Physical Chemistry

Crown compounds for anions. MNDO calculations of complexes of halide anions with cyclic pentameric difluoromethylidenemercury

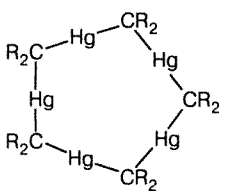
A. L. Chistyakov, I. V. Stankevich, N. P. Gambaryan, I. A. Tikhonova, and V. B. Shur*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: stan@ineos.ac.ru

Molecular and electronic structures of complexes of halide anions with cyclic pentameric difluoromethylidenemercury $[CF_2Hg]_5$ have been studied by the MNDO method. Calculations have been performed for $[L—X]^-$ halfsandwich complexes and bipyramidal complexes $[X—L—X]^{2-}$ having a shape of a spinning top (**L** is the mercury-containing macrocycle; X = F, Cl, Br, or I). It has been shown that in complexes of both types, halide anions are bonded to the mercury-containing macrocycle *via* three generalized chemical bonds: one headlight-shaped σ-bond and two two-lobe π-bonds. The complexes studied have been compared with the analogous complexes of the macrocycles containing three mercury atoms. The similarity and differences in the character of the generalized chemical bonds in relation to the size of the cycle have been considered.

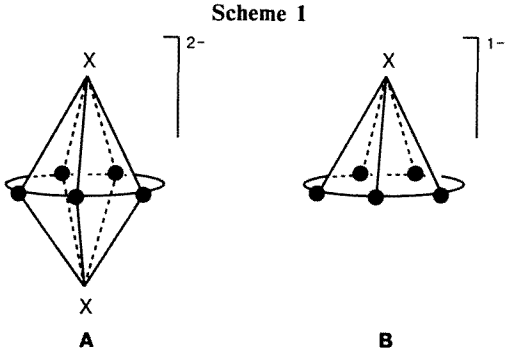
Key words: polymercury-containing macrocycles, halide anions, complexes; MNDO method; generalized chemical bonds.

Recently, it has been established that cyclic pentameric perfluoroisopropylidenemercury $[(CF_3)_2CHg]_5$ (**L1**), containing five Hg atoms in the planar ten-membered cycle,[1] is capable of binding halide anions to form $\{[(CF_3)_2CHg]_5X_2\}^{2-}$ complexes, where X = Cl (**1**),[2] Br (**2**),[3] or I (**3**).* X-ray structural study demonstrated that these complexes have the unusual shape of a spinning top (**A**), the equatorial girdle of which is the mercury-containing metallacycle, while the axis direction is defined by halide anions located above and below its plane at approximately equal distances from the mercury atoms (Scheme 1).



L1 (R = CF_3)
L2 (R = F)

Scheme 1



A **B**

* V. B. Shur, I. A. Tikhonova, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, A. Yu. Volkonsky, and E. V. Solodova, Unpublished results.

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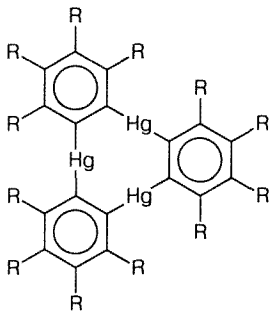
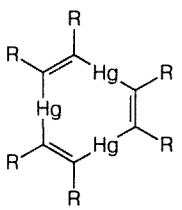
To elucidate the nature of the chemical bonds between halide anions and mercury-containing macrocycles in complexes **1**—**3**, we carried out quantum-chemical calculations of $[X—L—X]^{2-}$ bipyramidal complexes (X = F, Cl, Br, or I) of the same type for the analog of compound **L1**, namely, for cyclic pentameric difluoromethylidenemercury $[CF_2Hg]_5$ (**L2**). We have also performed calculations for macrocycle **L2** and its complexes (**B**) with halide anions of the halfsandwich type $[L2—X]^-$.

Here we report the results of the calculations and their interpretation in terms of generalized chemical bonds, which were successfully used previously in studies of π-complexes of transition metals[4] as well as complexes of halide anions with macrocycles **L3**—**L6** containing three Hg atoms (see Ref. 5).



L3 (R = H)
L4 (R = F)

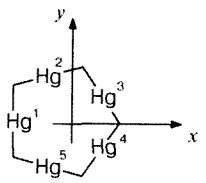


L5 (R = H)
L6 (R = F)

Results and Discussion

The geometric and electronic characteristics of the systems were calculated by the MNDO method[6] on a PC AT/386 computer using the MOPAC program.[7] The parameters for the Hg atom were taken from Ref. 8. The atomic numbering scheme for the macrocycle framework of molecule **L2** and coordinate axes are shown in Scheme 2.

Scheme 2



The coordinate axes were chosen so that the p_ρ-orbital of the Hg(1) atom (the symmetry axis of the p_ρ-AO passes through the center of the metallacycle) coincides with the p_x-AO, while the p-orbital that is involved in sp-hybridized AOs forming the Hg—C bonds coincides with the p_y-AO.

Macrocycle $[CF_2Hg]_5$. Calculations with the full optimization of geometric parameters of the mercury-containing macrocycle **L2** showed that this macrocycle has D_{5h} symmetry. The nuclear framework of the ten-membered cycle of **L2** is planar; the hybridization of the Hg atoms is close to the sp type (the C—Hg—C angle is 175°); a slight displacement of the Hg atoms toward the center of the cycle is in agreement with the data of X-ray structural analysis of macrocycle **L1** (see Ref. 1).

Molecule **L2** has the closed electron shell; the heat of formation of **L2** is negative (Table 1); the frontier MOs are nondegenerate; the ionization potential and the electron affinity are 8.4 and 2.5 eV, respectively. As in the case of metallacycles **L3**—**L6**, which we have calculated previously, the Hg atoms in macrocycle **L2** have two unoccupied p-AOs each, namely, p_ρ and p_z (see Table 2 in which the populations of the p_x- and p_z-AOs of the Hg(1) atom are given). These AOs are involved in the unoccupied MOs of the cycle, which are able to participate in formation of the generalized chemical bonds with halide anions.

Halfsandwich $[(CF_2Hg)_5X]^-$ complexes of type B. Calculations for the halfsandwich structures $[L2—X]^-$ (X = F, Cl, Br, or I) were carried out with full optimi-

Table 1. Heats of formation ($\Delta_f H°$),* heats (Δ_1) of reaction (1), heats (Δ_2) of reaction (2), optimized geometric parameters, and effective charges on the atoms of macrocycle **L2** and its complexes with halide anions $[L2—X]^-$ and $[X—L2—X]^{2-}$calculated by the MNDO method

System	Heat/kcal mol^{-1}		Distance/Å			Angle/deg		Charge/au			
	$\Delta_f H°$	Δ_1 [Δ_2]	Hg—X	Hg—C	h_C** (X···X)	C—Hg—C	Hg—C—Hg	C	Hg	F	X
L2	−38.3	—	—	2.197	—	174.8	102.8	0.139	0.338	−0.239	—
$[L2—F]^-$	−149.0	93.6	2.383	2.173	0.000	152.3	80.2	0.048	0.317	−0.251	−0.307
$[L2—Cl]^-$	−174.7	81.7	2.798	2.196	0.839	163.7	92.7	0.066	0.343	−0.261	−0.434
$[L2—Br]^-$	−159.4	83.8	2.884	2.198	1.113	163.6	93.2	0.068	0.337	−0.261	−0.420
$[L2—I]^-$	−183.0	138.3	2.849	2.211	1.057	162.1	92.0	0.065	0.301	−0.260	−0.227
$[F—L2—F]^{2-}$	−116.6	[−49.5]	2.443	2.183	(2.096)	144.9	72.9	−0.031	0.343	−0.277	−0.395
$[Cl—L2—Cl]^{2-}$	−205.7	[−23.9]	2.917	2.191	(3.051)	155.7	83.7	−0.001	0.356	−0.280	−0.488
$[Br—L2—Br]^{2-}$	−180.0	[−16.9]	2.995	2.195	(3.232)	156.9	84.9	0.004	0.350	−0.280	−0.482
$[I—L2—I]^{2-}$	−206.7	[17.3]	2.989	2.207	(3.305)	155.1	83.1	−0.003	0.298	−0.279	−0.342

* The heats of formation of the halide anions (MNDO), $\Delta_f H°$/kcal mol^{-1}, are: −17.1 (F^-), −54.7 (Cl^-), −37.5 (Br^-), and −6.4 (I^-).
** The distance between the X atom and the plane formed by the C atoms of the macrocycle.

Table 2. Wiberg indices (W), valences of atoms (V), and atomic orbital populations (Q) of macrocycle **L2** and complexes $[\mathbf{L2}—X]^-$ and $[X—\mathbf{L2}—X]^{2-}$ (C_{5v} symmetry) calculated by the MNDO method (au)

System	W		V		$Q_{Hg(1)}$				Q_X		
	Hg—X	Hg—C	Hg	X	s	p_x	p_y	p_z	s	$p_x = p_y$	p_z
L2	—	0.771	1.774	—	1.151	0.026	0.474	0.011	—	—	—
$[\mathbf{L2}—F]^-$	0.225	0.737	1.939	1.236	1.090	0.132	0.444	0.015	1.777	1.778	1.975
$[\mathbf{L2}—Cl]^-$	0.182	0.758	1.917	1.018	1.084	0.104	0.450	0.019	1.973	1.773	1.916
$[\mathbf{L2}—Br]^-$	0.186	0.757	1.919	1.044	1.089	0.102	0.449	0.022	1.981	1.781	1.877
$[\mathbf{L2}—I]^-$	0.243	0.741	1.954	1.354	1.109	0.123	0.442	0.026	1.890	1.727	1.882
$[F—\mathbf{L2}—F]^{2-}$	0.193	0.720	2.060	1.091	1.008	0.391	0.208	0.050	1.829	1.815	1.936
$[Cl—\mathbf{L2}—Cl]^{2-}$	0.164	0.744	2.027	0.937	1.018	0.151	0.426	0.048	1.984	1.836	1.832
$[Br—\mathbf{L2}—Br]^{2-}$	0.165	0.745	2.032	0.951	1.024	0.149	0.427	0.050	1.988	1.837	1.820
$[I—\mathbf{L2}—I]^{2-}$	0.206	0.728	2.093	1.172	1.048	0.164	0.417	0.072	1.928	1.792	1.830

zation of geometric parameters with retention of C_{5v} symmetry. A local minimum occurs on the potential energy surface of each complex. Heats of formation of the $[\mathbf{L2}—X]^-$ complexes and heats (Δ_1) of reactions (1) are given in Table 1; the orders of the bonds and the populations of the AOs are listed in Table 2.

$$\mathbf{L2} + X^- \rightarrow [\mathbf{L2}—X]^- + \Delta_1 \qquad (1)$$

From the data of Table 1 it follows that the heats of formation of all $[\mathbf{L2}—X]^-$ complexes are negative and all reactions (1) are exothermal. Among the $[\mathbf{L2}—X]^-$ complexes, the complex with the fluoride anion stands out. In this complex, the F^- anion is located in the center of the ring, which is a result of the small size of this anion and the large size of the macrocycle. A comparison of the data in Tables 1 and 2 with analogous parameters of the complexes of halide anions with macrocycles **L3**—**L6** containing three Hg atoms, which we calculated previously,[5] indicates that the general characteristics of the bonds between halide anions and the macrocycle are similar. In complexes of both types, the Hg atoms are displaced toward halide anions and deviate (except for the $[\mathbf{L2}—F]^-$ complex) from the plane, in which carbon atoms are located.

Analysis of the energy of the bond between the anion and the cycle, the valence of the halide anion, and the total electron density transfer from the halide anion to the macrocycle demonstrates that in the complexes with macrocycle **L2** containing five Hg atoms, these parameters are within the range of analogous values for the complexes with macrocycles containing three Hg atoms (for X = F, Cl, or Br; the complexes with the iodide anion are considered below). Therefore, the character of the bonding between halide anions and macrocycles **L2** and **L3**—**L6** is similar. In the halfsandwich complexes of pentameric difluoromethylidenemercury (**L2**), the halide anion is bonded to the ring in the same fashion as that observed in the corresponding complexes of metallacycles **L3**—**L6**, namely, *via* three generalized chemical bonds: one σ-bond and two π-bonds.[4,5]

Although the general similarity of the character of the bonding between halide anions and metallacycles occurs regardless of the number of Hg atoms in the cycle, the complexes with macrocycle **L2** have some peculiar features. First, because macrocycle **L2** contains a greater number of Hg atoms than **L3**—**L6**, it is reasonable that in complexes with **L2**, the bonding between halide anion and each individual Hg atom is weaker. This leads to somewhat larger Hg—X bond lengths and to smaller orders of these bonds (the Wiberg indices[9]) in complexes with macrocycle **L2**.

Second, the stability of the halfsandwich complexes of halide anions with macrocycles **L3**—**L6** increases in the order Br < Cl < I < F, whereas the stability of analogous complexes with **L2** increases in the different order: Cl < Br < F < I. For F^- and I^- anions, this permutation is quite natural because the conditions of the interaction between the metallacycle and the small fluoride anion should be impaired with increasing size of the metallacycle. At the same time, a favorable ratio between the sizes of the iodide anion and pentameric difluoromethylidenemercury, **L2**, leads to the fact that in the $[\mathbf{L2}—I]^-$ complex the strength of the bond between the I^- anion and the cycle, the electron density transfer from the anion to the cycle, and the valence of the iodine atom are larger than the corresponding parameters in the halfsandwich complexes of the iodide anion with molecules **L3**—**L6**.

In the halfsandwich complexes of halide anions with metallacycles **L3**—**L6**, a substantial decrease in the electron density transfer from the p_z-orbital occupied by the lone electron pair of the anion to Hg atoms was observed on going from Cl^-, Br^-, and I^- to F^- (see Ref. 5). This effect is even more pronounced in the $[\mathbf{L2}—F]^-$ complex: in this case, the electron transfer from the p_z-orbital of the F^- anion becomes quite insignificant. This is attributable to the fact that in the planar $[\mathbf{L2}—F]^-$ complex, the p_z-orbital of the F^- anion, which is located in the plane of the ring, is the π-orbital with respect to this plane, and only π-interaction with the p_z-orbitals of the Hg atoms of the macrocycle is possible for this orbital. The large Hg—F distance and a rapid decrease in the π-overlapping with increasing distance leads to an almost complete damping of the

interaction between the p_z-orbital occupied by the lone electron pair of the F^- anion and the metallacycle.

Furthermore, an increase in the size of the metallacycle should favor a relative increase in the interaction between its unoccupied orbitals and the p_x- and p_y-lone electron pairs of halide anions (compared to the s- and p_z-lone electron pairs) because the highest electron density of the p_x- and p_y-orbitals of X^- is localized in the region, which is far from the axis of the complex, whereas the s- and p_z-orbitals of X^- are localized near this axis. Actually, the characteristic feature of the complexes with macrocycle **L2** is a decrease in the electron density transfer from the halide anion to the metallacycle along the generalized σ-bond and an increase in the electron density transfer along the generalized π-bonds, in other words, an increase in the donation of electron density from the p_x- and p_y-lone electron pairs of halide anions. As a result, in $[\mathbf{L2}—X]^-$ complexes, the total electron density transfer from the halide anion to the macrocycle along two two-lobe generalized chemical π-bonds is greater than the transfer along the generalized σ-bond. In analogous complexes with metallacycles **L3**—**L6**, the electron transfer along the σ-bond is greater than the total transfer along the π-bonds in all the cases.[5]

Bipyramidal $[X—L2—X]^{2-}$ complexes of type A. Optimization of geometric parameters of $[X—\mathbf{L2}—X]^{2-}$ bipyramidal complexes (X = F, Cl, Br, and I) was carried out under the assumption that C_{5v} symmetry of the nuclear framework is retained. Calculations demonstrated that in all the cases, local minima occur on the potential energy surface. The lengths of both **L2**—X semiaxes are equal, and the systems have D_{5h} symmetry which is in agreement with the data of X-ray structural analysis of the $[X—\mathbf{L1}—X]^{2-}$ complexes (X = Cl, Br, or I).[2,3] The structures of the real $[X—\mathbf{L1}—X]^{2-}$ complexes are also characterized by anomalously short X···X distances, substantially shorter than twice the van der Waals radius of the halogen atom. Apparently, this shortening of the distances between halide anions is due to their strongly attracting interactions with the Hg atoms of macrocycle **L1**. An analogous, although more substantial, shortening of the X···X distances was also obtained in calculations of $[X—L—X]^{2-}$ complexes (**L** = **L1** or **L2**; see Tables 1 and 3).

On going from halfsandwich to bipyramidal complexes, the general characteristics of the bonds between the halide anions and the Hg atoms of metallacycle **L2** change only slightly (see Tables 1 and 2). As expected, the Hg—X distances in the bipyramidal dianions are slightly longer, whereas the corresponding Wiberg indices are smaller than those in the halfsandwich complexes. The changes in the valences of the Hg and X atoms are also reasonable: in the bipyramidal dianions, the valence of the four-coordinate Hg atoms is higher, whereas the valence for the halide anion is slightly lower than the corresponding values in the halfsandwich complexes. These natural deviations from the complete additivity do not contradict the conclusion that each of two halide anions in the bipyramidal complexes is bonded to the ring *via* three generalized chemical bonds: one σ-bond and two π-bonds. As in the case of the $[\mathbf{L2}—X]^-$ halfsandwich structures, the electron density transfer in the $[X—\mathbf{L2}—X]^{2-}$ complexes occurs predominantly along the generalized π-bonds rather than along the σ-bond, unlike the case for the bipyramidal complexes of halide anions with metallacycles **L3**—**L6**.

Table 3. Bond lengths d(Hg—X) and distances d(X···X) in the bipyramidal complexes of halide anions X^- with macrocycle **L1** based on the data of X-ray structural analysis (average values)[2,3] and the results of MNDO calculations

Complex	d(Hg—X)/Å		d(X···X)/Å		$2r_w$(X)*
	X-ray	MNDO	X-ray	MNDO	/Å
$[Cl—\mathbf{L1}—Cl]^{2-}[PPh_4]_2^+$	3.25	2.72	3.25	3.07	3.6
$[Br—\mathbf{L1}—Br]^{2-}[PPh_4]_2^+$	3.34	2.82	3.62	3.26	3.8
$[I—\mathbf{L1}—I]^{2-}[PPh_3Me]_2^+$	3.48	2.80	4.04	3.37	4.2

* Twice the van der Waals radius of the X atom.

It should be also noted that electrostatic destabilization of double-charged anions does not allow a direct comparison of the energy characteristics of the halfsandwich (**B**) and the bipyramidal (**A**) complexes. Addition reactions of the second halide anion to the halfsandwich complexes

$$[\mathbf{L2}—X]^- + X^- \rightarrow [X—\mathbf{L2}—X]^{2-} + \Delta_2 \qquad (2)$$

when X = F, Cl, or Br are endothermal (see Table 1). The possibility of the existence of the bipyramidal complexes of type **A** for these halogens is provided by high energy barriers to the removal of the halide anions from these complexes; these barriers are 10.8, 16.5, and 20.8 kcal mol^{-1} for X = F, Cl, and Br, respectively. Only for I^-, reaction (2) is exothermal.

It is interesting that in the case of mercury-containing metallacycles **L3**—**L6**, reaction (2) is exothermal when X = F^- as well. This difference between the complexes of the fluoride anion with macrocycles **L2** and **L3**—**L6** is also a manifestation of the discrepancy between the sizes of the F^- anion and metallacycle **L2** containing five Hg atoms. Note, however, that in the case of real macrocycle **L1**, which have substantially greater possibilities for delocalization of the electron density, reaction (2), according to the results of our calculations, is exothermal for all halide anions. This fact is a consequence of a decrease in the electrostatic destabilization of the double-charged anion on going from the complexes $[X—\mathbf{L2}—X]^{2-}$ to $[X—\mathbf{L1}—X]^{2-}$.

Therefore, the MNDO calculations correctly describe the principal features of the geometric and electronic structures of the bipyramidal complexes of halide anions with mercury-containing metallacycles, correlate with natural changes in the character of the bonding between halide anions and macrocycles on going from

the halfsandwich to bipyramidal complexes, and adequately reflect characteristic features of the bipyramidal complexes that are associated with the size of the cycle. However, it should be noted that the degree of interaction between halide anions and mercury-containing macrocycles determined by calculations is substantially overestimated. This leads to such peculiarities of the results of calculations, which are believed to be artifacts.

For example, a too strong interaction (according to calculations) of the Hg atoms with the halide anions manifests itself in a considerable (compared to the results of X-ray structural analysis; see Table 3) shortening of the Hg—X bonds and in an excessively small distances between the halide anions. It also causes a substantial decrease in the C—Hg—C and Hg—C—Hg angles compared to those experimentally observed (*cf.* Refs. 2 and 3 and Table 1). The latter fact leads to the unreasonable character of the charge redistribution in the metallacycle. Actually, as is evident from Table 2, the electron density on the C and F atoms increases so significantly upon complexation between **L2** and X^- that the electron density transfer from the halide anion to the metallacycle results in an increase rather than in a decrease in the positive charges on the Hg atoms (except for the case when X = I, where the part of the transferred electron density does remain on the Hg atoms as well).

Analysis of the populations of the AOs of the Hg atoms and the change in the populations in the series X = F, Cl, Br, I (see Table 2) demonstrates that the electron density on the unoccupied AOs of the mercury atoms of the initial metallacycle does increase, but this effect is masked by a considerable decrease in the populations of the AOs that are involved in the sp-hybridized AOs of the mercury atoms that form the Hg—C bonds (see the populations of the s- and p_y-orbitals of the Hg(1) atom in Table 2). A decrease in the populations of these AOs is a result of deviations of the hybridization of Hg atoms in the bipyramidal dianion from the sp type (change to sp^2- or even to sp^3-hybridization). In other words, anomalies of the changes in charges on the Hg atoms upon complexation are also due to the overestimation of the degree of interaction between the mercury atoms and the halide anions.

Calculations of the bipyramidal complex of metallacycle **L1** with bromide anions using the last version of the MNDO/PM3 method[10] demonstrated that in this case the Hg—Br bond lengths, the Br···Br distance, and the C—Hg—C and Hg—C—Hg angles are also substantially smaller that those experimentally observed[3] for the $[Br—\mathbf{L1}—Br]^{2-}$ complex.

Note, however, that although MNDO calculations overestimated, as was already mentioned, the degree of the interaction between halide anions and Hg atoms, the results of these calculations adequately reflect the principal features of the geometric and electronic structures of the bipyramidal complexes of halide anions with mercury-containing macrocycles.

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