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The Structural Chemistry of Organic Compounds of Mercury and Its Analogues (Zinc and Cadmium)

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Information on the structure of organometallic compounds of zinc, cadmium, and mercury published up to 1973 is summarised. Detailed consideration is given to true organometallic compounds, containing a metal-carbon bond. Compounds in which a carbon atom (hydrocarbon radical) is separated from the metal atom by a heteroatom are mentioned only for comparison, and no systematic description of their structures is given. The Review covers results obtained by X-ray and neutron diffraction, gas-phase, electron diffraction, and in part microwave and Raman spectroscopy. A list of 90 references is included.

CONTENTS

I. Introduction 73
II. Organomercury compounds 73
III. Organozinc and organocadmium compounds 81

I. INTRODUCTION

Structural examination of compounds of zinc, cadmium, and mercury—members of subgroup II*b* of Mendeleev's Periodic System and having outer electron shells of similar structure—reveals significant differences in their stereochemistry: whereas a tetrahedral bond configuration is more characteristic of zinc and cadmium, mercury prefers a linear configuration with two short bonds, and this geometry of mercury compounds is little distorted by additional coordination interactions. Orgel[1,2] explained the structure of this type of mercury compound with strongly electronegative ligands in terms of their conferring a high positive charge (formally +2) on its atom: transition from the $5d^{10}$ (Hg^{2+}) electronic configuration to $5d^{9}6s^{1}$ followed by d_z2s hybridisation requires relatively little energy (5.3 eV), considerably less than for zinc and cadmium. Such hybridisation presupposes the existence either of two stable bonds in the *z* direction and four weak bonds in the *xy* plane or four stable bonds in the *xy* plane and two weak bonds in the *z* direction. The former alternative is preferred, although this cannot be explained in terms of Orgel's concepts.

In compounds with less electronegative substituents, in which the mercury atom has a small positive charge (formally +1) and the $5d^{10}6s^{1}$ configuration, the energy necessary for the transition $5d^{10}6s^{1} \rightarrow 5d^{10}6p^{1}$ is really not so small (~ 6 eV).[2,3] Linear *sp* hybridisation is therefore most favourable, with the use of only one higher *p*-level. In zinc and cadmium the energy difference between *s* and *p* levels is smaller, which facilitates sp^3 hybridisation.

Since the structure of organomercury compounds differs from that of organozinc and organocadmium compounds, they are discussed in different Sections. The stereochemistry of organomercury compounds is dealt with in Section II, where ideas put forward by Grdenić[2] are used. Subsections II, 1 and II, 2 examine the structures of aliphatic and aromatic organomercury compounds respectively. The presence of intramolecular coordination is discussed in subsection II, 3, and finally crystal structures with intermolecular coordination of the mercury atom are described in II, 4. However, assignment to a particular subsection is often difficult, both owing to the impossibility of establishing coordination on the basis of available data and because the original paper lacks the appropriate information (in particular no analysis of intermolecular distances is given, and sometimes even the atomic coordinates are missing). Structures of organomercury compounds determined by X-ray diffraction are usually not very accurate, owing to the great difference in atomic number between mercury and the other atoms present in the molecule. Section III deals with the structures of organozinc and organocadmium compounds, which have been little studied.

II. ORGANOMERCURY COMPOUNDS

1. Aliphatic Derivatives

The first information on the structure of dimethylmercury was obtained during 1936-1937, when gas-phase electron diffraction gave values of 2.20 and 2.23 Å[4,5] for the mercury-carbon bond length in this molecule. However, 2.094(5) Å has since been obtained[6] from the Raman spectra. This value has recently been confirmed by a second electron diffraction investigation: the internuclear distance in the linear CH_3-Hg-CH_3 molecule is 2.083 Å.[7]

Compound	Hg-C, A	Hg-X, A	Ref.
CH_3HgCH_3	2.083 (5); 2.094 (5)	—	6,7
CH_3HgCl	2.061 (20)	2.282 (5)	8
CH_3HgBr	2.074 (15)	2.406 (5)	8
CH_3HgI	2.087 (10)	2.528 (5)	9

Closely similar values have been obtained by microwave spectroscopy for the methylmercury halides (Table). It is evident that the presence of a halogen atom in the molecule shortens the mercury-carbon bond, an effect which diminishes in the sequence Cl > Br > I, so that the bond length in methylmercury iodide is the same as in dimethylmercury.

X-Ray examination of several alkylmercury halides—methylmercury, ethylmercury, propylmercury, and butylmercury chlorides and ethylmercury bromide—by means of projections[10] gave values of 2.06(3), 2.50, and 2.51 Å for the bonds between mercury and carbon, chlorine, and bromine respectively. The mercury–halogen bond lengths differ significantly from the above values, probably because of the lower accuracy of X-ray examination. This method gave 2.43 Å for the mercury–bromine bond length in *trans*-2-chlorovinyl mercury bromide ClCH:CH.HgBr.[11]

From the bond lengths in the above compounds and in those of type HgX_2 investigated by electron diffraction in the vapour phase, with the Schomaker–Stevenson correction for the electronegativity difference, Grdenić proposed[2] the value 1.30 Å for the covalent radius of mercury with a linear bond configuration. This value corresponds satisfactorily to the additivity rule for free molecules of the types HgX_2 and $HgXX'$. This rule is not always satisfied in crystalline structures, owing to the influence of surrounding molecules.

sp-Hybridisation of the mercury atom presupposes that these dihalide molecules have a linear structure, but it is interesting to trace to what extent linearity is preserved in organomercury compounds. From the vibrational spectra of methylmercury cyanide CH_3HgCN it was concluded[12] that linearity of the C–Hg–C(N) fragment was disturbed in this compound. Examination of crystals by X-ray and neutron diffraction[13,14] showed in both cases that the angle at the mercury atom was 180 ± 2°. The Hg–CH_3 and Hg–CN bond lengths were 2.15(5) and 2.01(5) Å according to the X-ray results, and 2.08(2) and 2.05(1) Å respectively according to neutron diffraction. It is interesting that the latter method distinguished between the nitrogen and carbon atoms, and showed that mercury was attached to the carbon atom of the cyano-group.

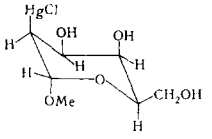
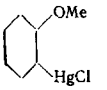


Figure 1.

X-Ray examination of DL-penicillaminatomethylmercury[15] indicated that the methylmercury group is attached to the amino-acid through a deprotonated mercapto-group $CH_3.Hg.S.C(CH_3)_2.CH(NH_3^+).COO^-,H_2O$. The CH_3–Hg–S fragment is nearly linear (176(2)° and 179(1)° in two independent molecules). The mean Hg–C and Hg–S bond lengths are 1.90(6) and 2.38(1) Å, and the angle at the sulphur atom is 109°.

A linear configuration has been found for mercury also in methoxycarbonylmercury chloride Cl–Hg–$COOCH_3$ (X-ray examination by projections).[16] The Hg–C and Hg–Cl bond lengths of 1.96 and 2.35 Å differ from those found in methylmercury chloride[8] and in mercury(II) chloride[2], but the poor accuracy makes the reality of these differences dubious.

X-Ray investigation[17] of two diastereomers—(I) $\alpha(dd,ll)$ and (II) $\beta(dl,ld)$—of 2-methoxycyclohexylmercury chloride



showed that in (I) the Hg–C and Hg–Cl bond lengths were 2.34 and 2.53 Å, with the ClHgC angle 178°; the corresponding values in (II) were 2.15, 2.50, and 180°. The molecules differ in the relative orientation of the substituents about the cyclohexane ring. Thus the intramolecular Hg...O distances in (I) and (II) are 4.06 and 3.06 Å.

Structure determination by means of X-rays showed[18] that the Hg–Cl bond length in methyl 2-chloromercury-2-deoxy-α-D-talopyranoside (Fig. 1) is 2.38(10) Å. Preliminary examination of dibenzylmercury crystals[19] established only the partial position of the mercury atom in the cell (space group $P4_2/n$, $z = 4$).

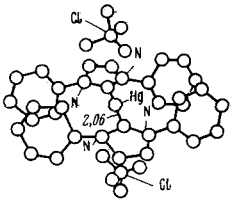


Figure 2.

The mercury–carbene complex $[Hg(C_{15}H_{12}N_2)_2](ClO_4)_2$ possesses an interesting structure (Fig. 2).[20] The cation is located at the centre of symmetry, so that the configuration of the mercury bonds is strictly linear. The Hg–C bond length of 2.06(1) Å coincides within the limits of accuracy with the sum of the covalent radii of mercury and sp^2 carbon (1.30 + 0.74 Å).

2. Aromatic Compounds

Measurements of the dipole moments of diarylmercury compounds indicate significant polarity[2,21,22], which might be explained by non-linearity of the C–Hg–C fragment. It was therefore of interest to undertake structure determinations on these compounds.

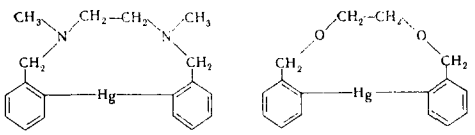
Two methods—X-ray structure determination[23–25] and gas-phase electron diffraction[26]—have been used to examine diphenylmercury. This planar molecule is situated at a centre of symmetry in the crystal, so that the C–Hg–C fragment is strictly linear. The structure was refined on the assumption that the Hg–C bond length was 2.10 Å: i.e. this parameter was not objectively determined. Electron diffraction in the gas phase led to the fairly accurate value of 2.092(5) Å for the Hg–C internuclear distance. The CHgC angle was not determined experimentally, but was assumed to be 180°.

Comparison of the mercury–carbon bond length thus obtained with that found in aliphatic organomercury compounds reveals no contraction on passing from sp^3 to sp^2 hybridisation of the carbon. On the other hand, it was of interest to ascertain the extent to which the state of

hybridisation of the carbon atom attached to mercury in organomercury halides affects the mercury–halogen bond length. Examination of phenylmercury bromide vapour by electron diffraction[27] showed, on the assumption that the C–Hg–Br fragment was linear, that the Hg–Br bond length was 2.435(4) Å, rather longer than the 2.40 Å in methylmercury bromide (see above): i.e. it was established that the organic substituent attached to the mercury atom influences the length of the mercury–halogen bond.

X-Ray structure determination on di-*p*-tolylmercury established that the mercury–carbon bonds were collinear[28,29] (the planar molecule was located at a centre of symmetry). The Hg–C bond length of 2.08 Å coincides within the limits of accuracy with the sum of the covalent radii. The great scatter in the carbon–carbon bond lengths and angles in the phenyl rings (1.39–1.44 Å and 116–124°) is an indication of the difficulty of locating light atoms in the structures of organomercury compounds.

In most of the symmetrical mercury compounds examined by X-ray diffraction the mercury atom is situated at a centre of symmetry, so that the C–Hg–C fragment has a strictly linear structure in the crystal. In bispentafluorophenylmercury $(C_6F_5)_2Hg$, in whose crystal structure the molecule is located at a common position [sic: the molecular crystal has four molecules in the unit cell (Ed. of Translation)], the CHgC angle is 176.2(1.2)°.[30] This value probably represents the limits within which linearity of X–Hg–X bonds can be disturbed by the packing of molecules in the crystal. It is noteworthy, however, that the distances between mercury and the *ortho*-fluorine atoms—3.32, 3.25, 3.22, and 3.14 Å—are fairly short. The possibility of specific Hg...F interaction is therefore not excluded; this would be analogous to (but weaker than) the coordination interaction of the mercury atom with the *ortho*(2,2′ and 6,6′)-chlorine atoms in bispentachlorophenylmercury[31] indicated by the nuclear quadrupole resonance spectrum. Such interaction may disrupt the linearity. In contrast to diphenyl- and di-*p*-tolyl-mercury, moreover, the $Hg(C_6F_5)_2$ molecule is non-planar in the crystal, with an angle of 59.4° between the planes of the benzene rings.



(I) $HgC_{18}H_{22}N_2$ (II) $HgC_{16}H_{16}O_2$

Figure 3.

The angle at the mercury atom also differs from 180° in the crystal structures of *NN*′-dimethylethylenediamine-ωω′-di-*o*-tolylmercury (I) and ethylenedioxy-ωω′-di-*o*-tolylmercury (II) (Fig. 3),[32] being respectively 172.3(9)° and 173.6(2.1)°. The Hg...O distances of 3.01(4) and 3.19(3) Å in (II) and the Hg...N distances of 2.92(2) and 2.97(2) Å in (I) were regarded as excluding coordination between the atoms, which might have led to some disturbance of bond linearity. Thus these disturbances are probably due to steric stresses.

X-Ray examination of 1-naphthylmercury iodide[33] revealed only the heavy atoms—mercury and iodine—separated by the bond length 2.61 Å.

Thus these subsections 1 and 2 show that a linear bond configuration is most common in organomercury compounds, with the mercury–carbon bond length generally within the range 2.06–2.10 Å.[34] Other bond configurations are rare and atypical in organomercury compounds.

3. Compounds with Intramolecular Coordination of Mercury with a Heteroatom

Coordination between the mercury atom and a heteroatom in the same molecule has recently been increasingly used to explain several anomalies in the physical properties of organomercury compounds, as well as to interpret many of their reactions[27]. In particular, special features of the infrared, nuclear magnetic resonance, and nuclear quadrupole resonance spectra and the dipole moments, as also anomalous effects of *ortho*-substituents, are explained by such coordination interaction[35–37].

X-Ray structure determination and electron diffraction are often used to ascertain the possible presence of intramolecular coordination interaction. The sole geometrical criterion of such interaction is the shortening of the distance between the atoms in comparison with the sum of their van der Waals radii. The presence of interaction can be deduced unambiguously from this criterion only if the contraction exceeds those which may arise from packing effects (~ 0.2 Å). Grdenić[2] suggested 1.50 Å, half the shortest interatomic distance in metallic mercury, as the van der Waals radius; and to allow for several specific coordination interactions he proposed the value 1.73 Å (half the next larger interatomic distance in metallic mercury). These recommendations were based on the intermolecular mercury–halogen distances in the structures of organomercury halides[10]. Since the minimum van der Waals radius proposed by Grdenić exceeds the covalent radius of mercury by only 0.2 Å, it is difficult in several cases to reach, on the basis of the above geometrical criterion, an unambiguous conclusion on the presence of weak coordination interaction. Additional criteria must therefore be adduced in order to establish such interaction.

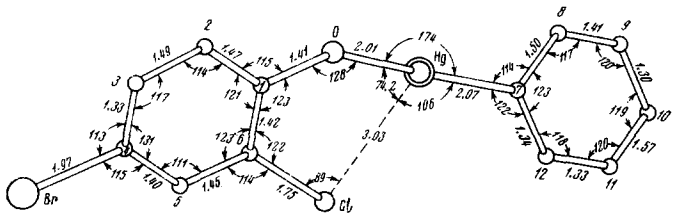
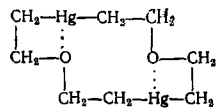


Figure 4.

X-Ray examination of phenylmercury 4-bromo-2-chlorophenoxide (Fig. 4) was undertaken[38] to establish the possibility of intramolecular interaction of the *ortho*-chlorine with the mercury. Such interaction is possible on appropriate rotation of the phenyl ring about the C–O single bond. The angle between the HgOC ω plane and the plane

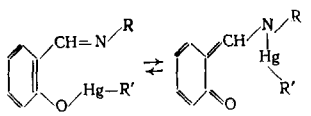
of the benzene ring $C_{(1)}...C_{(6)}$ is found experimentally to be 17°, when the molecule acquires a cisoid conformation, in which mercury and chlorine atoms approach to 3.03(2) Å. This distance is 0.3 Å shorter than the sum of the van der Waals radii of chlorine (1.8 Å) and mercury if the minimum 1.5 Å is adopted for the latter, and 0.5 Å shorter if 1.73 Å is used. It should be noted also that the OHgC angle away from the chlorine atom has diminished to 174(1)°, while the location of the chlorine atom relative to the C–Hg–O fragment is roughly symmetrical (to the extent that this is permitted by the geometrical rigidity of the "metal ring" HgOCCCl): the ClHgO and ClHgC angles are respectively 74° and 106°. All this is evidence of the presence of intramolecular Hg...Cl coordination. The Hg–C and Hg–O bond lengths are respectively 2.07 and 2.01 Å. Thus such interaction does not cause elongation of valency bonds and produces no significant change in hybridisation.

X-Ray structure determination on "diethylenemercury oxide" established [39] that the molecule was dimeric



with strong Hg...O coordination interaction at 2.21(10) Å (sum of covalent radii 1.96 Å) in a twelve-membered ring arranged about a twofold axis. It is strange, however, that such strong interaction barely disturbs the hybridisation of the mercury atom (CHgC angle 176°), which probably indicates the poor accuracy of the work (the structure was determined from projections). The length of the Hg–C bonds in this molecule is 2.14 Å.

An intensive study of metallotropic rearrangements, including metallotropic tautomerism, has begun recently. In particular, electron spectroscopy has provided evidence that phenyl- and methyl-mercury derivatives of *o*-iminomethylphenols are present in solution as equilibrium mixtures of metallotropic benzenoid and quinonoid tautomers, whose proportions vary with the temperature and the polarity of the solvent [40]:



(I) (II)

Transfer of the phenylmercury residue from one reaction centre to the other is facilitated by intramolecular coordination, which is possible if the molecule has a *cis*-conformation relative to the exocyclic carbon–carbon bond. X-Ray structure determination has shown [41] that phenylmercury *o*-methyliminomethylphenoxide is an *N*-derivative of *o*-methyliminomethylphenol with the *cis*-conformation. The triclinic cell contains two independent molecules, having the same geometry within the limits of accuracy. The structure of one of them is shown in Fig. 5. The mean Hg–N and Hg–C bond lengths are 2.12(3) and 1.98(4) Å.

The oxygen atom is distant 2.44 Å from the mercury atom, about 0.4 Å further than the length of the mercury–oxygen covalent bond and 0.4–0.6 Å closer than the sum of the van der Waals radii. In this case there is no doubt about the presence of coordination interaction. Here, as in the preceding structure, the bond angle opposite to the "additional" oxygen atom is diminished to 167°, the greater decrease being consistent with stronger intramolecular interaction between mercury and the heteroatom.

The presence of strong Hg...O coordination interaction implies that the quinonoid structure (II), whose predominance follows from the fact that mercury is covalently bound to the nitrogen atom, is accompanied by the benzenoid form (I).

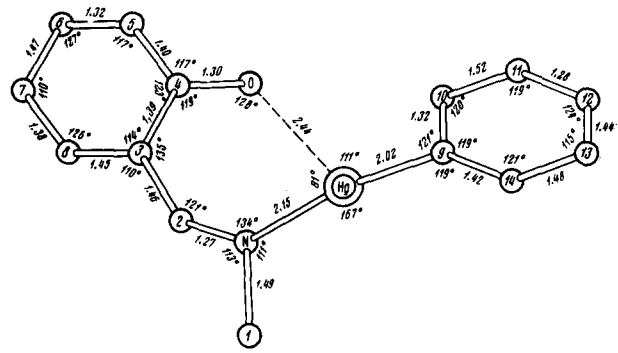


Figure 5.

A similar type of coordination of the mercury atom is found in 2-hydroxy-5-methylphenylmercury 4-methyl-2-nitrosophenoxide $C_7H_7OHg.C_7H_6ONO$ [42,43] (Fig. 6*a*). As in the preceding structure, the mercury atom is covalently bound through a carbon atom of the phenol ring and the nitrogen atom of the quinone monoxime. The unit cell contains two independent molecules, with mean Hg–N and Hg–C distances 2.14 and 2.04 Å. The C–N and N–O bonds (mean lengths 1.25 and 1.27 Å) are nearly double, since the molecular structure is best described by formula (II) (Fig. 6*b*).

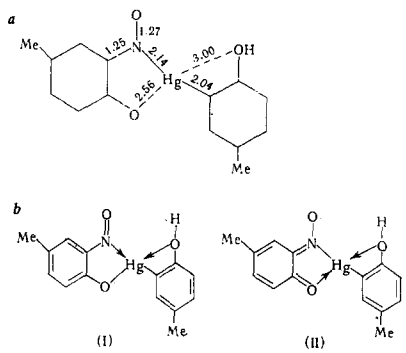


Figure 6.

The oxygen atom of the nitrosophenol is distant 2.56 Å from the mercury atom, which corresponds to coordination, but weaker than in phenylmercury *o*-methyliminomethylphenoxide. The probable reason for the weaker interaction is that a more symmetrical arrangement of the coordinated oxygen atom relative to the C–Hg–N fragment is

prevented by the geometrical rigidity of the five-membered "metal ring". The $O_{(1)}HgN$ and $O_{(1)}HgC$ angles are 71° and 115°, whereas in the salicylic derivative they are 81° and 111° respectively. The $N_{(1)}HgC$ angle away from the $O_{(1)}$ atom has also diminished to 174°. It is remarkable that a five-membered metal ring is formed in this structure, although the ligand is isoelectronic with salicylicidenimine, and on coordination of the mercury, not with the nitrogen but with the oxygen of the nitroso-group, would have formed a six-membered chelate metal ring analogous to that found in the above phenylmercury derivative of salicylicidenimine.

In all the above structures a shortening of the distance between the "additionally" coordinated heteroatom and mercury is sufficient to indicate interaction between these atoms without further corroboration. However, this is by no means always possible, and additional geometrical criteria of coordination must be used for such cases. They may be the deviation from the ideal XHgX angle opposite the "extra" atom, the symmetry of the position of the latter relative to the X–Hg–X fragment, and also the occurrence in the molecule of a conformation favourable to such interaction[44].

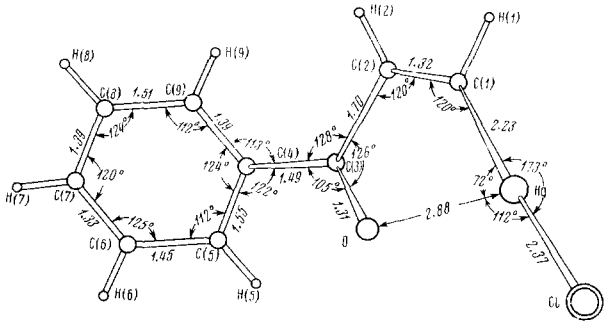


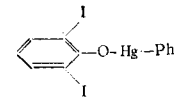
Figure 7.

An example is 2-benzoylvinylmercury chloride, whose *cis*-isomer was more stable than the *trans*-isomer, which was attributed[45] to intramolecular Hg...O coordination. X-Ray structure determination established a cisoid conformation[46] (Fig. 7), in which the oxygen atom lay in the direction of the mercury atom. The Hg...O distance of 2.88(10) Å agreed within the limits of accuracy with the sum of the van der Waals radii (2.9–3.1 Å). However, the molecular conformation and the diminution to 173(2)° in the ClHgC angle opposite the oxygen atom are evidence of the above coordination.

Examination of *cis*-2-chlorovinylmercury chloride by gas-phase electron diffraction[47] gave Hg–C and Hg–Cl bond lengths (2.14(1) and 2.27(1) Å) that can be regarded as normal. The non-bonded intramolecular Hg...Cl distance is 3.27 Å, and the sum of the van der Waals radii 3.3–3.5 Å. This distance was regarded as corresponding to intramolecular coordination. However, it is determined in considerable measure by the geometrical rigidity of the molecule, and cannot be used as an unequivocal criterion of coordination. Such interaction might be indicated by a decrease in the CHgCl angle away from the "extra" chlorine atom. Linearity of the C–Hg–Cl fragment is in fact disturbed (the angle is 168.5(1.5)°), but the side to which the Hg–Cl bond is deflected is not stated. The presence of coordination in this molecule is supported also by results obtained by other methods (dipole moments, anomalies of chemical behaviour, nuclear quadrupole resonance spectra)[48–50].

Only the coordinates of the mercury and halogen atoms have objectively been established in the crystal structure of trichloromethylmercury bromide CCl_3HgBr.[51] The Hg...Cl distances were not equivalent: two were 3.21 Å, and one 3.15 Å, the decrease being attributed to coordination. However, the poor accuracy does not allow this conclusion to be accepted as entirely reliable. Nevertheless, the presence of interaction is indicated by the nuclear quadrupole resonance spectra of trichloromethylmercury bromide and chloride and of bistrichloromethylmercury.

The Hg...I distance in the crystal structure of phenylmercury 2,6-di-iodo-4-methylphenoxide



was determined[52,53] as 3.14 Å, which corresponds to strong intramolecular coordination.

4. Crystal Structures of Organomercury Compounds with Intermolecular Coordination of the Mercury Atom

Coordinative saturation of mercury can be attained not only by the intramolecular interaction with the heteroatom discussed in the preceding subsection but also by interaction with donor atoms of a neighbouring molecule in the crystal.

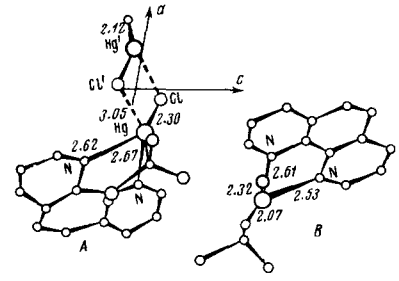


Figure 8.

X-Ray structure determination on the adduct of trichloromethylmercury chloride and 1,10-phenanthroline[54] indicated strong interaction between the mercury atom and the nitrogen atoms of the phenanthroline, with substantial disturbance of the linearity of the C–Hg–Cl fragment. The crystal structure contains two independent molecules A and B differing in geometry (Fig. 8), with CHgCl angles of 155° and 145° respectively. With such considerable disruption of the linear geometry of the mercury atom the Hg–C and Hg–Cl bond lengths—2.12 and 2.30 Å in A, and 2.07 and 2.32 Å in B—are almost the same as in linear

molecules. The Hg...N distances are 2.62 and 2.67 Å in A, and 2.53 and 2.61 Å in B. Coordination of the mercury atom in molecule B in the crystal conforms to a distorted tetrahedron; in A the additional effect of the close intermolecular Hg...Cl contact of 3.05 Å brings the coordination to distorted trigonal-bipyramidal.

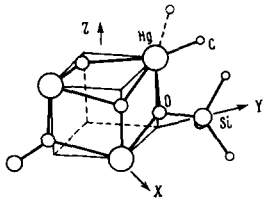


Figure 9.

Strong distortion of the linear geometry of the mercury atom has been found in methylmercury trimethylsiloxide[55]. The molecules are associated into tetramers (Fig. 9) having a cubane-like structure intermediate between the ideal cubane structure in the corresponding zinc and cadmium compounds (see below) and a structure with isolated molecules. Within the limits of accuracy the Hg–C and Hg–O distances of 2.09(40) and 2.11(20) Å correspond to normal covalent bonds in linear mercury molecules; the OHgC angle is 112(8)°. Thus even in this compound disturbance of the linear geometry of mercury is not accompanied by increase in Hg–O and Hg–C bond lengths. The coordination of mercury in the tetramer is supplemented by weak Hg...O interactions at distances of 2.75(20) Å to give a distorted tetrahedron. The arrangement of the methyl group attached to the mercury atom is random.

Several crystal structures have been described in which Hg...X coordination is achieved with considerably less distortion of the linear bond configuration of the mercury atom.

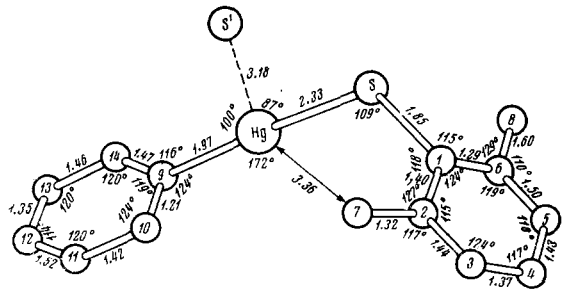


Figure 10.

An X-ray examination of phenylmercury 2,6-dimethylphenyl sulphide[44] had the aim of refining the van der Waals radius of the mercury atom, since intramolecular contact between the mercury atom and an electrically neutral methyl group should be present in this compound (Fig. 10). The Hg–C and Hg–X bond lengths are respectively 1.97 and 2.33 Å, and the SHgC angle is 172°. The angle between the HgSC(ω) plane and the plane of the thiophenol ring is 52.3°, with the mercury atom approaching a methyl group to 3.36 Å. On the assumption that contact occurs between the mercury atom and the carbon atom of the methyl group, whose hydrogen atoms do not prevent such contact, the van der Waals radius of the mercury atom is found to be ~ 1.6 Å, which lies between the two values suggested earlier[2]. The crystal structure involves intermolecular Hg...S′ coordination at 3.18 Å, which is 0.1–0.3 Å closer than the sum of the van der Waals radii. Such coordination is evidence also that the CHgS angle away from the S′ atom has decreased to 172° and that this atom is in a symmetrical position with respect to the C–Hg–S fragment. Furthermore, the angle at the sulphur atom (109°) is larger than the corresponding angle (100°) in the crystal structure of triphenyltin 2,4,6-trimethylphenyl sulphide[56], which may be due to a redistribution of electron density on the sulphur atom when it interacts with the mercury atom.

A similar increase in the angle at the sulphur atom (to 111°) was found in the crystal structure of mercury dimethanethiolate $(CH_3S)_2Hg$,[57,58] where intermolecular Hg...S interaction occurs at 3.25 Å, whereas in the structure of mercury diethanethiolate $(C_2H_5S)_2Hg$,[59] where such interaction is evidently absent (Hg...S = 3.56 Å), the HgSC angle is smaller (106°). The presence of coordination in the methyl derivative is confirmed by its higher melting point than those of the ethyl and propyl sulphides (175° compared with 76° and 71°C).

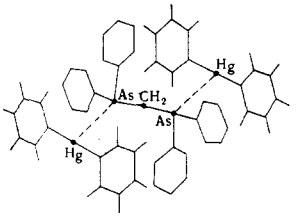
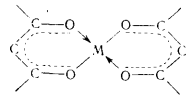


Figure 11.

The presence of Hg...As coordination has been established in the crystal structure of the 2 : 1 adduct of bispentafluorophenylmercury and bisdiphenylarsinomethane[60,61] (Fig. 11). The arsenic atoms are situated symmetrically with respect to the bispentafluorophenylmercury molecules: the AsHgC angles are 90(3)° and 96(3)°. The Hg...As distance of 3.40 Å is 0.1–0.3 Å less than the sum of the van der Waals radii, and the CHgC angle away from the arsenic atom has closed to 173(4)°. Further evidence of Hg...As interaction is that the angle between the planes of the pentafluorophenyl rings is 7°, whereas it is 59.4° in the crystal structure of bispentafluorophenylmercury (see subsection II, 2). Such a tendency of the latter molecule to achieve planarity in the adduct facilitates approach of the arsenic to the mercury atom.

X-Ray examination of bisdipivaloylmethylmercury has established[62,63] that the mercury atom, in contrast to the atoms of transition metals, which form chelate complexes



with dipivaloylmethane, is attached to the two central carbon atoms of the ligands (Fig. 12). Only one moiety of the molecule is involved in additional Hg...O coordination (in conformity with which the thermal vibrations are smaller in this half). Such interactions lead to a decrease (to 170°) in the angle away from the two interacting oxygen atoms, to a lengthening to 2,18(3) Å of the Hg–C bond in the moiety involved in interaction (the length of the second Hg–C bond is 2.13(3) Å), and also to an increase to 120° of the angle at the central carbon atom in this moiety, which indicates a contribution by the sp^2 state of this atom.

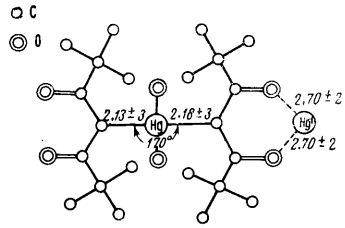


Figure 12.

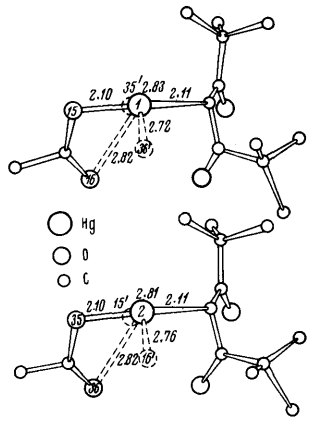


Figure 13.

In the crystal structure of dipivaloylmethylmercury acetate[64] the mercury atoms of two crystallographically independent molecules are involved in intermolecular coordination with oxygen atoms of acetate groups (Fig. 13): the oxygen atoms of the dipivaloylmethyl groups play no part in these interactions. The intramolecular Hg...O distances vary between 2.72 and 2.83 Å. The intramolecular Hg...O distance to the second oxygen atom of the acetate group (2.82 Å) is determined by the geometrical rigidity of the HgOCO fragment, so that we do not know whether it corresponds to interaction. Fig. 14 shows the coordination polyhedron of the mercury atom. As in certain other cases in which mercury is coordinated with more than two atoms corresponding to a more complicated polyhedron, the criterion of a decrease in bond angle at the mercury atom is ineffective or completely unsuitable.

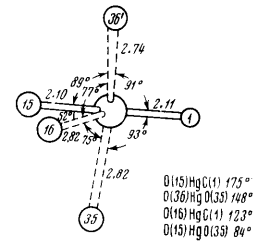


Figure 14.

A similar situation is found in the crystal structure of phenylmercury acetate[65] (Fig. 15). The Hg–$O_{(1)}$ and Hg–$C_{(1)}$ bond lengths are respectively 2.11 and 1.92 Å, and the OHgC angle is 170°. The distance to the second atom of the acetate group $O_{(2)}$ is 2.85 Å, but here, too, the question of intramolecular interaction is evidently unsettled. In the crystal the mercury atom is surrounded by oxygen atoms of neighbouring molecules at distances of 2.94, 2.95, and 3.11 Å. Although these distances coincide with the sum of the van der Waals radii (2.9–3.1 Å), the fairly symmetrical arrangement particularly of oxygen atoms about mercury in a plane approximately perpendicular to O–Hg–C suggests that they are responsible for coordination interactions. The original authors regard them as van der Waals contacts.

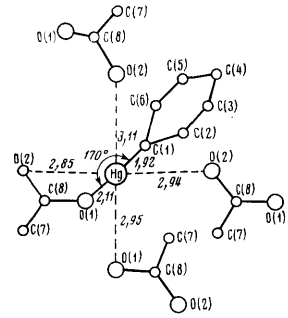


Figure 15.

An X-ray structure determination on 2-diethylaminoethylmercury chloride $(C_2H_5)_2N.CH_2.CH_2.HgCl$ was undertaken[66] to establish intermolecular Hg...N coordination in compounds of this type. The Hg–C and Hg–Cl bond lengths are 2.12 and 2.36 Å respectively. Coordination of the

mercury atom in the crystal is trebled by interaction with a nitrogen atom of a neighbouring molecule at 2.77(2) Å, with a decrease in the CHgCl angle to 173°.

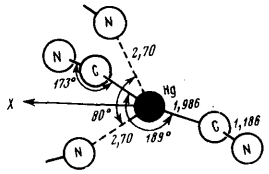


Figure 16.

X-Ray structure determination[67] and neutron diffraction[68] have given a closely similar intermolecular Hg...N distance in the mercury(II) cyanide crystal (2.70 and 2.74 Å). The former method shows that the CHgC angle away from the two coordinating nitrogen atoms (Fig. 16) has decreased to 171(2)°, and the Hg–C bond length is 1.986(16) Å. Neutron diffraction indicates that this angle is 175.0(2)°, and the bond length 2.015(3) Å. It is interesting to compare these results with those for methylmercury cyanide[13,14]. This molecule is linear, and the Hg...N distances (3.14 and 3.26 Å) are not shortened in the crystal. This is probably because replacing the cyanide group by methyl diminishes the positive charge on the mercury atom and weakens its ability to coordinate.

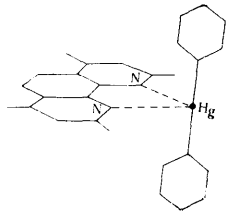
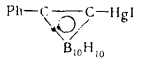


Figure 17.

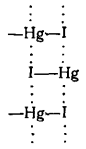
The crystal structure of the adducts of diphenylmercury with 2,9-di- and 2,4,7,9-tetra-methyl-1,10-phenanthroline[69] (Fig. 17) also show diminished coordinating power of mercury in the absence of electronegative substituents. One phenanthroline molecule is located near each diphenylmercury molecule in a plane approximately perpendicular to the C–Hg–C fragment and passing through the mercury atom (a second substituted phenanthroline molecule, not involved in contacts with the mercury atom, is also present). The Hg...N distances of 2.8–3.0 Å are greater in the two preceding structures, and close to the sum 2.8–3.0 Å of the van der Waals radii. Therefore coordination cannot be assumed on this basis alone, but its presence is suggested by such a specific relative arrangement of diphenylmercury and phenanthroline molecules.

X-Ray structure determinations on several barenyl derivatives of mercury halides[70] established the presence of strong intermolecular Hg...I interaction in phenylbarenylmercury iodide

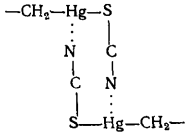


corresponding to 3.29 Å, which is 0.4–0.6 Å smaller than the sum of the van der Waals radii. Such interaction explains the spontaneous symmetrisation that occurs when the crystals are stored. Only the coordinates of the mercury and bromine atoms were determined in phenyl- and in methyl-barenylmercury bromide, and the Hg...Br distances shown to be respectively 3.42 and 3.56 Å, with the sum of the van der Waals radii 3.4₅–3.7 Å. However, the antiparallel arrangement of the Hg–Br fragments in the structure indicates weak intermolecular Hg...Br interaction.

Several crystal structures have been described in which the arrangement of heteroatoms in neighbouring molecules suggests the presence of coordination, although the atoms are no closer than the sum of the van der Waals radii. X-Ray examination of the compounds $CH_3O.C(CH_3)_2.C(CH_3)_2.CH_2.HgX$ showed[71] that, when X = I, the Hg–I bond length is 2.60 Å, and the intermolecular Hg...I distance 3.81 Å. Owing to weak intermolecular Hg...I interactions, infinite chains of antiparallel Hg–I fragments



appear in the crystal structure of this compound. In such compounds with X = SCN geometrical analysis of the coordinates of mercury and sulphur atoms reveals the formation of dimers



through the terminal nitrogen atoms of the thiocyanato-groups. The molecular configuration in the dimer corresponds to the isomer with closest approach of mercury and nitrogen atoms, probably as a consequence of coordination between them. Unfortunately, the Hg...N distances were not determined.

Intermolecular Hg..Cl interaction was established[72] in the crystal structure of 2-chlorovinylmercury chloride ClCH:CH.HgCl. The mercury atoms in three crystallographically independent molecules are coordinated by the chlorine atoms of neighbouring molecules; the Hg...Cl distances vary within the range 2.89–3.49 Å. The mean Hg–C and Hg–Cl bond lengths are respectively 2.10 and 2.30 Å. Unfortunately, no analysis of the coordinative environment of the mercury atoms is given in the paper.

X-Ray examination of phenylmercury halides established[73] that the Hg–Br bonds in the bromide have an antiparallel arrangement, with the mercury atom coordinated by four bromine atoms of neighbouring molecules (Hg...Br = 3.45 Å) in an octahedral environment. The Hg–C and Hg–Br bond lengths are 2.06 and 2.43 Å, and the CHgBr angle is 180°. The chloride and the iodide are isostructural with the bromide.

The crystal structures of *para*-derivatives of phenylmercury halides were also studied[74]. The coordinates of the mercury and chlorine atoms in *p*-tolylmercury chloride showed that the mercury atom is surrounded by three chlorine atoms of neighbouring molecules at 3.35, 3.35, and 2.99 Å. The packing of *p*-chlorophenylmercury chloride molecules in the crystal is closely similar to that of phenylmercury chloride, with a nearly antiparallel arrangement of Hg–Cl bonds. The tendency of the molecules to such an arrangement is so great that it is realised, although geometrical analysis shows that such packing will probably lead to the presence of closer intermolecular contacts.

An antiparallel arrangement of Hg–Br bonds was found also in *p*-tolylmercury bromide, in contrast to the corresponding chloride, and also leads to the presence of closer intermolecular contacts. This probably indicates that Hg...Br interaction is stronger than Hg...Cl interaction.

An antiparallel arrangement of Hg–Br bonds is impossible in the crystal structure of *p*-ethoxycarbonylphenylmercury bromide, containing a bulky *para*-substituent. The mercury atom in this crystal is surrounded by three bromine atoms of neighbouring molecules at distances 3.43, 3.43, and 3.55 Å (Hg–Br bond length 2.42 Å). *p*-Methoxyphenylmercury chloride, despite its large *para*-substituent, has the phenylmercury chloride type of crystal structure. This was explained by the "flexibility" of the methoxy-group, making it convenient for packing in the crystal.

III. ORGANOZINC AND ORGANOCADMIUM COMPOUNDS

The structures of the corresponding zinc and cadmium compounds have been studied considerably less than those of organomercury compounds. The reason is the great reactivity of the former, making their examination by X-ray or electron diffraction difficult.

The structures of dimethylzinc and dimethylcadmium, among organometallic compounds of type R_2M, have been studied by means of their Raman spectra[6]. Both molecules are linear. The Zn–C and Cd–C bond lengths are 1.929(4) and 2.112(4) Å, the latter thus being rather longer than Hg–C in dimethylmercury (2.094(5) Å). Thus the M–C bond length does not vary in parallel with the atomic number of the metal in the series zinc, cadmium, and mercury. A similar relation of bond lengths has been found for the dihydrides, in which the H–M distances in this series are 1.595, 1.762, and 1.740 Å. X-Ray examination of dimethylzinc[75] gave Zn–C = 1.96 Å, and a methyl group of a neighbouring molecule situated opposite the vacant *p*-orbitals of the zinc atom. This does not exclude weak interaction between them, like that observed in trimethylindium[75,76] and in trimethylaluminium[75,77].

Organozinc and organocadmium compounds in which the metal atom has a tetrahedral configuration are rather more stable, and have therefore been studied more thoroughly.

The crystal structure and the molecular structure of lithium tetramethylzincate were determined[78] by the powder method. The second of the two space groups $I\bar{4}2m$ and $I\bar{4}$, which differ in the orientation of the methyl groups, was chosen on the basis of crystallographic considerations. The zinc atom (Fig. 18) is located at a singular point on an inversion axis, and has distorted tetrahedral coordination. The Zn–C bond lengths of 2.07(15) Å were regarded as greater than the value of 1.929 Å in the linear molecule of dimethylzinc. However, the poor accuracy of this value does not permit the significance of such an increase to be assessed.

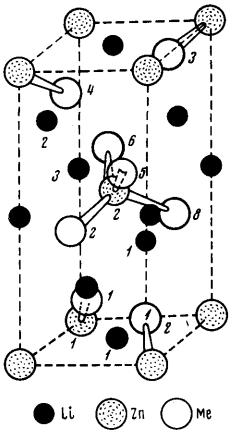


Figure 18.

Crystals of the isostructural potassium tetraethynylzincate and tetraethynylcadmate $K_2[Zn(C_2H)_4]$ and $K_2[Cd(C_2H)_4]$ have also been investigated by the powder method[79] (Fig. 19). In both compounds the metal atom has tetrahedral coordination. The $Zn–C_{(1)}$ distance of 2.0(1) Å was regarded as shortened by $d_\pi–p_\pi$ interaction, although the poor accuracy evidently gives no grounds for such conclusions. The Cd–C distance is 2.5(1) Å.

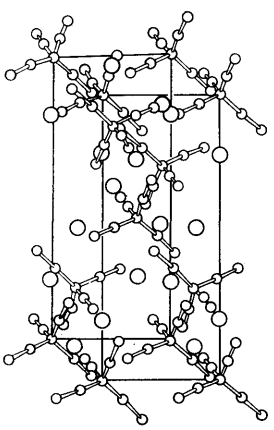


Figure 19.

The formation of tetra-, penta-, octa-, and poly-mers is very characteristic of organozinc and organocadmium compounds in the crystalline state. X-Ray examination of methylzinc methoxide[80,81] established the existence of a tetramer having a cubane structure (Fig. 20). Zinc and oxygen atoms occupy alternate corners of a distorted cube.

The Zn–C and Zn–O distances are 1.94 and 2.09 Å; the mean angles at the zinc and oxygen atoms are 83° and 96°.

On the basis of chemical and physicochemical investigations an analogous cubane structure was suggested[82–84] for the structurally unstudied compounds $[CH_3MOSi(CH_3)_3]_4$ (M = Zn, Cd) (Fig. 21) and $[CH_3ZnNP(CH_3)_3]_4$ (Fig. 22).

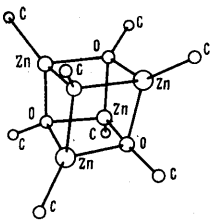


Figure 20.

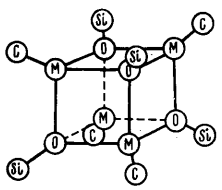


Figure 21.

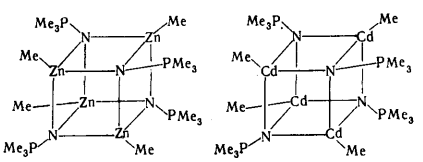


Figure 22.

X-Ray examination of the compound $Zn_7O_8(CH_3)_{14}$ shows[85] that it has a dicubane structure (Fig. 23) in which two kinds of zinc atoms differ in their coordination. The central zinc atom, located at a centre of symmetry, is octahedrally surrounded by methoxyl oxygen atoms at distances of 2.068–2.170 Å. The remaining zinc atoms have tetrahedral coordination with mean Zn–C distances of 1.953 Å, while the Zn–O distance varies between 2.026 and 2.147 Å.

The sulphur analogues—methylzinc isopropyl[86] and isobutyl[81] sulphides—have an interesting structure. The former is octameric (Fig. 24), but unfortunately the X-ray examination did not reveal the carbon atoms. The Zn–S distance varied in the range 2.161–2.489 Å. The zinc atoms in the latter compound (Fig. 25) are located at the vertices of a distorted square pyramid, and the sulphur atoms over the faces of this pyramid; bond lengths were not given.

Crystalline ethylzinc iodide does not have a tetrameric structure but is a coordination polymer[87,88] (Fig. 26), owing to the bulkiness of the iodine atom, which does not permit formation of a four-membered ring. This explains the difference in chemical behaviour (solubility in hydrocarbons) between this compound and the bromide and chloride, which have a tetrameric cubane structure in solution[89]. Nevertheless, the arrangement of zinc and iodine atoms is close to a cubane structure, which can be obtained (Fig. 27) simply by shifting two iodine atoms (as indicated by the arrows) in the four-membered fragment of the polymer. The zinc atom has a distorted tetrahedral coordination; the CZnI angle is 144.4(1.7)°, the Zn–C and Zn–I bond lengths are 1.95 and 2.64 Å, and the other two Zn–I distances to the iodine atoms of neighbouring fragments (C_2H_5ZnI) of the polymer are 2.91(6) Å.

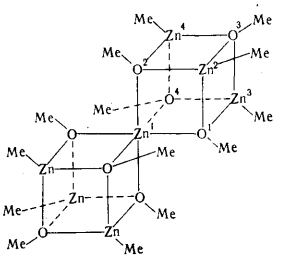


Figure 23.

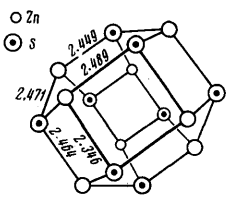


Figure 24.

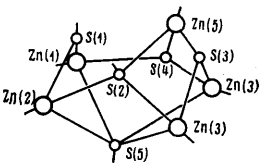


Figure 25.

The zinc atom in the crystal structure of the ionic methyldineopentylsulphonium tri-iododineopentylthiomethylzincate $[(C_5H_{11})_2SCH_3]^+[(C_5H_{11})_2SCH_2ZnI_3]^-$ is subject to distorted tetrahedral coordination[90] (Fig. 28) by three iodine atoms and one carbon atom. However, the Zn–I bonds have undergone more equalisation than in ethylzinc iodide (2.62, 2.63, and 2.68 Å), while the CZnI angle of 120°

shows maximum departure from the tetrahedral value; the Zn–C bond length is 2.14(3) Å.

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This Review shows that hardly any structural studies have been made on organic derivatives of zinc and especially of cadmium, mainly owing to the high reactivity of these compounds.

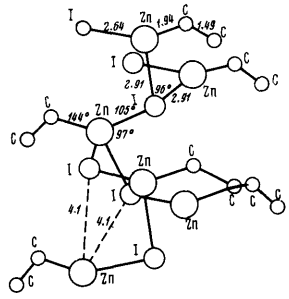


Figure 26.

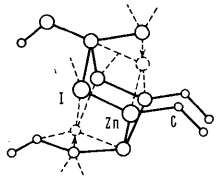


Figure 27.

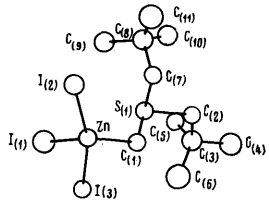


Figure 28.

The investigation of organomercury compounds, as already remarked, presents considerable difficulties owing to the great difference in atomic number between mercury and carbon. Only during recent years have papers appeared in which all the light atoms have been objectively revealed: in the vast majority of studies during the 1940s and 1950s either the coordinates of light atoms were not found at all or the accuracy of their determination was poor (~ 0.1 Å).

This aspect is especially significant in view of the fact that, in the investigation of organomercury compounds, interest lies not in establishing the structural formula, which usually requires no great accuracy, but in revealing weak intramolecular and intermolecular coordination interactions, whose analysis rests on fine changes in geometrical parameters (interatomic distances, bond angles). These interactions usually operate at large distances (~ 3 Å), close to the sums of the van der Waals radii. It is noteworthy, however, that the very concept of van der Waals radius was originally applied mainly to organogen elements, i.e. to non-metals and certain closely related classically non-transition elements (germanium, tin). However, the use of van der Waals radii of post-transition metals in which a *d*-shell has only just been filled, such as mercury, copper, etc., must evidently be approached with great caution.

The nature of the "additional" interactions discussed in the Review is not entirely clear. Electrostatic forces undoubtedly play an important part in many cases. However, it is difficult to explain the structure of many crystals, e.g. the adduct of diphenylmercury with phenanthroline, solely on the basis of electrostatic interactions. Not only further structural investigations but also appropriate quantum-chemical calculations are required to settle this question.

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