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Author's Review

## Structural Chemistry of Organomercury Compounds. Role of Secondary Interactions\*

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The structures of the organomercury compounds have been reviewed from the point of view of the secondary bonds which mercury atom forms with the surrounding atoms. These bonds, though rather labile, exhibit a definite influence on the crystal structure which is manifested in a peculiar coordination around the mercury atom. This influence has to be studied systematically since the mercury coordination polyhedra in the crystal structure of organomercury compounds are far from being regular. The review has been restricted to the structures in which the secondary bonds of mercury are shorter than the sum of the van der Waals radii. The upper limit of the distances within the coordination polyhedron cannot be well substantiated while the distances larger than the sum of the van der Waals radii may be also influential in the structure. The influence of the long-range contacts, both on the molecular structure as a whole as well as on the stability of the secondary bonds, may be quite essential. The long-range contacts actually reproduce the solvation effect in chemical reactions in solutions. From this point of view the X-ray diffraction data are useful for the study of the chemical reaction mechanism in the organic chemistry of mercury.

### INTRODUCTION

The structural chemistry of mercury compounds is one of the most interesting areas of the structural chemistry of metals. This is due largely to the fact that the mercury atom actually does not form regular coordination polyhedra and, on the contrary, that polyhedra which are intermediate to canonic or strongly distorted ones are often realized. A detailed and comprehensive analysis of the data on the structure of mercury compounds was carried out by D. Grdenić in his review<sup>1</sup> which is still regarded as the most cited and authoritative source in this area. At the same time, the section of that review dealing with the structure of organomercury compounds is rather brief in view of the absence at that time of extensive and reliable experimental data. However, in recent years a great number of sufficiently accurate structural investigations of organomercury compounds has been published. The accumulated data need systematization, which is the purpose of the present review.

\* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

However, we did not try to discuss all structural data available on this subject. In particular, the review does not include numerous papers by a group of Canadian authors dealing with the study of the interaction of  $\text{MeHg}^+$  with biological systems. Moreover, the present review does not cover all the data published prior to about 1975 as their accuracy is insufficient for detailed discussion. The review is concerned exclusively with compounds of bivalent mercury, for in the investigated organic derivatives it occurs only in this state.

The main stereochemical feature of  $\text{Hg(II)}$  compounds is a distinctly pronounced tendency of the mercury atom to form two strong predominantly colinear bonds, i. e. to be in the state of  $sp$ -hybridization. This tendency is observed both in inorganic mercury compounds of the type  $\text{XHgX}'$  with  $X$  and  $X'$  being inorganic groups or heteroatoms where rather often distortion of the linear configuration of the mercury atom bonds may still be very large, and in organic derivatives (of the type  $\text{RHgR}'$  with organic radicals  $R$  and  $R'$ ) as well as in mixed organo-inorganic derivatives  $\text{RHgX}$ . In the derivatives of the latter type a significant distortion of the linear configuration of the mercury atom bonds is also observed, although unlike compounds of the  $\text{XHgX}'$  type, such examples among the mixed  $\text{RHgX}$  compounds are, in general, less numerous.

According to D. Grdenić's terminology<sup>1</sup> in all the mentioned types of compounds displaying a tendency to the  $sp$ -hybridized state of the  $\text{Hg}$  atom, the latter reveals »characteristic« linear coordination. At the same time, in crystals of mercury compounds its atom, besides forming two strong  $sp$ -bonds, also participates, as a rule, in weaker interactions with heteroatoms having lone electron pairs. Such interactions are usually referred to as secondary bonds<sup>2</sup>. When taking into account these secondary bonds, the effective coordination of the mercury atom appears to be more complicated. In all cases when a distortion of the characteristic linear coordination of the mercury atom is observed it is in fact due to secondary bonds.

## I. MAIN GEOMETRICAL PARAMETERS OF THE COORDINATION ENVIRONMENT OF THE MERCURY ATOM IN ORGANOMERCURY COMPOUNDS

### 1. »Standard« $\text{Hg}-\text{C}$ Bond Length

Since the present review is concerned with structures of organomercury compounds of the types  $\text{RHgR}'$  and  $\text{RHgX}$ , i. e. compounds involving at least one  $\sigma$ -bond  $\text{Hg}-\text{C}$ , it is necessary to find out what value should be accepted as the standard  $\text{Hg}-\text{C}$  bond length and in what range it may vary. For this purpose, we shall consider the results obtained by X-ray crystal structural analysis and gas electronography of organomercury compounds, wherein there are no additional contacts of the mercury atom with heteroatoms, which could be considered as secondary bonds. This restriction is due to the fact that the secondary bonds may lead to a change in the lengths of the covalent bonds, as will be shown below. A few known examples of molecules which satisfy the above condition are given in Figure 1.

The  $\text{Hg}-\text{C}(sp^2)$  and  $\text{Hg}-\text{C}(sp^3)$  bond lengths in unfluorinated compounds are 2.06–2.09 and 2.05–2.09 Å, respectively, i. e. within the limits of the experimental accuracy they do not depend on the carbon atom hybridization state. On the whole, the 2.05–2.09 Å range represents those limits wherein the value of the unperturbed  $\text{Hg}-\text{C}$  bond length may be found. These values correspond to the sums (2.04 and 2.07 Å) of the carbon atom covalent radius

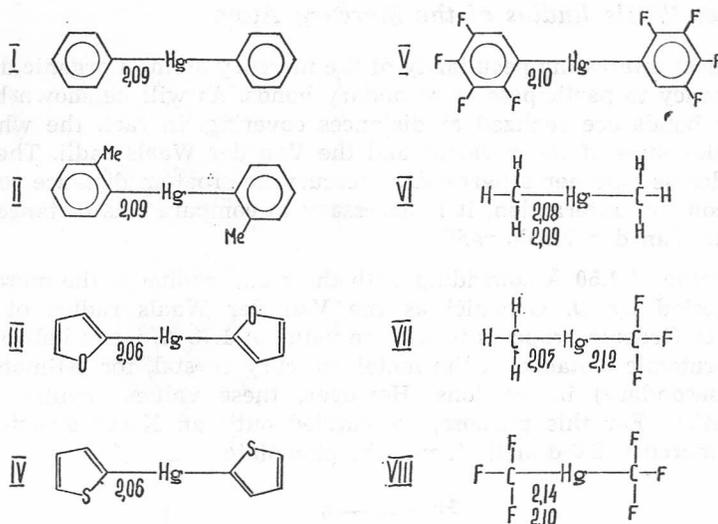


Figure 1. Hg—C bond distances (Å) in organomercury compounds without secondary bonds: I-diphenylmercury<sup>3</sup> II-di(o-tolyl)mercury<sup>4</sup>, III-di(2-furyl)mercury<sup>5</sup>, IV-di(2-thienyl)mercury<sup>6</sup>, V-bis(2,3,4,5-tetrafluorophenyl)mercury<sup>7</sup>, VI-dimethylmercury (the first value from<sup>8</sup>, the second value from<sup>9</sup>, VII-methyltrifluoromethylmercury<sup>10</sup>, VIII-di(trifluoromethyl)mercury (the first value from<sup>11</sup>, the second value from<sup>12</sup>).

( $sp^2$ —0.74 Å<sup>13</sup>,  $sp^3$ —0.77 Å<sup>14</sup>) and the mercury atom radius according to Grdenić (1.30 Å<sup>1</sup>).

In fluorinated organomercury compounds V, VII, VIII the Hg—C bond lengths are in the range of 2.10—2.14 Å; hence the electronegative substituents in the organic groups at the mercury atom are capable of inducing some elongation of this bond.

It is interesting to determine the limits of the Hg—C bond elongation which can be induced by steric strains. Such a situation is likely to occur in the molecules IX—XI (Figure 2). In these molecules the Hg—C bond length varies in the range of 2.06—2.15 Å. Thus, steric strains can cause a small elongation of the Hg—C bond.

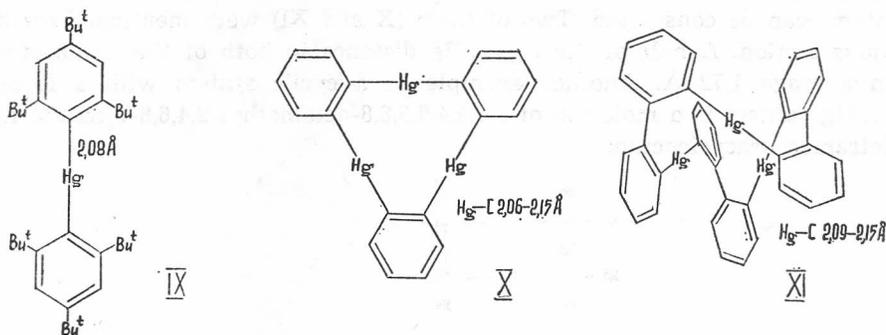
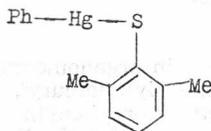


Figure 2. Some sterically overcrowded molecules of organomercury compounds: IX-bis(2,4,6-tri-*tert*-butylphenyl)mercury<sup>15</sup>, X-tribenzo [b,e,h] [1,4,7] trimercuronine<sup>16</sup>, XI-trimeric-2,2'-biphenylenemercury<sup>17</sup>.

## 2. Van der Waals Radius of the Mercury Atom

The most interesting peculiarity of the mercury atom in organic derivatives is its tendency to participate in secondary bonds. As will be shown below, the secondary bonds are realized at distances covering, in fact, the whole range between the sums of the covalent and the Van der Waals radii. Therefore, in order to decide whether a particular mercury-heteroatom distance corresponds to the secondary interaction, it is necessary to compare this distance with the sum of the Van der Waals radii.

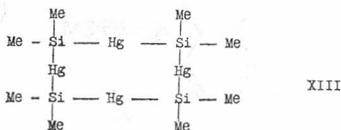
The value of 1.50 Å coinciding with the metal radius of the mercury atom was suggested by D. Grdenić<sup>1</sup> as the Van der Waals radius of mercury. However D. Grdenić proposes to use the value of 1.73 Å, i. e. a half of the next short interatomic distance in the metal mercury crystal, for estimation of the specific (secondary) interactions. However, these values require additional substantiation. For this purpose, we carried out<sup>18</sup> an X-ray structural study of phenylmercury 2,6-dimethylaminothiophenolate.



XII

In this molecule rotation around the formally single S—C bond may lead to a short contact of the Hg atom with one of the methyl groups. In fact, in the crystal, the Hg atom is close to one of the Me-groups of the same molecule at a distance of 3.36 Å. Consideration of the intermolecular distances has shown that this distance is not shortened due to the molecular packing in the crystal. Assuming that the contact of the Hg atom with the carbon atom of the Me-group is realized and that the Van der Waals radius of carbon is equal to 1.70 Å\*, this distance corresponds to the Van der Waals radius of mercury being 1.5—1.6 Å. A close value of the Van der Waals radius of mercury of 1.6 Å results from the intermolecular Hg...F contacts in the crystal structure of F<sub>3</sub>CHgCF<sub>3</sub><sup>11</sup>.

Other models, in particular cyclic molecules involving contacts between Hg atoms can be considered. Two of them (X and XI) were mentioned in the previous section. A half of the Hg...Hg distance in both of these molecules is on average 1.72 Å. Another example of a cyclic system with a forced Hg...Hg contact is a molecule of 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasilolane-1,3,5,7-tetramercurycyclooctane<sup>19</sup>.



XIII

\* Here and below we use the Van der Waals radii suggested by Bondi<sup>89</sup> for all atoms with the exception of mercury.

In this molecule the Hg...Hg half-distance is 1.64 Å. Forced Hg...Hg contacts are also found in mercurimethane molecules (Figure 3). The range of Hg...Hg distances in these molecules is 3.25—3.393 Å, which corresponds to a Van der Waals Hg radius of 1.6—1.7 Å.

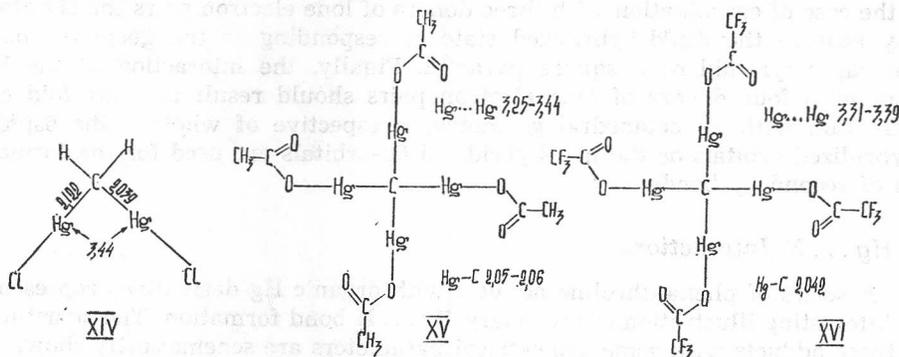


Figure 3. Hg...Hg distances in mercurimethane molecules: XIV-bis(chloromercuri)methane<sup>20</sup>, XV-tetrakis(acetoxymethylmercuri)methane<sup>21,22</sup> XVI-tetrakis(trifluoroacetoxymercuri)methane<sup>21,23</sup>.

On the basis of analysis of the intermolecular distances Hg...Hg, Hg...N, Hg...O, Hg...S, Hg...halogen, Hg...carbon of aromatic rings in many crystal structures, Canty<sup>24</sup> suggested that the Van der Waals radius of mercury is in the range of 1.7—2.0 Å.

Thus, it follows from the experimental data that the Van der Waals radius range for mercury is very wide, viz. from 1.5 to 2.0 Å. This result is probably not accidental and it implies that representation of the Van der Waals surface of the mercury atom by a sphere proves to be too rough. In view of this ambiguity it seems better to use the minimal values derived for the Van der Waals »radius« of mercury, viz. 1.5—1.6 Å, to decide whether a particular distance of mercury-heteroatom corresponds to a secondary bond.

## II. INTRA- AND INTERMOLECULAR SECONDARY BONDS OF THE MERCURY ATOM IN CRYSTALS OF ORGANOMERCURY COMPOUNDS

This section deals with crystal and molecular structures of organomercury compounds of the  $RHgR'$  and  $RHgX$  types wherein the Hg atom, apart from the formation of two strong covalent bonds, is involved also in additional interactions (secondary bonds) with one or several electron-donating heteroatoms (X, Y...). These heteroatoms may belong either to the same or to the surrounding molecules and correspondingly intra- or intermolecular secondary bonds are formed.

Since the Hg atom in organomercury compounds has vacant 6p- and 6d-orbitals, it may be expected in general to display a very diverse coordination geometry. When the Hg atom interacts with one donor of a lone electron pair, which leads to the coordination number 3, the  $6sp^2$ -hybridized state with a planar trigonal geometry or a T-shaped coordination with participation of the non-hybridized 6p-orbitals may arise.

If the Hg atom interacts with two donors of lone electron pairs, formation of the  $6sp^3$ -hybridized state should lead to a tetrahedral geometry, whereas participation of the non-hybridized  $6p$ -orbitals would correspond, in this case, to a geometry of the bisphenoid ( $TeCl_4$ ) type or, probably, to a distorted square. In the case of coordination with three donors of lone electron pairs the Hg atom may acquire the  $6sp^3d$ -hybridized state corresponding to the geometry of a trigonal bipyramid or a square pyramid. Finally, the interaction of the Hg atom with four donors of lone electron pairs should result in a six-fold coordination with an octahedral geometry, irrespective of whether the  $6sp^3d^2$ -hybridized orbitals or the non-hybridized  $6p$ -orbitals are used for the formation of secondary bonds.

### 1. Hg...N Interactions

A series of phenanthroline adducts with organic Hg derivatives represents an interesting illustration of secondary Hg...N bond formation. The structures of these adducts with some geometrical parameters are schematically shown in Figure 4. In all these structures the plane of the phenanthroline system is almost normal to the covalent bonds of the Hg atom or is in the bisectral plane of the C—Hg—C(Cl) unit if these bonds are not colinear. In crystals of XVII the secondary Hg...N bonds are realized at distances in the range 2.8—3.0 Å, i. e. close to the sum of Hg and N Van der Waals radii of 3.05—3.15 Å. However, the relative arrangement of phenanthroline and diphenylmercury molecules, which is not typical of a close packing of planar molecules in a crystal, shows that these distances are due to specific interaction. With an increase in the electronegativity of groups or atoms forming covalent bonds with the Hg atom one may observe a strengthening of the secondary Hg...N bonds. It manifests itself not only in the shortening of the Hg...N distances, but also in rehybridization of mercury atom bonds which is characterized by an increasing deviation from the collinearity of its two shortest (covalent) bonds. The  $\sigma^*$  constants characterizing the electronegativity of the substituents at the Hg atom are as follows: Ph 0.62,  $CCl_3$  2.62, Cl 2.68, CN 3.25<sup>31</sup>. Thus, the gradual strengthening of the secondary Hg...N interaction in the structures XVII, XVIII, XXIIA is associated with an increase in the total electronegative effect brought about by two substituents at the mercury atom. The difference in the structure of two crystallographically independent molecules XXIIA and XXIIIB is due to different surroundings of the Hg atoms of these molecules in the crystal: besides contacts formed by molecule XXIIA, the Hg atom of the molecule XXIIIB has an additional contact with the Cl atom of the neighbouring molecule which also corresponds to the secondary bond (Hg...Cl 3.05 Å, the sum of the Van der Waals radii being 3.35—3.45 Å).

The data given in Figure 4 show that even in the case of structure XXII, where the Hg...N interaction is the strongest, there is no complete rehybridization of the Hg atom bonds to the  $sp^3$ -state with a regular tetrahedral geometry. The coordination polyhedron of the Hg atom in the series of adducts under consideration either represents a bisphenoid (XVII—XXI) or is intermediate between bisphenoid and tetrahedron (XXII). In all cases formation of secondary bonds does not cause an elongation of the covalent bonds. Thus, the non-hybridized or almost non-hybridized vacant  $6p$ -orbitals of the mercury atom participate in the formation of secondary bonds.

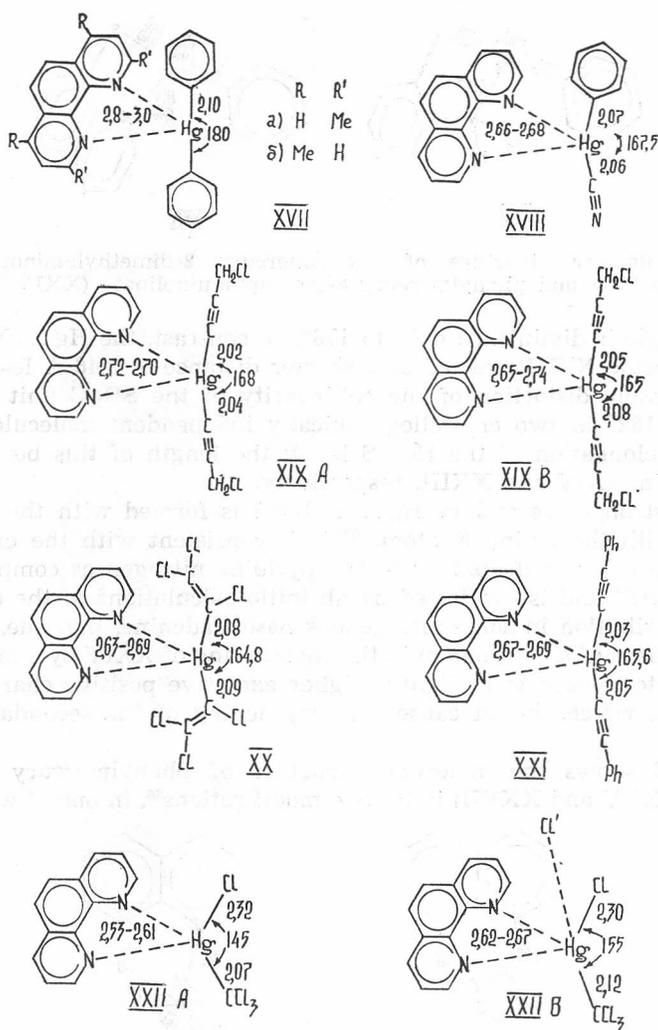


Figure 4. Structures and some geometrical parameters of a series of phenanthroline adducts with organomercury compounds (A and B-crystallographically independent molecules). XVII,<sup>25</sup> XVIII,<sup>26</sup> XIX,<sup>27</sup> XX,<sup>28</sup> XXI,<sup>29</sup> XXII<sup>30</sup>

Now it is interesting to consider molecules wherein a 5-membered chelate ring is closed due to the secondary Hg...N bond. Examples of such molecules are phenylmercuric derivatives of 2-dimethylaminothiophenol (XXIII)<sup>32</sup> and 8-mercaptoquinoline (XXIV)<sup>33</sup> whose structures are shown in Figure 5. In molecule XXIII the Hg...N distance corresponding to the secondary bond equals 2.657 Å. The N atom of the dimethylamino group has a pyramidal bond configuration (the sum of the bond angles is 336.9°), the orbital of its lone electron pair being oriented towards the Hg atom (the Hg...N—C angles are 100.3—112.3°). The Hg...N interaction in this molecule does not lead to a significant distortion of collinearity of the mercury atom covalent bonds, as

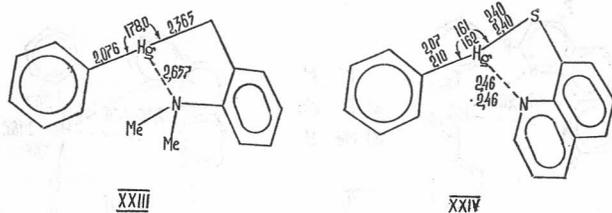


Figure 5. Molecular structure of phenylmercury 2-dimethylaminothiophenolate (XXIII)<sup>32</sup> and phenylmercury 8-mercaptoquinolinolate (XXIV)<sup>33</sup>.

the CHgS angle is diminished only to 178°. In contrast, the Hg...N secondary bond in molecule XXIV realized at a shorter distance of 2.46 Å leads not only to a considerable distortion of the collinearity of the SHgC unit (the angles are 161 and 162° in two crystallographically independent molecules) but also to a certain elongation of the Hg—S bond: the length of this bond is 2.40 Å and 2.365 Å in XXIV and XXIII, respectively.

Thus a stronger secondary Hg...N bond is formed with the pyridine N atom than with the amino N atom. This is consistent with the experimental data on the greater nucleophilicity of the pyridine nitrogen as compared to the amine nitrogen<sup>34</sup> and is confirmed by ab initio calculations of the electrostatic potential distribution in some nitrogenous bases (adenine, thymine, cytosine)<sup>35</sup>.

Replacement of a heteroatom in the chelate ring of XXIV by a more electronegative O atom leads to a slightly higher excessive positive charge ( $\delta^+$ ) on the Hg atom, which should cause a strengthening of the secondary Hg...N bond.

Figure 6 shows the molecular structure of phenylmercury 8-hydroxyquinolinolate (XXV and XXVII) in its two modifications<sup>36</sup>, in one of which (XXV)

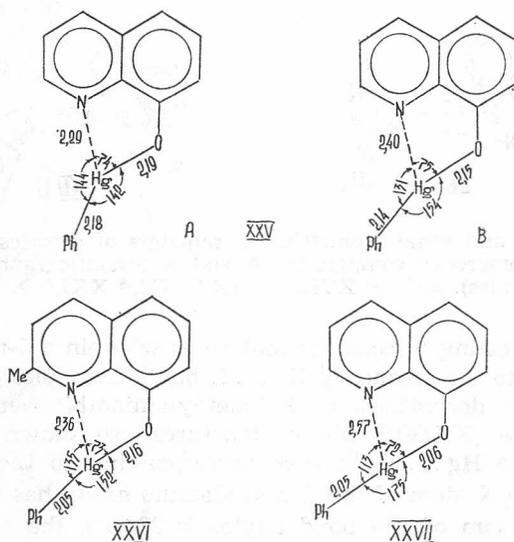


Figure 6. Molecular structures of phenylmercury 8-hydroxyquinolinolate in two crystal modifications (XXV and XXVII) and phenylmercury 2-methyl-8-hydroxyquinolinolate (XXVI)<sup>36</sup>.

there are two crystallographically independent molecules (A and B), as well as the structure of phenylmercury 2-methyl-8-hydroxyquinolate (XXVI)<sup>36</sup>. The geometrical parameters of the molecules (including two crystallographically independent molecules of XXV) shown in Figure 6 are essentially different. It is reasonable to believe that the Hg atom in molecule XXVA has a planar trigonal coordination (however, with a forced decrease of the endochelate angle resulting from the closure of this cycle) since the exochelate bond angles are in fact equal. In such a coordination the difference between the lengths of the covalent Hg—O bond (2.19 Å) and the secondary Hg...N bond (2.29 Å) turns out to be the smallest. In molecule XXVB the secondary bond is weaker: the Hg...N distance (2.40 Å) and the CHgO bond angle (154°) are greater than in molecule XXVA. The Hg atom in molecule XXVB has a coordination intermediate between a planar trigonal and T-shaped as the exochelate bond angles are essentially different. Such a situation is also found in the molecule XXVI. The secondary interaction in the molecule XXVII is even weaker: the Hg...N distance is 2.57 Å, the CHgO angle being increased to 175°, i. e. the Hg atom has a T-shaped coordination. At the same time in all four molecules considered the Hg atom coordination including the secondary bonds turns out to be planar (the sum of the bond angles of the Hg atom being 360, 360, 359.9 and 359.6°, respectively).

Above we mentioned a case when two independent molecules have essentially different geometries (phenanthroline adduct with Cl<sub>3</sub>CHgCl), which is due to the different molecular environments in the crystal. Probably, the difference in the geometrical parameters of molecules XXV—XXVII can also be accounted for by this effect. These experimental facts lead to an important general conclusion on the closeness of the energies of secondary bonds (at least not extremely strong) and intermolecular interactions in the crystal, and, consequently, on the possible influence of the crystal field on the geometrical parameters of secondary coordination.

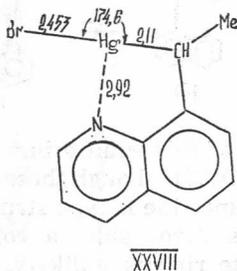


Figure 7. Molecular structure of 8-( $\alpha$ -bromomercurethyl)quinoline (XXVIII)<sup>37</sup>.

The replacement of the heteroatom (S or O) in the chelate ring by a »non-conducting« C(sp<sup>3</sup>) atom results in a weakening of the Hg...N interaction, for the energetically favourable delocalization of the electron density in the chelate ring becomes impossible. The structure of the 8-( $\alpha$ -bromomercurethyl)quinoline molecule XXVIII<sup>37</sup> is shown in Figure 7. The Hg atom has a planar T-shaped coordination. The Hg...N distance of 2.92 Å is close to the sum of the Van der Waals radii 3.15 Å and corresponds to a very weak secondary bond.



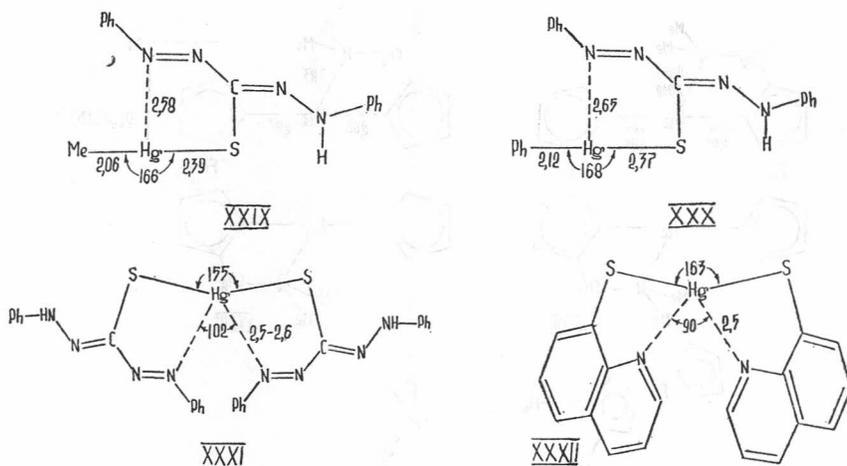
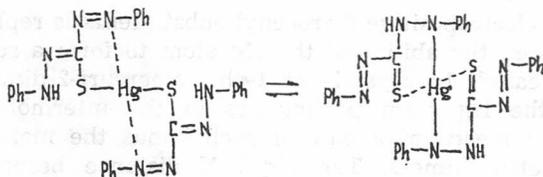


Figure 9. Molecular structures of methylmercury dithizonate (XXIX)<sup>39</sup>, phenylmercury dithizonate (XXX)<sup>39</sup>, bis(dithizonato)mercury (XXXI)<sup>40</sup> and bis(8-thioquinolinato)mercury (XXXII)<sup>41</sup>.

present in the S-form, i. e. the Hg atom forms a covalent bond with the S atom and a secondary bond with the N atom. The molecule of the mercury dithizone complex (XXXI) has the same structure in the crystal<sup>40</sup>, i. e. two stronger bonds are formed by the Hg atom to the S atoms. The possibility of a more complete delocalization of the electron density in the chelate ring of molecules XXIX and XXX results in a greater rehybridization of the Hg atom bonds. In fact, these molecules correspond to those points in Figure 5 (indicated by crosses) which are found below the general  $\alpha$  vs.  $1$  plot. The same tendency is also observed when we compare molecules XXXI and bis(8-mercaptoquinolinato)mercury (XXXII)<sup>41</sup>.

Crystals and solutions XXXI as well as those of XXIX and XXX are yellow. However, if solutions of XXXI are irradiated with visible light, they turn blue due to the following exchange reaction between the covalent and secondary bonds proceeding in solution (see<sup>39</sup> and references therein):



Molecules XXIX and XXX, which are slightly different in geometry, may be regarded as two points on the pathway of this reaction.

The structures of some aminomethylferrocenylmercury derivatives are shown in Figure 10. The Hg...N distances in the two crystallographically independent centrosymmetric molecules of bis(dimethylaminomethyl) derivative of 1,1-dimercuriferrocenophane (XXXIII)<sup>42</sup> are 2.92 and 3.05 Å, respectively, i. e. close to the sum of the Van der Waals radii. The 5-membered chelate ring closed by the secondary Hg...N bond is not planar, but the Me<sub>2</sub>N-group

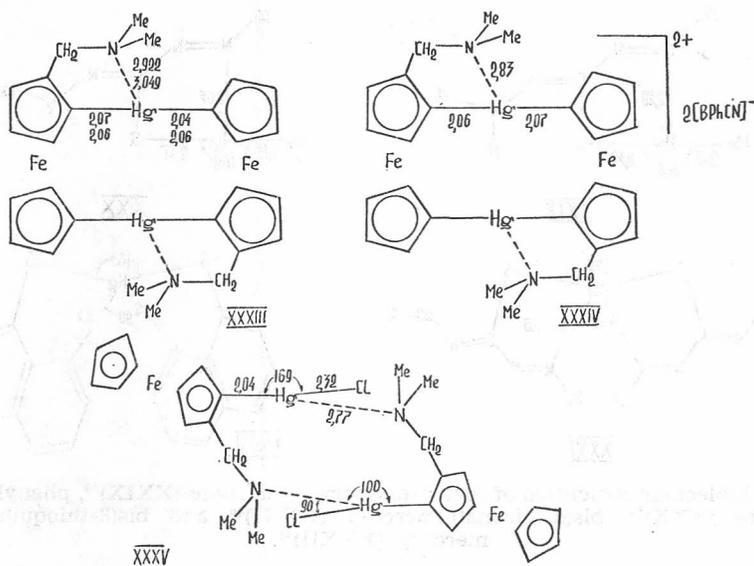


Figure 10. Structures of ferrocenyl mercury derivatives XXXIII<sup>42</sup>, XXXIV<sup>43</sup> and XXXV<sup>44</sup>.

is oriented in such way that the orbital of the lone electron pair of the N atom is directed towards the Hg atom. The weakness of the secondary bond in this molecule is due to the fact that, first, the »non-conducting« CH<sub>2</sub> group is involved in the chelate ring, secondly, the donor of the lone electron pair is the less nucleophilic amine N atom and, thirdly, the covalent bonds of the Hg atom are formed with electropositive ferrocenyl radicals.

When passing from this molecule to the corresponding dication in the salt XXXIV<sup>43</sup>, the participation of the Hg atom in the delocalization of the positive charges leads to some excessive charge ( $\delta^+$ ) on this atom. As a result, the secondary Hg...N bond becomes stronger. The chelate ring in the centrosymmetric dication XXXIV is planar and the Hg...N distance is decreased to 2.83 Å.

If one of the electropositive ferrocenyl substituents is replaced by an electronegative Cl atom, the ability of the Hg atom to form a secondary Hg...N bond is considerably increased. In crystals of 1-chloromercuri-2-dimethylaminoferrocene (XXXV)<sup>44</sup> the Hg atom participates in the intermolecular secondary Hg...N bond. By means of a pair of such bonds the molecules are linked into centrosymmetric dimers. The Hg...N distance becomes still shorter (2.77 Å), while the angle between the Hg—C and Hg—Cl bonds which is opposite to the N atom is diminished to 169°. The preference of the intermolecular coordination in this case is apparently due to the better geometrical conditions for the Hg...N interaction. In fact, in the case of an intramolecular coordination, the Hg...N distance in a planar chelate ring with undistorted bond angles at its atoms would be equal to 2.83 Å. The shortening of this distance may be achieved only by deformation of the bond angles in the chelate ring. At the same time, with intermolecular coordination no distortion of the bond angles is required and, furthermore, the lone electron pair orbital

of the N atom may be oriented more symmetrically with respect to the covalent bonds of the Hg atom than in the case of a rigid 5-membered chelate ring.

Most favourable for the secondary Hg...X interaction is the position of the X heteroatom in the plane through the Hg atom and perpendicular to its covalent bonds. The farther the heteroatom is situated from this plane, the less effective is the overlap of the interacting orbitals of the Hg and X atoms, i. e. the weaker is the secondary bond. In molecules where the closure of the 4-membered chelate ring is possible (see examples in Figure 11), the secondary

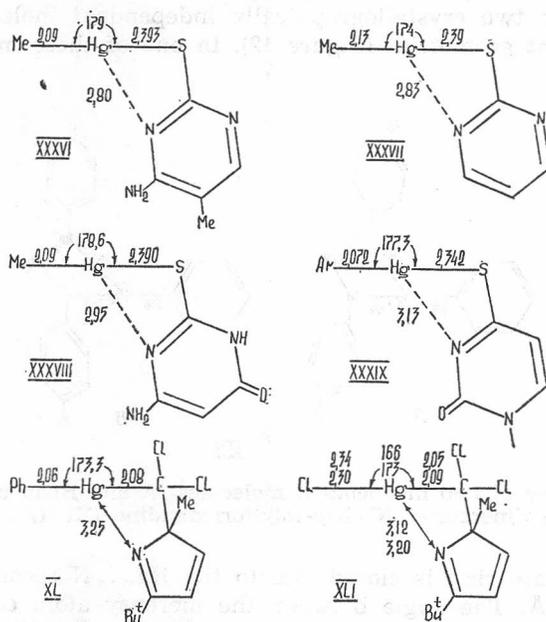


Figure 11. Structure of some molecules with a possible closure of the 4-membered chelate ring due to the secondary Hg...N interaction: XXXVI<sup>45</sup>, XXXVII<sup>46</sup>, XXXVIII<sup>45</sup>, XXXIX<sup>47</sup>, XL and XLI<sup>48</sup>.

Hg...N bond in general is weaker than in molecules with 5-membered chelate rings. In molecules of (4-amino-5-methyl-2-pyrimidinethiolate)ethylmercury (XXXVI)<sup>45</sup> and (2-pyrimidinethiolato)methylmercury (XXXVII)<sup>46</sup> (despite participation of the  $sp^2$ -hybridized N atom of the pyridine type in the secondary interaction) the secondary interaction is realized at distances of 2.80 and 2.83 Å, respectively, i. e. essentially greater than 2.46 Å in molecules of phenylmercury 8-mercaptoquinolinato (XXIV). Besides, the Hg...N interaction in the molecules XXXVI and XXXVII does not, in fact, result in a rehybridization of the Hg atom bonds. A still greater weakening of the intramolecular secondary Hg...N bonds in (4-amino-6-oxopyridine-2-thiolato)-methylmercury (XXXVIII)<sup>45</sup> and in *p*-(1-methyluracyl-4-thiolato)mercuribenzoic acid (XXXIX)<sup>47</sup> is apparently due to a decrease in the nucleophilicity of the coordinating N atom as a result of the presence of the electronegative carbonyl substituent in the heterocycle.

On passing to molecules XL and XLI<sup>48</sup>, i. e. when a 6-membered *N*-heterocycle is replaced by a 5-membered and a *S* heteroatom in the chelate ring is replaced by a  $C(sp^3)$  atom, we observe an extreme weakening or even the absence of a secondary  $Hg \dots N$  interaction. Two factors are responsible: the violation of delocalization of the electron density because of the »non-conductivity« through the  $C(sp^3)$  atom and the less favourable orientation of a lone electron pair of the *N* atom for an interaction with the *Hg* atom.

A somewhat different situation is observed in potentially tautomeric molecules with a possible closure of the 4-membered chelate ring by the secondary bond. In crystals of *N*-phenylmercuri-*N,N'*-di-*p*-tolylformamidine (XLII)<sup>49</sup> there are two crystallographically independent molecules with substantially different geometries (Figure 12). In one of these molecules (A) the

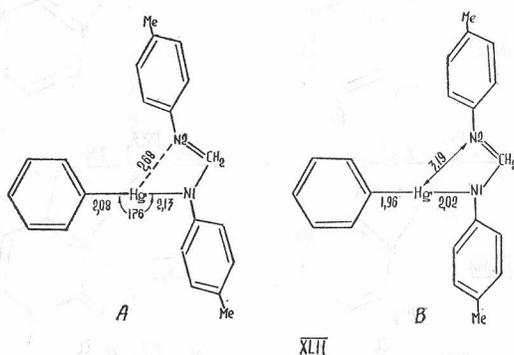
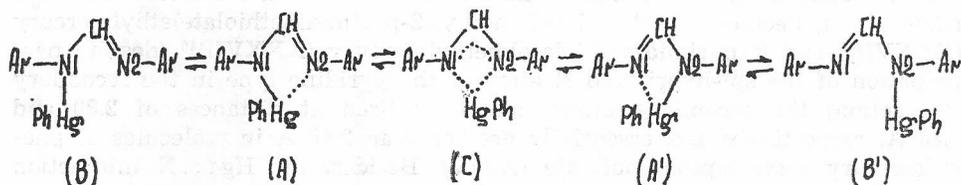


Figure 12. Geometry of two independent molecules (A and B) in crystals of *N*-phenylmercuri-*N,N'*-di-*p*-tolylformamidine (XLII)<sup>49</sup>.

4-membered chelate ring is closed due to the  $Hg \dots N$  secondary bond at a distance of 2.68 Å. The angle between the mercury atom covalent bonds is actually not reduced. In molecule B the intramolecular secondary bond is extremely weakened (the  $Hg \dots N$  distance 3.19 Å). Molecules A and B simulate two consecutive states in the pathway of the following degenerate tautomeric transformation proceeding in the solution via the intermediate mesomeric structure C:



The structure of the organomercuric salts  $MeHgL^+Z^-$  with a polydentate *N*-containing ligand *L* is also of great interest. In this case it is a priori unknown whether the mercury atom of the  $MeHg$  moiety is bonded to donor centres of the ligand *L* symmetrically or whether in such cations this atom also tends to retain the  $sp$ -hybridized state. The structure of the  $MeHgL^+$  cations in a number of their nitrates<sup>50-54</sup> is shown in Figure 13. The sym-

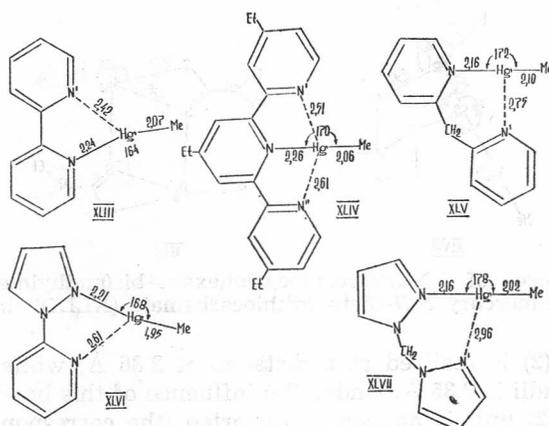


Figure 13. Structure of the  $\text{MeHgL}^+$  cations in their nitrates (L — a polydentate N-containing ligand): XLIII<sup>50,51</sup>, XLIV<sup>52,53</sup>, XLV<sup>52,53</sup>, XLVI<sup>54</sup>, XLVII<sup>54</sup>.

metrical bonding of a polydentate ligand L is not found in any of the cations. In all the structures studied only one of the N atoms of the ligand L forms a »covalent« (donor-acceptor) bond with the mercury atom of the  $\text{MeHg}^+$  unit. All other  $\text{Hg}\dots\text{N}$  interactions are realized with the participation of the vacant 6p-orbitals of the Hg atom. In (2,2'-bipyridyl)methylmercury nitrate (XLIII)<sup>50,51</sup> both  $\text{Hg}\dots\text{N}$  distances, 2.14 and 2.42 Å, are longer than the covalent  $\text{Hg}-\text{C}$  bond length (2.03—2.16 Å<sup>55-58</sup>), yet the shorter  $\text{Hg}-\text{N}$  bond is almost colinear (the angle is 164°) with the  $\text{Hg}-\text{C}$  bond. In the cation XLVI<sup>54</sup> the difference in the  $\text{Hg}\dots\text{N}$  distances (2.21 and 2.61 Å) is larger than in the cation XLIII. In this case the shorter  $\text{Hg}\dots\text{N}$  bond is more colinear with the  $\text{Hg}-\text{C}$  bond (the angle is 168°), than in cation XLIII.

In the complex XLIV<sup>52,53</sup> with a tridentate tripyridyl ligand the shortest of the  $\text{Hg}\dots\text{N}$  bonds 2.26 Å is formed with its central N atom. The competition of two secondary  $\text{Hg}\dots\text{N}$  bonds with the peripheral N atoms of the ligand having a limited flexibility results in the weakening of each of these bonds. The  $\text{Hg}\dots\text{N}'$  and  $\text{Hg}\dots\text{N}''$  distances are 2.51 and 2.61 Å, respectively, whereas the  $\text{CHgN}$  angle which is opposite to the  $\text{N}'$  and  $\text{N}''$  atoms is reduced to 170°.

As should be expected, the weakest secondary  $\text{Hg}\dots\text{N}$  bonds are found in cations XLV and XLVII<sup>52-54</sup> wherein the methylene group is involved in the chelate ring. The  $\text{Hg}-\text{N}$  distances (2.14 Å in both cases) are the shortest and lie within the limits characteristic of the corresponding covalent bond (2.02—2.18 Å<sup>55-60</sup>), whereas the  $\text{Hg}\dots\text{N}'$  distances (2.75 and 2.96 Å) are the longest in this series of compounds.

## 2. $\text{Hg}\dots\text{S}$ and $\text{Hg}\dots\text{I}$ Interactions

Sulfur and iodine atoms are »soft« donors of lone electron pairs. Therefore, these atoms may be expected to form rather strong secondary bonds with the mercury atom. The structures of 1,2-dimercaptocyclohexanobis(methylmercury) (XLVIII)<sup>61</sup> and methylmercury *N,N*-diethyldithiocarbamate (XLIX)<sup>62</sup> in crystal are shown in Figure 14. In the molecule XLVIII the intramolecular secondary

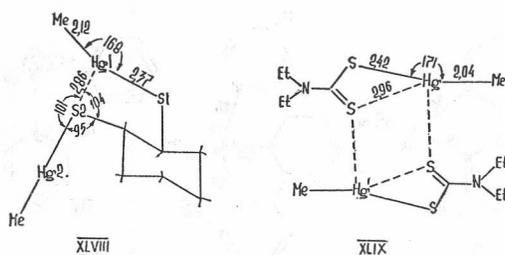


Figure 14. Structures of 1,2-dimercaptocyclohexano-bis(methylmercury) (XLVIII)<sup>61</sup> and methylmercury *N,N*-diethyldithiocarbamate (XLIX)<sup>62</sup> in crystals.

bond Hg(1) ... S(2) is realized at a distance of 2.86 Å, while the sum of the Van der Waals radii is 3.35 Å. Under the influence of this bond the collinearity of the MeHg(1)S(2) unit is noticeably distorted (the corresponding bond angle is 168°). It should be noted that the angle between the covalent bonds of the second mercury atom Hg(2) of this molecule which does not participate in the additional interactions is equal to 177°. The S(2) atom coordination and its bond angles with the participation of Hg(1), Hg(2) and C(2) atoms (101, 104, 95°) show that the orbital of one of lone electron pairs of the S(2) atom, irrespective of the presumed state of its hybridization ( $sp^2$  or  $sp^3$ ), is oriented towards the Hg(1) atom.

Crystals of XLIX are built of centrosymmetric dimers formed by means of intermolecular secondary Hg ... S(2) bonds, 3.15 Å in length. Thus the diethyldithiocarbamate ligand turns out to be chelate-bridging and participates not only in the intermolecular Hg ... S(2') bond, but also in the intramolecular secondary Hg ... S(2) bond of 2.96 Å. Under the influence of two secondary Hg ... S bonds the collinearity of the covalent-bonded triad SHgC (the angle is 171°) is distorted.

The structures of two dimeric compounds  $\{[(Ph_3P)C_5H_4HgI]I\}_2$  (L)<sup>63,64</sup> and  $\{[(Me_2S)C_5H_4HgI]I\}_2$  (LI)<sup>65</sup> with substituted ylide (onium) cyclopentadienyl groups at the Hg atoms are shown in Figure 15. Molecules L and LI are

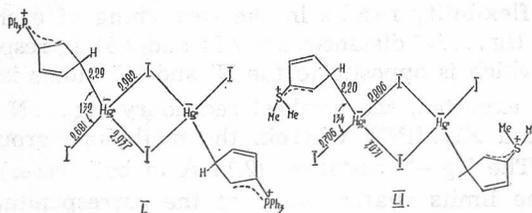


Figure 15. Structure of two ylide mercury complexes  $[(Ph_3P)C_5H_4HgI]I$  (L)<sup>63,64</sup> and  $[(Me_2S)C_5H_4HgI]I$  (LI)<sup>65</sup>.

examples of a few organomercury compounds with a characteristic coordination of the Hg atom other than linear, viz. distorted tetrahedral. However, even in these compounds the Hg atom tends to retain the  $sp$ -hybridized state, as in both cases one may distinguish two shortest bonds Hg—C (2.29 and 2.20 Å) and Hg ... I(1) (2.681 and 2.706 Å) with the largest angle between them (132 and 134° in L and LI, respectively). The other two bonds Hg ... I(2) and Hg ... I(2') (2.937, 2.982 and 2.896, 3.031 Å) may be regarded as secondary.

Under the influence of these secondary bonds a distortion of the C—Hg—I sp<sup>2</sup>-unit occurs accompanied by the elongation of the Hg—C bond in comparison to its standard value (2.05—2.09 Å). These two structures represent an example of an extreme strengthening of the secondary bonds when the distinction between »covalent« and »secondary« bonds of the Hg atom becomes almost formal.

### 3. Hg...O Interactions

The oxygen atom usually has two lone electron pairs and, therefore, it may in principle act as a donor. However, because of its higher electronegativity in comparison to N, S and I atoms the oxygen atom can participate in the formation of sufficiently strong secondary Hg...O bonds, only in very rare cases, the Hg...O interaction is most frequently electrostatic in character. Here an exception is also represented by the potentially tautomeric molecules wherein the secondary Hg...O bond may be sufficiently short and accompanied by a noticeable rehybridization of the Hg atom bonds. Examples of such molecules are shown in Figure 16.

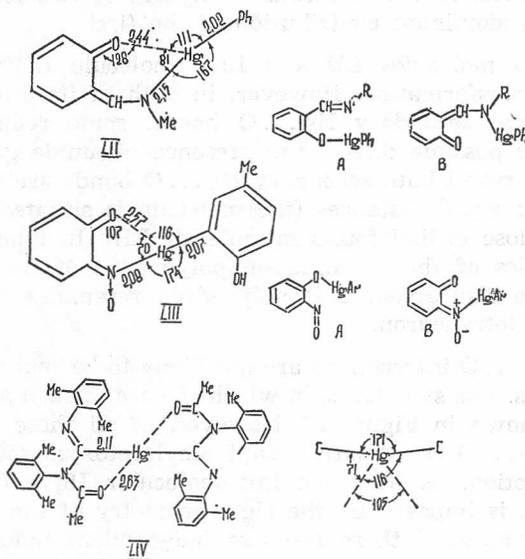


Figure 16. Structures of two potentially tautomeric molecules LII<sup>66</sup> and LIII<sup>67</sup> (A and B — tautomeric forms) and of the molecule LIV<sup>68</sup> with the intramolecular secondary Hg...O bond.

Due to the Hg...O interaction the 6- and 5-membered chelate rings are closed in molecules of phenylmercurysalicylalmethyliminato (LII)<sup>66</sup> and *o*-nitrosophenoxyl(*o*-hydroxy-*m*-tolyl)mercury (LIII)<sup>67</sup> respectively. The Hg...O distances are 2.44 and 2.57 Å, the sum of the Van der Waals radii being 3.0—3.1 Å, and the angle between the covalent bonds of the Hg atom is equal to 167 and 170°, respectively. The oxygen atom in both molecules is in the sp<sup>2</sup>-hybridized state. The orbital of one of the lone electron pairs of the O atom in these two molecules is directed towards the Hg atom. However, in the

6-membered chelate ring this orbital may be oriented more symmetrically with respect to the covalent Hg atom bonds (the angles are  $81^\circ$  and  $111^\circ$ ) than in the 5-membered chelate ring (the angles are  $70^\circ$  and  $116^\circ$ ). This results in a weakening of the Hg...O interaction in LIII as compared with LII. It is interesting to note that in the phenylmercury salicylalmethyliminato solution there exists an equilibrium between the benzoid (A) and quinoid (B) forms and its position can be changed by varying temperature or solvent polarity. Two tautomeric forms of compound LIII are also shown in Figure 16. However, in the original paper<sup>67</sup> there is no information concerning the behaviour of this compound in solution.

In the crystal both molecules exist predominantly in the quinoid N-form (B) (for LIII this is confirmed also by the distribution of the bond lengths in the salicylalmethyliminato part of the molecules; for LIII the experimental accuracy is not high enough to allow the same conclusion to be made only on the basis of the bond lengths between light atoms). At the same time, the strong Hg...O interaction indicates a significant contribution of the benzoid structure (A) in both cases. Therefore, the structure of these molecules is more correctly represented as a resonance hybrid of two forms, quinoid and benzoid, with a predominant contribution of the first.

In contrast to molecules LII and LIII, molecule LIV<sup>68</sup> is not capable of a tautomeric transformation. However, in both of its 5-membered chelate rings closed by the secondary Hg...O bonds, some redistribution of the electron density is possible due to the presence of amide groups and double C=N bonds. As a result both secondary Hg...O bonds are realized at rather short (2.63 Å) and equal distances (the molecule is situated on the two-fold axis), which are close to that found in molecule LIII. In Figure 16 the geometrical characteristics of the coordination polyhedron of the Hg atom in the molecules LIV are also given. This polyhedron resembles a bisphenoid or a strongly distorted tetrahedron.

Secondary Hg...O interactions are not likely to be realized in the 4-membered chelate rings. The structures, in which closure of such a ring is potentially possible are shown in Figure 17. However, in all these cases there is no intramolecular Hg...O coordination. Dipivaloylacetoxymercurimethane (LV)<sup>69</sup> presents no exception, as here the intramolecular Hg...O(2) contact at a distance of 2.82 Å is imposed by the rigid geometry of the acetate group. In crystals of this compound there are two independent molecules and the O atoms of the acetate groups of two adjacent molecules participate in the coordination of the Hg atom. The coordination polyhedron of the Hg atom represents a bisphenoid with an angle between the secondary intermolecular Hg...O bonds equal to  $148^\circ$ . A similar coordination polyhedron of the Hg atom is found in crystals of bis(dipivaloylmethanate)mercury (LVI)<sup>70</sup> where the O atoms of one dipivaloylmethanate group participate in two intermolecular secondary Hg...O bonds and the O...Hg...O angle is decreased to  $63^\circ$  due to the rigidity of this group. Thus the geometry of the secondary bonds in structures LV and LVI is rather far from an ideal arrangement (when all angles at the Hg atom are  $90^\circ$  or  $180^\circ$ ) determined by the interaction of the orbitals of the lone electron pairs of O atoms with the vacant 6p-orbitals of the mercury atom.

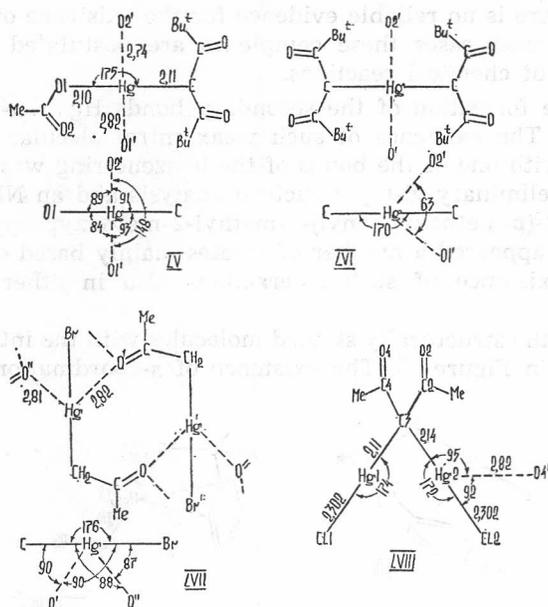


Figure 17. Examples of crystal structures of organomercury compounds with the intermolecular Hg...O coordination: LV<sup>69</sup>, LVI<sup>70</sup>, LVII<sup>71</sup>, LVIII<sup>72</sup>.

In crystals of 2-oxopropylmercury bromide (LVII)<sup>71</sup> the geometry of the secondary bonds, on the contrary, is close to ideal: all the angles involving the secondary Hg...O bonds are close to 90°. The interaction of the O atom of the carbonyl group with the Hg atoms of two adjacent molecules in the crystal leads to a decrease in the stretching frequency of this group ( $\nu = 1645 \text{ cm}^{-1}$ , while for the non-coordinated CO-group of RCOR' with R and R' = Alk  $\nu = 1710\text{--}1720 \text{ cm}^{-1}$ ). In crystals of 3,3-bis(chloromercuri)pentane-2,4-dione (LVIII)<sup>72</sup> one of the mercury atoms Hg(2) participates in the intermolecular secondary bond with the O(4) atom of the adjacent molecule. The distances between the second mercury atom Hg(1) and the nearest heteroatoms exceed the sums of the Van der Waals radii, i. e. do not correspond to specific interactions. The O atom of only one carbonyl group participates in the secondary bond with the Hg atom, and in the IR-spectrum the stretching vibration band of the group ( $1596 \text{ cm}^{-1}$ ) is shifted to the low-frequency region relative to the corresponding band of the other non-coordinated carbonyl groups ( $1667 \text{ cm}^{-1}$ ). The Hg(2) atom has a T-shaped coordination with an appropriate bond rehybridization: the angle C(3)Hg(2)Cl(2) opposite to the O(4') atom is decreased to 172°.

#### 4. Hg... $\pi$ -System Interactions

Donor properties may be exhibited not only by heteroatoms, but also by  $\pi$ -systems. The interaction of  $\pi$ -electron systems with transition metal atoms using their low-energy vacant d-orbitals is commonly known. Such interaction with non-transition and post-transition metals is considerably less typical as in this case, outer orbitals of the metal atoms with a higher energy are in-

volved. So far there is no reliable evidence for the existence of stable mercury  $\pi$ -complexes. In most cases these complexes are postulated or proved only as intermediates of chemical reactions.

However, the formation of the secondary bonds Hg... $\pi$ -system does not raise any doubt. The existence of such weak intramolecular secondary bond of the Hg atom with one of the bonds of the benzene ring was first recognized in 1968<sup>78</sup> by a preliminary X-ray structure analysis and an NMR study of the conformation of 3-(*p*-methoxyphenyl)-2-methyl-2-methoxypropyl-mercury chloride. Later there appeared a number of studies mainly based on NMR data<sup>74-80</sup> indicating the existence of such interactions also in other organomercury compounds.

Examples of the structurally studied molecules with the interaction Hg... $\pi$  bond are shown in Figure 18. The existence of  $\pi$ -coordination in these mole-

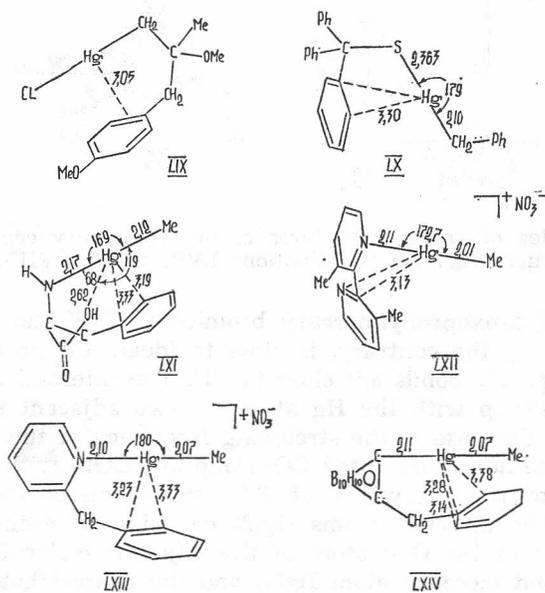


Figure 18. Examples of structures with the  $\pi$ -interaction Hg...aromatic bond: LIX<sup>78</sup>, LX<sup>82</sup>, LXI<sup>83</sup>, LXII<sup>84</sup>, LXIII<sup>85</sup>, LXIV<sup>86</sup>.

cules in solution was established by NMR spectra. In all the cases presented the distance from the Hg atom to the middle of the  $\pi$ -bond exceeds 3 Å, i. e. is rather long, and the distance from the Hg atom to the carbon atoms of this  $\pi$ -bond is close to the sum of the Van der Waals radii. However, in most cases the existence of the  $\pi$ -interaction is confirmed by the very fact of realization of such a molecular conformation (from among many possible conformations) which is most favourable for secondary bonding. An exception is the (3,3'-dimethyl-2,2'-bipyridyl)methylmercury cation (LXII)<sup>84</sup>. Hence the N atom of one of the pyridine rings forms a covalent bond with the Hg atom, the dihedral angle between the planes of the first and the second rings is equal to 100.5°. However, as it is pointed out<sup>84</sup>, the geometry of the cation LXII does not contradict the NMR data indicating a  $\pi$ -interaction<sup>81</sup>, though

this geometry does not prove such an interaction either, as the cation conformation observed in the crystal may be entirely defined by the steric interaction of the ortho-Me-groups of the pyridyl rings.

In the structure of *N*-(L-tyrosinato)methylmercury (LXI)<sup>83</sup>, apart from the  $\pi$ -coordination, there exists a secondary Hg...O bond which prevails over the secondary  $\pi$ -bond, as the covalent bonds of the Hg atom are bent from the O atom (the NHgC angle is 169°), although the molecular conformation is favourable for both secondary interactions.

Contrary to the molecules LIX—LXIII where the  $\pi$ -interaction of the Hg atom is realized with one bond of the aromatic ring, the secondary interaction in the molecule of 1-methylmercury-2-benzyl-*o*-carborane (LXIV)<sup>86</sup> may be considered as a  $\pi$ -allyl coordination. The average Hg...C distances in two crystallographically independent molecules are 3.14, 3.28, and 3.38 Å.

#### CONCLUSION

The data discussed above indicate a great variety of the structural chemistry of organomercury compounds. The most interesting feature is the ability of the mercury atom to form secondary bonds. These bonds are rather labile, i. e. in the plot of interaction energy vs. interatomic distance these bonds are represented by shallow and flat minima.

We have not considered by any means all cases of secondary interactions of the mercury atoms in crystals. As a rule, we restricted the discussion to examples of such interactions which are realized at distances shorter than the sums of the Van der Waals radii. However, since the observed mercury...heteroatom distances fall in practically the whole wide range between values close to the sums of the covalent radii and values considerably larger than the sums of the Van der Waals radii, there is no clear-cut boundary between situations where »there is a secondary bond« and where »there is no secondary bond«. Thus the upper boundary of the existence of secondary bonds chosen by us (i. e. the sum of the Van der Waals radii) is, strictly speaking, not well substantiated. Moreover, the contacts of the mercury atom at large distances, which we did not take into account, may, in a number of cases, influence both the structure and the chemical behaviour of the corresponding compounds. In the present paper this concept has been sufficiently well illustrated by examples of the structures of phenylmercury-8-hydroxyquinolate and 2-methyl-8-hydroxyquinolate and adduct of trichloromethylmercury chloride with phenanthroline as well as some others. However, the consideration of all mercury atom contacts in general does not allow us to single out the main structural features of secondary bonds. Therefore we excluded those contacts which are longer than the assumed above upper boundary of existence of the secondary bonds.

However, one should certainly remember that the influence of these long-range contacts both on the molecular structure, as a whole, and especially on the stability of the secondary bonds may be quite essential. The long-range contacts actually reproduce the solvation effect in chemical reactions in solutions. Therefore the varying structure of a certain part of the molecule in crystals of a series of related compounds or in different crystal modifications of a given compound simulates different points on the pathways of chemical reactions, particularly of the nucleophilic substitution at the mercury atom in

solutions. This reaction proceeds via the formation and strengthening of the secondary bond and leads ultimately to such a weakening of the covalent bond that it becomes a secondary bond, while the former secondary bond becomes a covalent bond. Such a treatment represents, as is known, a new approach to the study of chemical reaction mechanisms on the basis of X-ray crystal structure data. This approach is being successfully developed for organic derivatives of tin and antimony<sup>88,87,88</sup> and may also be applied to mercury compounds.

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## SAŽETAK

### Strukturna kemija organoživinih spojeva. Uloga sekundarnih interakcija

L. G. Kuz'mina i Yu. T. Struchkov

U ovom je radu dan pregled struktura organoživinih spojeva s obzirom na sekundarne veze atoma žive s atomima što je okružuju. Ove veze, iako slabe, utječu na kristalnu strukturu što se ogleda na koordinaciju oko atoma žive. Taj utjecaj treba proučavati sistematično jer koordinacijski poliedri oko atoma žive u kristalnim strukturama organoživinih spojeva nisu pravilni. Pregled se ograničava na strukture u kojima su sekundarne veze atoma žive kraće od zbroja Van der Waalsovih radijusa. Teško je odrediti gornju granicu udaljenosti u koordinacijskom poliedru jer i udaljenosti veće od zbroja Van der Waalsovih radijusa mogu imati utjecaja na strukturu. Utjecaj duljih kontakata je važan za strukturu molekule kao cjeline, ali i za stabilnost sekundarnih veza. Ti dulji kontakti u stvari reproduciraju efekt solvatacije kod kemijskih reakcija u otopinama. U tom pogledu su podaci rendgenske difrakcije korisni za proučavanje mehanizama kemijskih reakcija u organskoj kemiji žive.