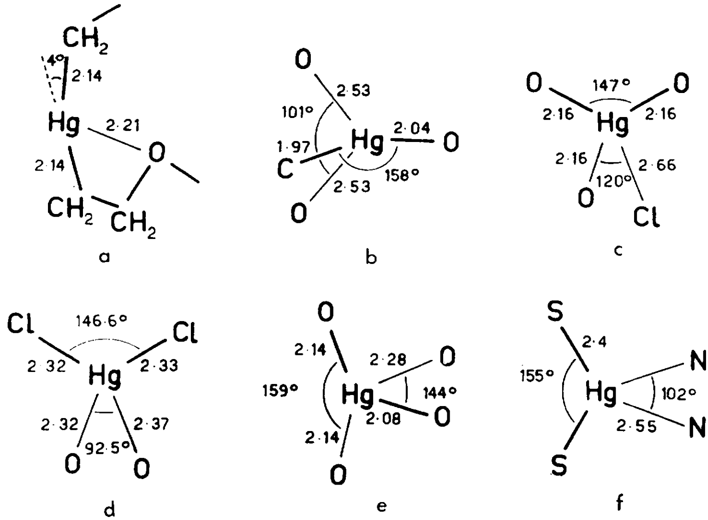


FIG. 3. *Examples of trigonal* (a) *and tetrahedral effective co-ordination of mercury:* (a) *mercury diethylene oxide,*[17] (b) *mercuric oxycyanide,*[98] (c) *trimercuric oxychloride,*[51] (d) *bis(triphenylarsine oxide)mercuric chloride,*[124] (e) *anhydrous mercuric sulphate,*[24] (f) *mercuric dithizonate.*[66]

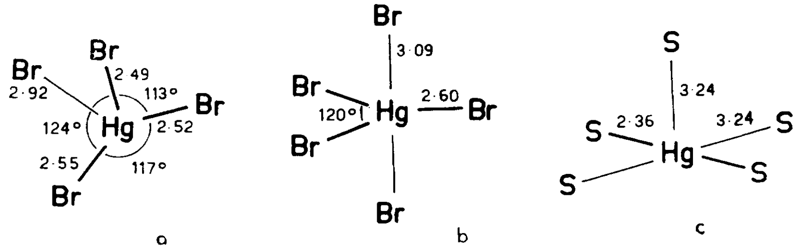


FIG. 4. *Examples of tetrahedral* (a), *bipyramidal* (b), *and pyramidal,* (c) *effective co-ordination of mercury. The distorted tetrahedron* (a) *in* $(Me_4N)HgBr_3$,[35] *and the trigonal bipyramid* (b) *in imidomercuric bromide*[76] *are based on trigonal characteristic co-ordination, while the pyramid in dimethylthio mercury*[70] *originated from digonal characteristic co-ordination.*

compounds from ionic to molecular, and mercury co-ordination could be correlated with all influencing factors, *e.g.* ionic radii, polarisability, electronegativity, etc. It has been found that the electronegativity difference $[x(\mathrm{Hg}) - x(\mathrm{L})]$ is most suitable for a rational classification of the crystal structures of mercury compounds. The value $x(\mathrm{L}) = 2{\cdot}5$ is a critical one, because for $x(\mathrm{L}) > 2{\cdot}5$ the characteristic co-ordination is generally digonal and for $x(\mathrm{L}) < 2{\cdot}5$ the characteristic and effective co-ordination is generally tetrahedral. Sulphur and iodine occupy a transitional position, digonal co-ordination being more stable for sulphur (cinnabar more stable than metacinnabarite) and tetrahedral for iodine

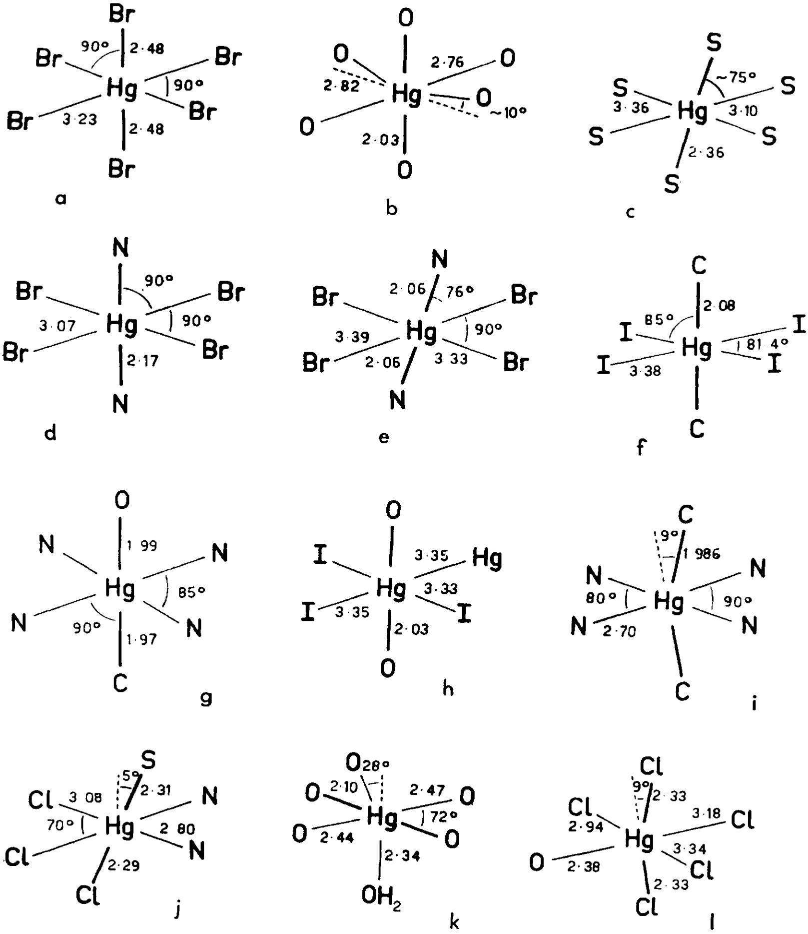


FIG. 5. *Examples of octahedral effective co-ordination based on digonal characteristic co-ordination of mercury:* (a) *mercuric bromide,*[27] (b) *orthorhombic mercuric oxide,*[44] (c) *cinnabar,*[63] (d) *cubic*[81] *and* (e) *orthorhombic*[82] *amidomercuric bromide,* (f) KI,Hg $(CN)_2$,[100] (g) *mercuric oxycyanide,*[98] (h) $(HgO)_2$,NaI,[56] (i) *mercuric cyanide,*[97] (j) *chloromercuric thiocyanate,*[69] (k) *mercuric sulphate monohydrate,*[58a] (l) *the addition compound of mercuric chloride with coumarin.*[13]

(red modification of mercuric iodide more stable than yellow one). Thus $x(S) > x(I)$. Digonal characteristic co-ordination is the most common because the majority of mercury compounds contain ligands with $x(L) \geqslant 2{\cdot}5$, and in this group octahedral effective co-ordination predominates. Even with very close approaches of the additional ligands, the co-ordination polyhedron is irregular. The most symmetrical is a square bipyramid which is flat along its tetrad axis. These octahedra are usefully classified into two groups depending whether the basic L–Hg–L skeleton is linear or bent. The first group contains the point groups C_i (very frequent), D_{4h}, C_{4v}, D_{2h}, C_{2v}, C_2, C_s, C_1, and the second the point groups C_s, C_{2v}, C_2, and C_1 (Figure 5). Tetrahedral effective co-ordination is very rare for $x(\mathrm{L}) > 2{\cdot}5$ and may be the result of steric factors in the crystal structure, *e.g.*, mercuric sulphate[24] or cyanomercuric oxide, $(\mathrm{CNHg})_2\mathrm{O}$.[25] The size of the atoms and packing conditions do influence the final arrangement, but $x(\mathrm{L})$ gives a satisfactory correlation for most structures.

5. Crystal and Molecular Structures of Mercury Compounds

(a) *Halogenomercurate*(II) *Compounds.*—The crystal structures of the mercuric halides are an example of a morphotropic transition dependent on the electronegativity of the halogen (4·0, 3·0, 2·8, and 2·5 for F, Cl, Br, and I, respectively). The structures of the chloride, bromide, and iodide are given in Figure 6. While mercury has distorted octahedral stereochemistry in the chloride, the structure is essentially molecular,[26] because two pairs of Hg · · · · · Cl distances (3·34 and 3·63 Å) are larger than the sum of the van der Waals radii (3·30 Å). Mercuric bromide has a layer structure of a deformed brucite type,[27] with six Hg–Br distances less than $R(\mathrm{Hg}) + R(\mathrm{Br})$.

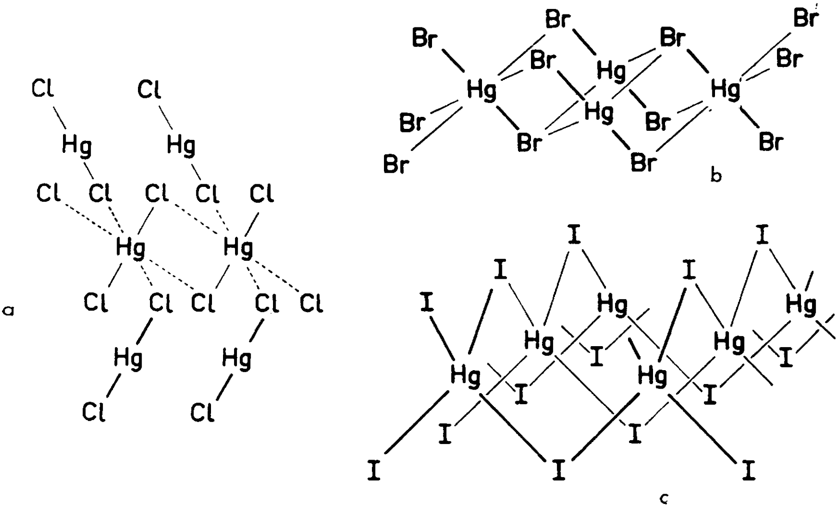


FIG. 6. *The environment of mercury in the crystal structures of mercuric chloride* (a), *bromide* (b), *and iodide* (c).

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[24] Bonefačić, *Croat. Chem. Acta.*, 1962, **34**, 119; 1963, **35**, 195.

[25] Ščavničar, *Z. Krist.*, 1963, **118**, 248.

[26] Braekken and Harang, *Z. Krist.*, 1928, **68**, 123; Braekken and Scholten, *Z. Krist.*, 1934, **89**, 448; Grdenić, *Arhiv Kem.*, 1950, **22**, 14.

[27] Verweel and Bijvoet, *Z. Krist.*, 1931, **77**, 122; Braekken, *Z. Krist.*, 1932, **81**, 152.

Thus the effective co-ordination is octahedral (Figures 5 and 6). The crystal structure of the iodide is composed of layers of fully corner-linked HgI_4 tetrahedra.[28] The mercuric halides are a good example of allotropy. The yellow unstable modification of the iodide crystallises with the $HgBr_2$ structure,[28,29] while the bromide probably has an unstable modification with the $HgCl_2$ structure.[29] In the vapour state, mercuric chloride, bromide, and iodide consist of linear molecules. The behaviour of the fluoride is not known, but should be similar in the vapour.

Halogenomercurates of the type $(M^{l+})_{b-2a/l}Hg_aX_b$ (M is a simple or complex cation, X is Cl, Br, I) are well known, the most common belonging to the classes $(M^+)_2HgX_4$ and $(M^+)HgX_3$. Recently some pyridinium tetrafluoromercurate(II) derivatives have also been made.[30] The properties of these compounds in solutions and in the melt have been extensively investigated[3] and have been recently reviewed.[31] Here the discussion is restricted to their crystal structures.

The electronegativity rule is again relevant. The characteristic co-ordination for chloro-complexes is generally digonal, though there are exceptions (see below), while that for iodo-complexes is trigonal or tetrahedral. Relatively little is known about the structures of crystalline bromonercurates, and the structures of the tetrafluoromercurates[30] have not yet been determined.

The crystal structure of yellow, tetragonal Ag_2HgI_4 has cubic close packed iodine atoms, with some of the tetrahedral holes filled by silver and mercury atoms in a regular manner. It is ordered below 50·7°, but the red cubic modification obtained above this temperature has a disordered zinc blende structure.[32] The isomorphous Cu_2HgI_4 shows analogous thermochromic properties. Tetraiodomercurate ion are found in $[Me_3S]_2HgI_4$,[33] but the complete structure has not yet been reported. The structure of $[Me_3S]HgI_3$ ($m = 3$) has been mentioned (Figure 2, Table 4), while $[Me_4N]HgI_3$ is isomorphous[34] with $[Me_4N]HgBr_3$, the structure of which [35] has been considered (Figure 4, Table 4).

There is one exception to the electronegativity rule conclusion that in chloromercurate the characteristic co-ordination of mercury should be digonal. The tetrachloromercurate of the alkaloid perloline contains tetrahedral $HgCl_4{}^{2-}$ ions.[36] In $[Me_4N]HgCl_3$, which is isomorphous[34] with the corresponding tribromo-derivative,[35] the characteristic co-ordination is trigonal (Table 3). A classification of the other known chloro-

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[28] Havighurst, *Amer, J. Sci.*, 1925, **10**, 556; Bijvoet, Claasen, and Karssen, *Proc. k. ned. Akad. Wetenschap.*, 1926, **29**, 529.

[29] van Nest, *Z. Krist.*, 1909, **47**, 263.

[30] Dotzer and Meuwsen, *Z. anorg. Chem.*, 1961, **301**, 79.

[31] Wait and Janz, *Quart. Rev.*, 1963, **17**, 225.

[32] Ketelaar, *Z. Krist.*, 1931, **80**, 190; 1934, (A), **87**, 435; Wells, ref. 1, pp. 174, 533.

[33] Fenn, Oldham, and Phillips, *Nature*, 1963, **198**, 381.

[34] Fatuzzo, Nitsche, Roetschi, and Zingg, *Phys. Rev.*, 1962, **125**, 514.

[35] White, *Acta Cryst.*, 1963, **16**, 397.

[36] Jeffreys, Sim, Burnell, Taylor, Corbett, Murray, and Sweetman, *Proc. Chem. Soc.*, 1963, 171.

mercurate structures has been given.[37] As $m = 2$ and $n = 6$ in all these compounds, then the configuration of the anion does not follow from the stoicheiometry. Thus K_2HgCl_4,H_2O does not contain discrete $HgCl_4^{2-}$ ions,[38,39] but distorted $HgCl_6$ octahedra form columns sharing two opposite edges (Figure 7a). There is a linear Cl–Hg–Cl skeleton (Hg–Cl 2·29 Å), with two pairs of longer bonds (2·29 and 3·13 Å).[38] If two of these

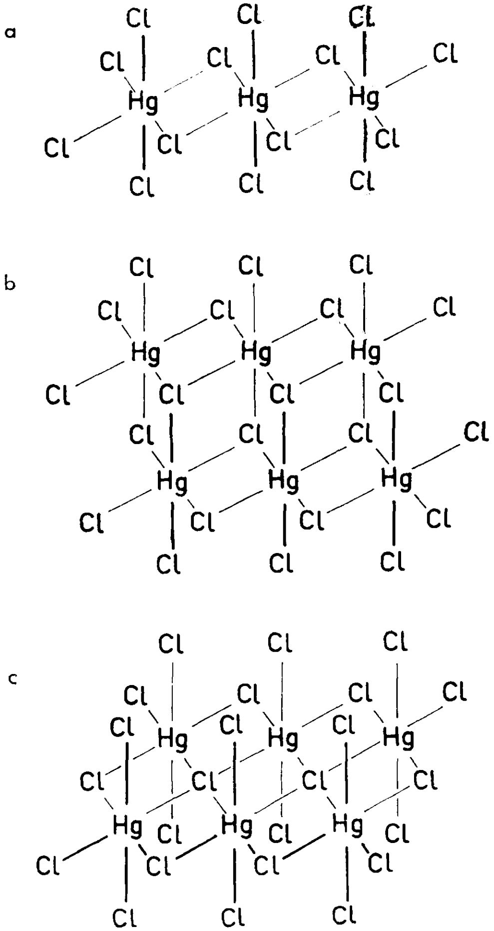

FIG. 7. *The chloromercurate anions in the crytsal structures of mercury chloro-complexes (idealised)*: (a) *ribbon of* $(HgCl_4)_a^{2a-}$ *in* K_2HgCl_4,H_2O,[38,39] (b) *twofold ribbon of* $(Hg_2Cl_6)_a^{2a-}$ *in* $NaHgCl_3$[40] *and related compounds*,[41,42] *and* (c) *layer of* $(HgCl_3)_a^{a-}$ *in* $NH_4{\cdot}HgCl_3$.[43]

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[37] Damm and Weiss, *Z. Naturforsch.*, 155, **10***b*, 535.

[38] Zvonkova, Samodurova, and Vorontsova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **102**, 1115.

[39] MacGillavry, de Wilde, and Bijvoet, *Z. Krist.*, 1938, *A*, **100**, 212.

linked octahedral columns are condensed by sharing three edges of an octahedron,the polymeric $(Hg_2Cl_6)_a^{2a-}$ ion is formed. This has been found in the structures of $NaHgCl_3$,[40] $NaHgCl_3,2H_2O$,[41] and $Na_2Hg_2Cl_5OH$ (Figure 7b).[42] NH_4HgCl_3 is not isomorphous with the sodium salt, but has a layer structure[43] in which $HgCl_6$ octahedra share four chlorine atoms (at 2·96 Å), and have colinear Hg–Cl bonds of 2·34 Å (Figure 7c). The corresponding cæsium compound has a cubic structure[38] in which mercury and cæsium occupy perowskite positions, the environment of each mercury being two chlorines at 2·29 Å and four at 2·70 Å. Three acids, $H_2HgCl_4,3H_2O$, $H_2Hg_2Cl_6,xH_2O$, and HHg_2Cl_5, have been identified in the solid state.[37] The first is isostructural with K_2HgCl_4,H_2O and thus may be written $(H_3O)_2HgCl_4,H_2O$. The detailed structures of the others are not known, but are considered to involve $HgCl_6$ octahedra.[37]

(b) *Mercuric Oxide, Oxyhalides, and Related Compounds.*—Both modifications, orthorhombic[44] and hexagonal[45], of mercuric oxide, are based on O·Hg·O·Hg·O·Hg zig-zag chains (Figure 8), which are planar in the former and spiral in the latter. In both $n = 6$ and $m = 2$, and the characteristic Hg–O distance is 2·03 Å. Four oxygen atoms from adjacent chains are only slightly closer than the sum of the van der Waals radii, *viz.* at 2·79 Å (two) and 2·90 Å (two) in the hexagonal form, and at 2·82 Å (four) in the orthorhombic form. The crystal structure parameters have been refined by neutron-diffraction methods, and hence are very accurate.

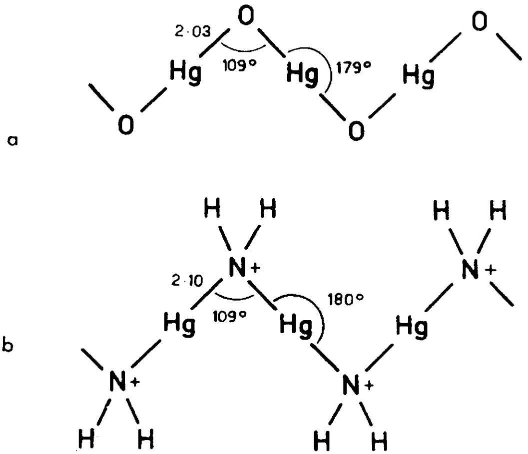

FIG. 8. *The characteristic mercury—oxygen and mercury—nitrogen chain structures:* (a) *mercuric oxide,*[44–47] (b) *the amidomercuric cation as,* e.g. *in* H_2NHgCl.[82]

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[40] Weiss and Damm, *Z. Naturforsch.*, 1954, **9***b*, 82.

[41] Ninković, *Bull. Inst. Sci. "Boris Kidrič", Belgrade*, 1957, **7**, 81; Malčić, *Bull, Inst. Nuclear Sci. "Boris Kidrič", Belgrade*, 1959, **9**, 115.

[42] Weiss and Damm, *Z. Naturforsch,*. 1955, **10***b*, 537.

[43] Harmsen, *Z. Krist.*, 1938, *A*, **100**, 208.

[44] Aurivilius, *Acta Chem. Scand.*, 1944, **8**, 523; 1956, **10**, 852.

[45] Aurivilius and Carlson, *Acta Chem. Scand.*, 1957, **11**, 1069; 1958, **12**, 1297.

TABLE 5. *Structure types of mercuric oxyhalides* $Hg_aCl_2O_{a-1}$ *in relation to oxygen : mercury atomic ratio*

a	Formula	O/Hg	Structure	Ref.
1	$HgCl_2$	0	Cl–Hg–Cl	26
3/2	$2HgCl_2,HgO$	1/3	$(ClHg)_3O^+Cl^-$	49, 50
3	$HgCl_2,2HgO$	2/3	$Hg(OHgCl)_2$	51
4	$HgCl_2,3HgO$	3/4	Related to kleinite, a naturally occuring oxychloride containing nitrogen. Probably distorted tridymite-like structure	52, 44, 47, 2
5	$HgCl_2,4HgO$	4/5	$(Hg_4Cl_4)^{4+}(Hg_6O_8)^{4-}$	53
5	$HgBr_2,4HgO$	4/5	$(Hg_4Br_4)^{4+}$ $(Hg_6O_8)^{4-}$	53*
∞	HgO	1/1	Chains of Hg–O–Hg–O–Hg–O	44—47

* *Added in Proof.*—The structure of $HgBr_2,4HgO$, as determined recently by Aurivilius (*Arkiv Kemi*, 1965, **23**, 469), is best defined as $Hg(OHg)_4Br_2$.

Many basic mercuric halides or oxyhalides of the general formula $Hg_aCl_2O_{a-1}$ (a = 1·5, 2, 3, 4, 5) have been described.[48] Recent investigations have shown that the characteristic co-ordination is digonal [x(Cl) = 3·0, x(O) = 3·5], and the effective co-ordination is tetrahedral or octahedral.[49–53] The structures are strikingly dependent on the oxygen : mercury ratio, and each species has its own distinct structure (Table 5).

With increasing oxygen content, the structures become more differentiated into mercury–chlorine and mercury–oxygen structural elements, until complete separation into alternating layers of complex halide cations and complex oxide anions occurs[53] with an atomic ratio O:Hg = 4:5. The structure of $2HgCl_2,HgO$ contains the tris(chloromercuri)oxonium ion. This should be pyramidal if the Hg–O links are covalent single bonds. However *X*-ray diffraction has shown the ion to be approximately planar[49,50] (Figure 9c), which might indicate partial double bond character for the Hg–O links. Neutron-diffraction analysis[54] shows a slight deviation from planarity. The O–Hg–Cl bonds are linear (Hg–O = 2·03 Å, Hg–Cl = 2·28 Å) and mercury has a very distorted octahedral environment. The structures of the analogous tris(methylmercuri)oxonium compounds[55] are now being investigated.

[46] Aurivilius and Heidenstamm, *Acta Chem. Scand.*, 1961, **15**, 1993.

[47] Aurivilius, *Acta Cryst.*, 1956, **9**, 685.

[48] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 4. Longmans, Green and Co., London, 1957.

[49] Weiss, Nagorsen, and Weiss, *Z. Naturforsch.*, 1953, **8b**, 162; Weiss, Nagorsen, and Weiss, *Z. anorg. Chem.*, 1953, **274**, 151.

[50] Grdenić and Šćavničar, *Nature*, 1953, **172**, 584; Šćavničar and Grdenić, *Acta Cryst.*, 1955, **8**, 275.

[51] Šćavničar, *Acta Cryst.*, 1955, **8**, 379.

[52] Heritsch, *Tschermaks mineralog. u. petrolog. Mitt.*, 1949, **1**, 300.

[53] Weiss, Nagorsen, and Weiss, *Z. Naturforsch.*, 1954, **9*b***, 81.

[54] Aurivilius, *Acta Cryst.*, 1963, **16**, A25.

[55] Grdenić and Zado, *Croat. Chem. Acta*, 1957, **29**, 425; Grdenić and Zado, *J.*, 1962, 521.

Mercuric oxide forms compounds with salts other than those of mercury. The crystal structure of $(HgO)_2,NaI$ consists of layers formed from HgO chains intermingled with iodide ions.[56] The effective co-ordination of each mercury is octahedral, if the fairly close approach of a mercury atom in an adjacent layer is considered to be significant (Hg · · · · · Hg = 3·334 Å).

(c) *Salts of Oxy-acids.*—Digonal characteristic co-ordination is expected [x(O) = 3·5]. The following crystal structures have been investigated:

(1) anhydrous salts: $HgSO_4$[24,57]
(2) hydrated salts: $HgSO_4,H_2O$[58]
(3) basic salts: $HgSO_4,2HgO$[59–61], $2HgSO_4,HgO,2H_2O$,[61]
$Hg(XO_3)_2,HgO,H_2O$[62] (X is Cl, Br)
(4) complex or double salts: $K_3[Hg(NO_2)_4]NO_3$.[23]

Mercuric sulphate and selenate are isomorphous, as are dioxotrimercuric sulphate, selenate, and chromate.[57]

In anhydrous mercuric sulphate the stereochemistry of mercury is distorted tetrahedral. The O–Hg–O bond angles in two mutually normal planes are 159° and 144°, while the Hg–O bond lengths are 2·14 (two) for the former, and 2·08 and 2·28 Å for the latter OHgO groups. The hydrate has a completely different structure based[58a] on H_2OHgO_5 octahedra arranged in parallel chain, which are crosslinked through sulphate ions. The characteristic H_2O–Hg–O bonds are bent to 169°, the H_2O–Hg and Hg–O distances being 2·24 and 2·17 Å, respectively.[58b] The Hg–O distances of the more remote neighbours are 2·50 Å (two) and 2·51 Å (two) [N.B. $R(Hg^{2+}) + R(O^{2-}) = 2{\cdot}44$ Å]. The structure of the basic mercuric sulphate, $Hg_3O_2SO_4$, (turpeth mineral)[59] has been solved quite recently.[60,61] The structure is formed from layers of polymeric mercurioxonium cations (Figure 9d) with sulphate anions between them. Thus the compound is $(Hg_3O_2)_a^{2a+}(SO_4^{2-})_a$. The characteristic Hg–O distances are 2·03 Å, and mercury has octahedral effective co-ordination. A polymeric oxonium ion (Figure 9b) has also been found[62] in crystals of basic mercuric chlorate and bromate monohydrate, $Hg(XO_3)_2,H_2O$, and the correct formulation of these salts is therefore $(HgOH)_a^{a+}(XO_3^-)_a$. The occurrence of mercurioxonium ions in basic mercuric salts is thus fairly general. Similar behaviour is found for ammonia derivatives of mercury compounds, where mercuriammonium ions occur. The compound $2HgSO_4,HgO,2H_2O$ has a complex structure[61] with two crystallographically different mercury atoms.

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[56] Aurivilius, *Acta Chem. Scand.*, 1960, **14**, 2196; 1964, **18**, 1305.

[57] Aurivilius and Malmros, *Acta Chem. Scand.*, 1961, **15**, 1932.

[58] (a) Bonefačić, *Acta Cryst.*, 1961, **14**, 116; (b) Templeton, Templeton, and Zalkin, *Acta Cryst.*, 1964, **17**, 933 (refinement by the use of three-dimensional *X*-ray diffraction data).

[59] Paić, *Bull. Soc. chim. France*, 1930, **47**, 1254; Paić, *Ann. Chim.* (*France*), 1933, **19**, 427.

[60] Nagorsen, *Angew. Chem.*, 1962, **74**, 119.

[61] Bonefačić, Thesis, University of Zagreb, 1963; Bonefačić, *Acta Cryst.*, 1963, **16**, A30.

[62] Weiss, Lyng, and Weiss, *Z. Naturforsch.*, 1960, **15b**, 678.

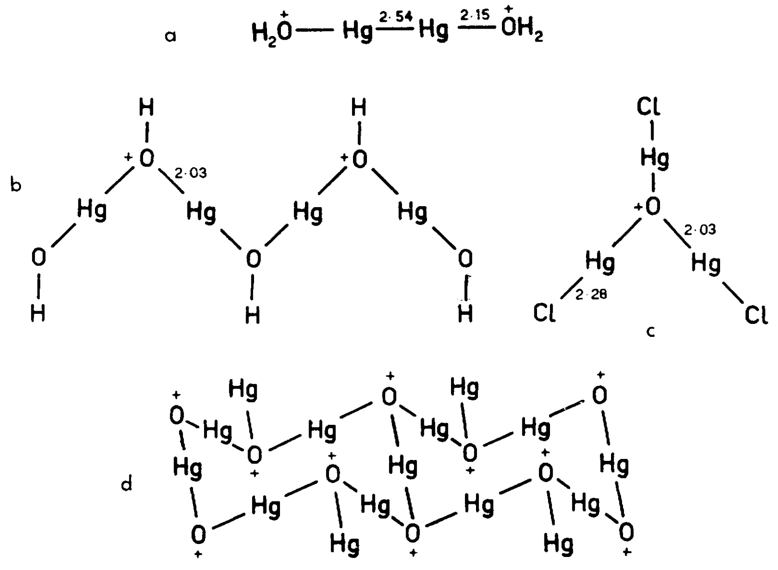

FIG. 9. *The oxonium ions in the crystal structures of different mercury compounds:* (a) *the hydrated mercurous ion in* $Hg_2(NO_3)_2,2H_2O$,[16] (b) *the hydroxomercuric ion in basic mercuric chlorate and bromate*,[62] (c) *the tris(chloromercuri)oxonium ion in* $2HgCl_2,HgO$,[49,50] *and* (d) *a* $(Hg_3O_2)_a{}^{2a+}$ *layer in the basic mercuric sulphate.*[60,61]

Only one of them has Hg–O bond lengths corresponding to covalent bond formation ($Hg–OH_2$ = 2·12 Å). All other Hg–O distances are larger than 2·41 Å. There is no characteristic mercuri-oxide chain in the structure, which must be considered to be essentially ionic.

The structure[23] of potassium tetranitritomercurate(II) nitrate also seems to be essentially ionic. The nitrogen atoms of the nitrite ions surround mercury tetrahedrally, but eight oxygen atoms at 2·4 Å do not follow necessarily the tetrahedral symmetry.

(d) *Compounds with Mercury–Sulphur Bonding.*—As the electronegativity of sulphur is 2·5, both tetrahedral and digonal characteristic co-ordination is observed. The stable modification of mercuric sulphide (cinnabar) has octahedral effective co-ordination.[63] The compound is isostructural with the hexagonal form of mercuric oxide.[45] The characteristic S–Hg–S bonds are bent to an angle of 172·4°, and the Hg–S length (2·36 Å) is equal to the sum of the digonal covalent radii. Two other pairs of Hg–S distances (3·10 and 3·30 Å) are less than the sum of the van der Waals radii. Both black mercuric sulphide, obtained by precipitation from solution, and metacinnabarite crystallise as the metastable cubic modification, the structure of which is related to those of cadmium and zinc sulphides.

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[63] Aurivilius, *Acta Chem. Scand.*, 1950, **4**, 1413.

Tetrathiocyanatomercurates contain the tetrahedral $Hg(SCN)_4^{2-}$ ion, in which the Hg–S bond lengths are equal to the sum of the tetrahedral covalent radii. The double salt, $Hg(SCN)_2,Ni(SCN)_2,2H_2O$, has been shown[64] to be nickel tetrathiocyanatomercurate(II) dihydrate. It contains tetrahedral $Hg(SCN)_4^{2-}$ ions (Hg–S = 2·50 Å), and nickel cations in an octahedral environment of two oxygen and four thiocyanate nitrogen atoms (Ni–O and Ni–N = 2·08 Å). In the compound $KHg(SCN)_3$, mercury has digonal characteristic and distorted tetrahedral effective co-ordination. The characteristic S–Hg–S linkage is bent (155°), and two sulphurs (at 2·78 Å) from adjacent thiocyanate ions complete a distorted tetrahedral environment[65] of the type in Figure 3f. The analogous ammonium salt is isostructural, and mercuric dithizonate has a similar structure.[66] The crystal chemistry of mercuric thiocyanate has been discussed.[67,68] Mixed derivatives of the type XHgSCN (X is Cl or Br) have digonally bonded mercury in distorted octahedral environment[69] (Figure 5f).

In dimethylthiomercury, $Hg(SMe_2)_2$, mercury has two short linear bonds and a unique square pyramidal effective co-ordination.[70] The structures of RSHgCl[71] and $(EtS)_2Hg$[72] seem to need further refinement.

The structure of the sulphochloride $Hg_3S_2Cl_2$ consists of layers of polymeric mercurisulphonium cations and halide ions[73] and is similar to that of the basic mercuric sulphate shown in Figure 9d. The S–Hg–S bonds are linear (Hg–S = 2·44 Å) with the sulphur atom at the apex of a trigonal pyramid and an Hg–S–Hg angle of *ca.* 95°. The analogous mercuric seleno- and tellurohalides have similar structures. Mercurisulphonium ions probably occur as commonly as the oxonium analogues. The sulphonium compounds are more stable, tris(methylmercuri)sulphonium ions having exceptional stability.[74]

(e) *Compounds with Mercury–Nitrogen Bonding*.—The large number of mercury compounds with ammonia and its derivatives were originally classified into three groups:[75] (1) mercuric ammines, *e.g.* "fusible white precipitate" or the various addition products of amines with mercuric salts; (2) mercuric amides, *e.g.* "infusible white precipitate" and analogous

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[64] K'uo-Hsiang Chou and Porai-Koshits, *Kristallografiya*, 1960, **5**, 462.

[65] Zhdanov and Sanadze, *Zhur. fiz. Khim.*, 1952, **26**, 469.

[66] Harding, *J.*, 1958, 4136.

[67] Zhdanov, Communications au XIIIe Congrès International de Chimie Pure et Appliquee, Stockholm, 1953, Editions de l'Academie des Sciences de l'U.R.S.S., Moscou, 1953, p. 175.

[68] Zhdanov and Zvonkova, *Trudy Inst. Krist. Akad. Nauk S.S.S.R.*, 1954, **10**, 30.

[69] Zvonkova and Zhdanov, *Zhur. fiz. Khim.*, 1952, **26**, 586.

[70] Bradley and Kunchur, *Chem. and Ind.*, 1962, 1240; *J. Chem. Phys.*, 1964, **40**, 2258.

[71] Johansson, *Arkiv Kemi Min., Geol., Ser. A*, 1939, **13**, 1.

[72] Wells, *Z. Krist.*, 1937, *A*, **96**, 43[illegible].

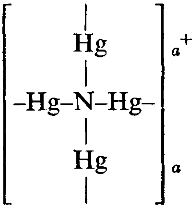
[73] Puff and Kohlschmidt, *Naturwiss.*, 1962, **49**, 299; Puff and Küster, *Naturwiss.*, 1962, **49**, 299; **49**, 464.

[74] Grdenić and Markušić, *J.*, 1958, 2434.

[75] Ley in Abegg und Auerbach, "Handbuch der anorganischen Chemie," vol. 2, Part 2, S. Hirzel, Leipzig, 1906, p. 666.

amidomercuric derivatives; (3) Millon's base and its salts. This classification still remains good in principle. *X*-Ray analysis has shown that the structure of these compounds are generally based on substituted ammonium ions. Brodersen and Rüdorff have given the following classification:[76]

(1) isolated linear groups: $^{+}H_3N\text{–}Hg\text{–}NH_3^{+}$	*e.g.* "fusible white precipitate $Hg(NH_3)_2Cl_2$
(2) polymeric zig-zag chains: $\text{—}^{+}NH_2\text{–}Hg\text{–}NH_2^{+}\text{–}Hg\text{–}$	*e.g.* infusible white precipitate $HgNH_2Cl$
(3) hexagonal puckered layers: $[Hg_3(NH)_2]_a^{2a+}$	*e.g.* dimercury imidobromide Hg_2NHBr_2, *viz.* $[Hg_3(NH)_2]_a^{2a+}(Br^-)_a(HgBr_3^-)_a$
(4) three-dimensional framework:	*e.g.* Millon's base and its salts



$$\left[\begin{array}{c} | \\ Hg \\ | \\ \text{–}Hg\text{–}N\text{–}Hg\text{–} \\ | \\ Hg \\ | \end{array}\right]_a^{a+}$$

tetrahedra

$(Hg_2N)OH,2H_2O$

$(Hg_2N)I,nH_2O$

There are also some Hg–N compounds in which nitrogen apparently retains an unshared electron pair, *e.g.* mercuric derivatives of acid amides and hydrazides.[77]

In many of the known structures the mercury–nitrogen bonds are colinear, mercury having octahedral effective co-ordination. The Hg–N bond length is equal to or less than the sum of the covalent radii. Hence the Hg–N bond is covalent and the positive charge is located on nitrogen. Four adjacent atoms or ions approach closer than the sum of the van der Waals radii to complete the co-ordination octahedron (*e.g.* Figure 5d, e).

Diamminemercuric halides $(NH_3)_2HgX_2$ (X is Cl or Br) have a statistical cubic structure, built of unit cubes of halide ions.[78] In each cube, one of the six possible positions at the centre of a face is occupied by a mercury atom, so that the linear $^{+}H_3N\text{–}Hg\text{–}NH_3^{+}$ ions are randomly orientated along one of the three axes with nitrogen atoms approximately at the centre of each cube. The structures of the analogous alkylamine derivatives[79] are still unknown. The complex Py_2HgCl_2 is less stable, losing pyridine at room temperature. The Hg–N distance (2·60 Å) is considerably larger than the sum of the covalent radii. There are two short (2·34 Å) and two longer (3·25 Å) Hg–Cl bonds.[80]

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[76] Brodersen and Rüdorff, *Z. Naturforsch.*, 1954, **9b**, 164; Brodersen, *Acta Cryst.*, 1955, **8,** 723.

[77] Brodersen, *Chem. Ber.*, 1957, **90,** 2703; Brodersen und Kunkel, *Z. anorg. Chem.*, 1959, **298,** 34.

[78] Bijvoet and MacGillvary, *Chem. Weekblad*, 1935, **32,** 346; MacGillvary and Bijvoet, *Z. Krist.*, 1936, *A*, **94,** 231.

[79] Hofmann and Marburg, *Annalen*, 1899, **305,** 196.

[80] Grdenić and Krstanović, *Arhiv Kem.*, 1955, **27,** 143.

Amidomercuric chloride and bromide are actually salts of a polymeric mercuriammonium ion (Figure 8b). The bromide is cubic when pure,[81] otherwise it is orthorhombic, as is the chloride.[82]

Dimercurihydrazonium chloride, $Hg_2(N_2H_2)Cl_2$, has a layer structure with a *trans*-conformation, and its formation may be interpreted as resulting from dehydrogenation of aminomercuric chloride:[83]

$$2HgNH_2Cl = Hg_2(N_2H_2)Cl_2 + H_2$$

An analogous chain structure has been found in ethylenediamine-mercury(II) chloride.[84] In "imidomercury bromide", Hg_2NHBr_2, layers of $HgBr_3^-$ ions alternate with $[Hg_3(NH)_2]_a^{2a+}$ layers which also contain bromide ions.[76] The compound is therefore written: $[Hg_3(NH)_2]_a^{2a+}$ $(Br^-)_a$ $(HgBr_3^-)_a$. The cation layer has the same structure as $(Hg_3O_2)_a^{2a+}$ (Figure 9), oxygen atoms being replaced by NH groups. There are two kinds of effective mercury co-ordination in the structure, octahedral and trigonal bipyramidal. Steric conditions do not allow the accommodation of an anion other than bromide.

Millon's base and its salts are known in cubic[85a] and hexagonal[85b,86] modifications. In the cubic form, only the nitrate is stable, whereas the hydroxide and other salts are stable in the hexagonal modification.[86] The cubic modification has a cristobalite structure, and the hexagonal form a tridimite type of structure in which silicon is replaced by nitrogen and oxygen by mercury. The NHg_2 framework so formed is a polymeric cation, $(NHg_2)_a^{a+}$, having interstitial holes sufficiently large to accommodate different anions. A regular tetrahedron of mercury atoms surrounds each nitrogen (Hg–N = 2·04—2·09 Å, depending on the anion). Additional close approaches give mercury octahedral effective co-ordination. The structure has been confirmed by infrared spectroscopy[87] and anion-exchange experiments.[88] The fluoride, $HgNH_2F$, is a double fluoride of the ammonium ion and Millon's base[89] $[(NHg_2)F,NH_4F]$. The interstitial space is sufficiently large to accommodate ammonium as well as fluoride ions. The hydrated acid fluoride[89] should probably be formulated $(NHg_2)F,(H_3O)F$, while the nitrate, sulphate, phosphate, and

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[81] Rüdorff and Brodersen, *Z. anorg. Chem.*, 1952, **270**, 145; Brodersen and Rüdorff, *Z. anorg. Chem.*, 1954, **275**, 141.

[82] Lipscomb, *Acta Cryst.*, 1951, **4**, 266; Nijsen and Lipscomb, *Acta Cryst.*, 1952, **5**, 604.

[83] Brodersen, *Z. anorg. Chem.*, 1956, **285**, 5; Brodersen, *Z. anorg. Chem.*, 1957, **290**, 24.

[84] Brodersen, *Z. anorg. Chem.*, 1959, **298**, 142.

[85] (a) Lipscomb, *Acta Cryst.*, 1951, **4**, 156; (*b*) Nijsen and Lipscomb, *Acta Cryst.*, 1954, **7**, 103.

[86] Brodersen and Rüdorff, *Angew. Chem.*, 1952, **64**, 617; Rüdorff and Brodersen, *Z. anorg. Chem.*, 1953, **274**, 323.

[87] Brodersen and Becher, *Chem. Ber.*, 1956, **89**, 1487.

[88] Arora, Lipscomb, and Sneed, *J. Amer. Chem. Soc.*, 1951, **73**, 1015; Seeger and Pualuan, *Bol. Soc. Chilena Quim.*, 1962, **12**, 25.

[89] Brodersen and Rüdorff, *Z. anorg. Chem.*, 1956, **287**, 24.

arsenate should have a similar structural framework.[90] The structure of the degradation product of Millon's base has been studied.[91]

The structures of a number of phosphine and arsine derivatives of mercuric salts have also been investigated.[92] In $PbHgP_{14}$ mercury is surrounded by four phosphorus atoms in a slightly deformed tetrahedron[93] with Hg–P = 2·52 Å.

(f) *Compounds with Mercury–Carbon Bonding.*—Potassium tetracyanomercurate(II), which is isomorphous to the analogous zinc compound,[94] was the first mercury compound to be examined by *X*-ray methods, but the exact structure is still not known. Mercuric cyanide is molecular rather than ionic.[95] The full structure was determined by Zhdanov and Shugam,[96] and neutron diffraction has subsequently been used to obtain the light-atom positions accurately.[97] The $Hg(CN)_2$ molecules, which are linear in solution or vapour, are bent in the crystal lattice because of Hg–N interactions. The effective co-ordination is distorted octahedral (Figure 5), the C–Hg–C bond angle being 171°, and the Hg–C and Hg–N bond lengths 1·986 and 2·70 Å, respectively. The former is significantly shorter than the sum of the digonal covalent radii, hence the Hg–C link may have some double-bond character. Mercuric oxycyanide, $HgO,Hg(CN)_2$, is actually cyanomercuric oxide, $(NCHg)_2O$.[98,99] Mercury has digonal characteristic co-ordination (Hg–C = 1·97 Å), but the two mercury atoms in each $(NCHg)_2O$ unit have different effective co-ordination numbers, *viz.* tetrahedral (C, 3O) and octahedral (C, O, 4N). The closest mercury-to-oxygen approach between two molecules, 2·53 Å, is exceptionally short for an intermolecular contact (cf. Hg–O bond length of 2·04 Å), but this does not influence the Hg–C length. However, in the structure of $KI,Hg(CN)_2$ the close approach of four iodine atoms (3·383 Å) causes a slight lengthening of the Hg–C bonds[100] (2·079 Å).

Comparatively little is known about the crystal structures of R_2Hg organomercurials. Both phenyl radicals of diphenylmercury are coplanar[101,102] in the crystal structure, but this seems less likely in solution.[19–21] All cyclic organomercurials so far investigated contain essentially linear C–Hg–C bonds. Thus "*o*-phenylenemercury" which was considered

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[90] Airoldi, *Ann. chim. (Rome)*, 1958, **48**, 491.

[91] Weber, *Naturwiss.*, 1957, **44**, 465.

[92] Evans, Mann, Peiser, and Purdie, *J.*, 1940, 1209.

[93] Krebs and Ludwig, *Z. anorg. Chem.*, 1958, **294**, 257.

[94] Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 774.

[95] Hassel, *Z. Krist.*, 1926, **64**, 218.

[96] Zhdanov and Shugam, *Zhur. fiz. Khim.*, 1945, **19**, 433.

[97] Hvoslef, *Acta Chem. Scand.*, 1958, **12**, 1568.

[98] Šćavničar, *Acta Cryst.*, 1960, **13**, *A*, 57; Šćavničar, *Z. Krist.*, 1963, **118**, 248.

[99] Weiss and Hofmann, *Z. Naturforsch.*, 1960, **15*b***, 679.

[100] Kruse, *Acta Cryst.*, 1963, **16**, 105.

[101] Kitaigorodskii and Grdenić, *Izvest. Akad. Nauk S.S.S.R., Odtel. Khim. Nauk.*, 1948, 262.

[102] Ziolkowska, *Roczniki Chem.*, 1962, **36**, 1314; Ziolkowska, Myasnikova, and Kitaigorodskii, *Zhur. strukt. Khim.*, 1964, **5**, 737.

to be 9,10-dimercura-anthracene is actually trimeric,[103] the molecule containing six linear C–Hg–C bonds.[104] "Pentamethylenemercury" for which a structure having a ring of five carbons and one mercury atom has been suggested,[105] is actually dimeric,[106] but is not isostructural with mercury diethylene oxide.[107] The latter has a twelve-membered ring, in which the C–Hg–C bonds are slightly bent (176°), due to mercury–oxygen interaction (Hg · · · · · O = 2·21 Å). "2,2-Biphenylenemercury" is not 9-mercurafluorene, but is a cyclic tetramer.[108]

The crystal structures of mixed organomercurials RHgX (X is Cl, Br, or I) are characterised by linear C–Hg–X bonds and octahedral effective co-ordination. In alkyl derivatives the structure is dictated by a tendency for parallel alignment of CHgX groups.[109] There is disagreement between the Hg–Cl distance for MeHgCl as obtained by *X*-ray methods (solid state)[109] and microwave spectroscopy (vapour state)[110] (2·50 and 2·282 Å, respectively). Such a difference between the bonding in the two states seems improbable. The *X*-ray value is doubtful, since it was obtained from two-dimensional Fourier synthesis from a small number of reflexions. Thus a three-dimensional Fourier synthesis of the electron density is desirable. For methylmercuric bromide the difference is much smaller [2·50 Å (*X*-ray), 2·406 Å (microwave)]. Chlorovinylmercuric bromide has a similar structure[111] with an Hg–Br length of 2·43 Å.

The available data suggests that the Hg–C bond is longer in aryl- than in alkyl-mercuric derivatives, and thus may be more ionic in the former. For crystalline aryl derivatives, the dependence of the Hg–C bond length on the nature and position of substituents in the aromatic ring has yet to be determined. A common property of most known organomercurials is a low ability to accept further ligands. Thus, in crystals of mixed mercurials the additional Hg · · · · · X contacts are only slightly less than the sum of the van der Waals radii. However, perfluoroalkylmercurials[112] and perfluoroarylmercurials[113] do give co-ordination derivatives. Thus $Hg(CF_3)_2$ forms the complex anions,[112] $Hg(CF_3)_2X^-$ and $Hg(CF_3)_2X_2^{2-}$ (X is halogen), while $Hg(C_6F_5)_2$ forms bipy$Hg(C_6F_5)_2$.[113]

(g) *Mercurous Compounds.*—Derivatives containing mercury bonded to halogens, oxygen, and nitrogen are known. The compounds are of particular interest because of the presence of metal–metal bonding. Although mercury has a formal oxidation state of one, the structures are based on

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[103] Wittig and Bickelhaupt, *Chem. Ber.*, 1958, **91**, 883.
[104] Grdenić, *Chem. Ber.*, 1959, **92**, 231.
[105] Hilpert and Grüttner, *Ber.*, 1914, **47**, 186.
[106] Grdenić and Goričan, unpublished molecular weight determination.
[107] Grdenić, *Acta Cryst.*, 1952, **5**, 367.
[108] Wittig and Lehmann, *Chem. Ber.*, 1951, **90**, 876.
[109] Grdenić and Kitaigorodskii, *Zhur. fiz. Khim.*, 1949, **23**, 1162.
[110] Gordy and Sheridan, *J. Chem. Phys.*, 1954, **22**, 92.
[111] Kitaigorodskii, *Izvest. Akad. Nauk. S.S.S.R.*, *Otdel. khim. Nauk*, 1947, 259.
[112] Lagowski, *Quart. Rev.*, 1959, **13**, 233, and references therein.
[113] Chambers, Coates, Livingstone and Musgrave, *J.*, 1962, 4367.

digonally co-ordinated mercury as in mercuric compounds. The presence of linear XHg·HgX bonds in mercurous halides has been long established,[28] but less is known about the structures of other derivatives.

The most important interatomic distances in the structures of the mercurous halides are given in Table 6. The Hg–Hg bond distance increases from fluoride to iodide, although the opposite is expected because of the probable higher ionic character of the Hg–F bond. This behaviour can be attributed to the repulsion between the electron clouds of the ligand and the secondary mercury atoms, *i.e.* by a *trans*-influence, which therefore weakens the Hg–Hg bond more in the iodide than in the fluoride. However, the Hg–Hg bond distance of 2·90 Å found in mercurous diacetylhydrazide,[114] $Hg_2N_2(CO{\cdot}CH_3)_2$, cannot be explained in this way, as the nitrogen electron cloud is unlikely to exert such a strong repulsive influence, and this behaviour is not yet understood.

TABLE 6. *Interatomic distances in crystal structure of mercurous halides*

	Hg_2F_2	Hg_2Cl_2	Hg_2Br_2	Hg_2I_2
Hg–X	2·31[c]	2·52[a]; 2·41[b]	2·53[a]; 2·45[b]	2·68[a]
Hg–Hg	2·43[c]	2·53[a]; 2·45[b]	2·58[a]; 2·50[b]	2·69[a]
X · · · X along the (*c*-axis direction)	no contact	3·33[a]; 3·70[b]	3·40[a]; 3·55[b]	3·55[a]

[a]Havighurst, *J. Amer. Chem. Soc.*, 1926, **48,** 2113. [b]Belov and Mokeeva, *Trudy Inst. Krist,. Akad. Nauk S.S.S.R.*, 1949, **5,** 57. [c]Grdenić and Djordjević, *J.*, 1956, 1316.

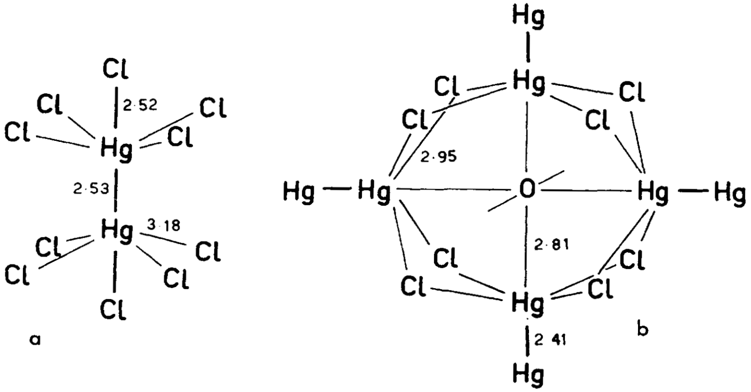

FIG. 10. *The environment of mercury* (a) *in mercurous chloride*[28] *and* (b) *in mercurous oxychloride* Hg_6Cl_4O (*mineral eglestonite*[115]).

The occurrence of the oxonium ion, $[H_2O{\cdot}Hg{\cdot}Hg{\cdot}OH_2]^{2+}$, in the structure of mercurous nitrate dihydrate[16] shows that the mercurous ion is a strong electron acceptor along the metal–metal bond axis. The Hg–O distances are close to the sum of the covalent radii. Further examples of

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[114] Brodersen and Kunkel, *Chem. Ber.*, 1958, **91,** 2698.

the Hg–Hg-to-oxygen relationship are found in the structures of mercurous oxychlorides. The *X*-ray diffraction pattern of the mineral eglestonite is best interpreted by the formula Hg_6Cl_4O.[115] The effective co-ordination is similar to that of mercurous chloride (Figure 10). Two chlorine atoms are replaced by one oxygen atom and the Hg–Hg groups are reorientated. The oxygen is quite loosely accommodated in an octahedral hole at the centre of the cube, the Hg–O distance being 2·80 Å, which is more than the greatest Hg–O distance observed at all (2·66 Å in the addition compound of mercuric chloride and 1,4-dioxan[116]). The Hg–Hg distance is 2·41 Å. Oxymercuric mercurous chloride,[117] $2HgO,Hg_2Cl_2$, consists of slightly deformed mercurous chloride molecules and mercuric oxide chains with rather close intermolecular approaches. The dipole moment of mercurous trichloroacetate, 2·65 D, excludes a rigid chelate structure.[118]

The nature of "alkylmercurous" compounds (RHg) is not yet fully understood. To explain their high electrical conductivity, it has been suggested that they are organic metals.[119] Recent results exclude their formulation as organomercurous compounds, RHg·HgR, or as amalgams between mercury and organic free radicals.[120]

(h) *Amalgams.*—In a comprehensive discussion of the structural chemistry of mercury, the amalgams should not be entirely omitted. As alloys they have to be treated from the standpoint of the theory of metals, and their structural inter-relations in terms of the crystal chemistry of intermetallic phases. Most of them have a peculiar structure in which some mercury atoms are grouped more closely than others. Characteristic arrangements are triangles and pentagons in Mn_2Hg_5,[121] isolated squares in Na_3Hg_2,[122] or squares shared in puckered ribbons in NaHg.[122]

6. General Concepts of the Stereochemistry of Mercury

There are two main features in the stereochemistry of mercury which have to be explained: (1) reduction of the characteristic co-ordination number from six or four (as with zinc and cadmium) to two, and (2) additional ligand approaches leading to distorted effective co-ordination, generally distorted octahedral.

An explanation of both phenomena has been given by Orgel.[8,9] In the third transition series *d–s* mixing is more energetically favourable for d^{10} ions than in the first or second series. Hybridisation of the d_{z^2} and *s* orbitals gives two new orbitals, and, depending on which of these is filled,

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[115] Hedlik, *Tschermaks mineralog. u. petrolog. Mitt.*, 1949, **1**, 378.
[116] Hassel and Hvoslef, *Acta Chem. Scand.*, 1954, **8**, 1953.
[117] Šćavničar, *Acta Cryst.*, 1956, **9**, 956.
[118] Davidson and Sutton, *J.*, 1942, 565.
[119] Coates, *Quart. Rev.*, 1950, **4**, 217.
[120] Gowenlock and Trotman, *J.*, 1957, 2114; Gowenlock, Pritchard, Jones, and Ovenall, *J.*, 1958, 535.
[121] de Wet, *Acta Cryst.*, 1961, **14**, 733.
[122] Nielsen and Baenziger, *Acta Cryst.*, 1954, **7**, 277; Duwel and Baenziger, *Acta Cryst.*, 1955, **8**, 705; 1960, **13**, 476.

mercury can either form two short strong bonds in the **z** direction and four weak ones in the **xy** plane, or four strong ones in the **xy** plane and two weak in the **z** direction. The former arrangement is preferred, though no explanation is yet available. The tendency for digonal co-ordination can also be explained[123] by the fact that mercury has a larger *s–p* separation than cadmium or zinc, which makes sp^3 or sp^2 hybridisation more difficult for mercury, hence favouring *sp* hybridisation. Nyholm[123] has shown that, while the $d^{10} \rightarrow d^9s$ separation favours the third series when the charge on the metal is high, the order is not maintained when the charge is low. However, in the latter case the $d^{10}s \rightarrow d^{10}p$ separation in the third series is high, favouring *sp* hybridisation.

For distorted octahedral mercury complexes based on digonal characteristic co-ordination, the residual charge on mercury in the linear L_2Hg skeleton must be reasonably high or further co-ordination would not occur. Thus it is valid to use *ds* hybridisation to explain the stereochemistry. However the low acceptor properties of organomercurials show that in these compounds the charge on mercury is low, and *sp* hydridisation probably predominates.

Added in Proof.—Some structural data have been obtained recently confirming the main structural principles outlined above.

5(b). It has been established by *X*-ray single-crystal and powder methods that the alkali metal oxomercurates(II) are isostructural.[125] The HgO_2^{2-} ion is linear with an Hg–O bond length of 1·95 Å. There are no other mercury-to-oxygen contacts in the structure and the effective co-ordination of mercury is octahedral if four equidistant mercury atoms at 3·42 Å are included. An interesting oxygen bridge structure has been found for the dimeric 1:1 tri(phenylarsine oxide) adduct with mercuric chloride.[126] The $HgCl_2$ molecule is as strongly deformed as in the 2:1 adduct.[124] In the 1:1 addition product of mercuric chloride with cyclohexane-1,4-dione[127] the Cl–Hg–Cl bond angle is 173° and the Hg–Cl and Hg · · · · · O distances are 2·30 and 2·79 Å respectively. The effective co-ordination of the mercury atom is a deformed octahedron.

Remarkable refinements of the structure of trischloromercurioxonium chloride have been made by neutron diffraction[128] as well as by three-dimensional *X*-ray diffraction methods.[129] The oxygen atom is displaced out of the plane of mercury atoms by $0{\cdot}43 \pm 0{\cdot}04$ Å so that the oxonium ion has the shape of a very flat pyramid with a vertex angle of 175·5°.

5(c). In anhydrous mercuric sulphate[130] the mercury atom is co-ordinated by four oxygen atoms at distances 2·12 (two atoms), 2·29, and

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[123] Nyholm, *Proc. Chem. Soc.*, 1961, 273.

[124] Bränden, *Acta Chem. Scand.*, 1963, **17**, 1363.

[125] Hoppe and Röhrborn, *Z. anorg. Chem.*, 1964, **329**, 110.

[126] Bränden, *Arkiv kemi.*, 1964, **37**, 485.

[127] Groth and Hassel, *Acta Chem. Scand.*, 1964, **18**, 1327.

[128] Aurivilius, *Arkiv kemi*, 1964, **22**, 517.

[129] Aurivilius, *Arkiv kemi*, 1964, **22**, 537.

[130] Kokkoros and Rentzeperis, *Z. Krist.*, 1963, **119**, 234.

2·43 Å in a deformed tetrahedron, the bond angle corresponding to the two shortest Hg–O approaches being 157·4°.

5(d). Interesting structural differences have been found among the mercury mercaptides. In t-butylmercury mercaptide[131] mercury has tetrahedral co-ordination in a polymeric structure with Hg–S bond lengths to 2·59 and 2·66 Å. The ethyl derivatives according to the authors' unpublished results has a simple molecular structure. The adducts of mercuric chloride with diethyl sulphide[132] and with tetrahydrothiophen[133] are sulphonium salts, *i.e.*, $(Et_2SHgCl)^+Cl^-$ and $(C_4H_6SHgCl)^+Cl^-$. The characteristic mercury co-ordination in both structures is digonal with a departure from linearity shown by angles of 158° in the former and 143° in the latter compound. The effective co-ordinations are octahedral and trigonal-bipyramidal, respectively. The Hg–S bonds (2·41 and 2·40 Å) are shortened in comparison with those given in Table 2.

In the crystal structure of the clathrate $CoHg_2(SCN)_6,C_6H_6$ mercury again has tetrahedral co-ordination[134] but it is deformed in such a way that a side of the benzene molecule approaches the mercury atom with C · · · · · Hg distances of 3·52 and 3·66 Å. $Co(NCS)_6$-octahedra are joined by mercury–sulphur bridges, the benzene molecules being accommodated in holes. In the 1,6-dithiacyclodeca-*cis*-3,*cis*-8-diene adduct (1:2) one molecule of mercuric chloride is linear and the second is deformed.[135] In the bis(thiourea) complex a cation $(thiourea)_2HgCl$ with mercury in the planar trigonal characteristic co-ordination has been found, the effective co-ordination having not been reported.[135] The adduct with phenoxathiin[135] has the mercury atom in an effective octahedral co-ordination with the structural pattern similar to that found in bispyridine adduct.[80] The preliminary structure investigation of two mercury thiourea complexes has also been reported.[136]

5(f) The crystal of di-*p*-tolylmercury contains planar centrosymmetrical molecules so that the high dipole moment in solution must be due either to atom polarisation or to solvation.[137]

The author thanks Professor R. S. Nyholm, F.R.S., for suggesting this review and for stimulating discussion.

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[131] Kunchur, *Nature*, 1964, **204**, 468.
[132] Bränden, *Arkiv kemi*, 1964, **22**, 83.
[133] Bränden, *Arkiv kemi*, 1964, **22**, 495 and p. 561.
[134] Grønbaek and Dunitz, *Helv. Chim. Acta*, 1964, **47**, 1889.
[135] Cheung, McEwen, and Sim, *Nature*, 1965, **205**, 383.
[136] Korczynski, *Roczniki Chem.*, 1963, **37**, 1645; 1963, **37**, 1647.
[137] Kunchur and Mathew, *Proc. Chem. Soc.*, 1964, 414.