

Crown compounds for anions. A new approach to the description of chemical bonds in the complexes of halide anions with polymercury-containing macrocycles ¹

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Abstract

The nature of chemical bonds between halide anions and polymercury-containing macrocycles has been investigated. For this purpose, calculations of the complexes of halide anions with cyclic trimeric *o*-phenylenemercury (*o*-C₆H₄Hg)₃, cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄Hg)₃, cyclic pentameric perfluoroisopropylidenemercury [(CF₃)₂CHg]₅ and some of their simpler hypothetical analogs have been carried out by the MNDO method. Complexes of the half-sandwich [L–X][–], bipyramidal [X–L–X]^{2–} and sandwich [L–X–L][–] (X = Hal, L = mercury-containing macrocycle) types have been calculated. It has been established that a uniform description of the bonding in such complexes, not depending on the number of Hg atoms in the macrocycle, can be reached within the framework of the concept of generalized chemical bonds. © 1997 Elsevier Science S.A.

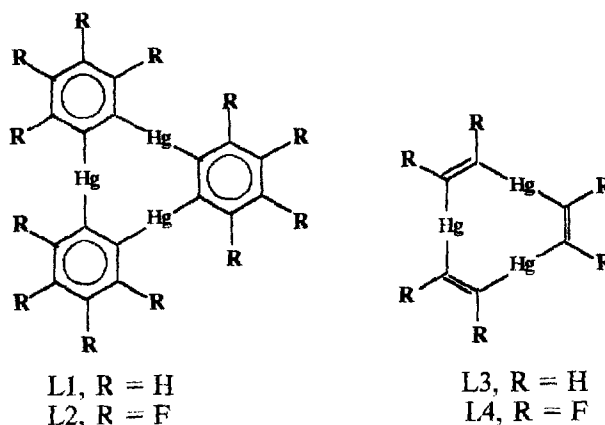
Keywords: Polymercury-containing macrocycles; Halide anions; Complexes; MNDO method; Generalized chemical bonds

1. Introduction

The problem of creating effective crown compounds for binding of anions is of great importance to the areas of molecular recognition and ion transport, as well as to organic synthesis and catalysis. One of the ways of developing such crown compounds is based on using macrocyclic multidentate Lewis acids as anion receptors. At present, a large number of papers on anion binding properties of polytin-, polysilicon- and polymercury-containing macrocycles has been published (see e.g. Refs. [1–13]). The possibility of application of such macrocycles in phase transfer catalysis of electrophilic reactions has also been reported [4,8,9].

On starting our studies in 1987 on anion complexation by macrocyclic multidentate Lewis acids, we chose two known mercury-containing macrocycles, i.e. cyclic trimeric *o*-phenylenemercury (*o*-C₆H₄Hg)₃ (**L1**) [14] and cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-

C₆F₄Hg)₃ (**L2**) [15,16] as Lewis acidic hosts. Both macrocycles have planar structures with C–Hg–C bond angles close to 180° [14,16], indicating the sp hybridization of the mercury atoms. It turned out that these macrocycles were capable of readily binding halide anions (Cl[–], Br[–], I[–]) in halomethane, ethanol and acetone solutions [4,5] to form complexes which, in the case of **L2**, could be isolated in the analytically pure state.



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¹ Dedicated by his coauthors to the memory of Professor Yu.T. Struchkov.

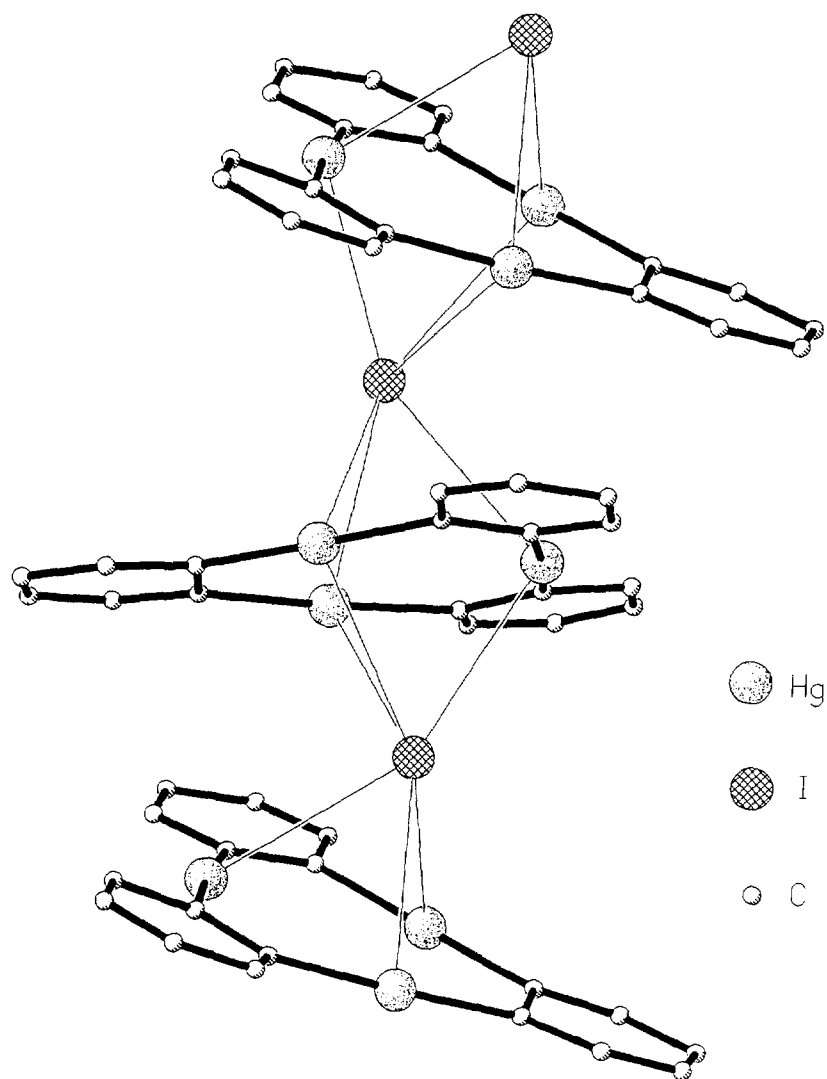


Fig. 1. The fragment of infinite polyanionic chain $\{[(o\text{-C}_6\text{F}_4\text{Hg}_3\text{I})_n]^{n-}\}$ in the structure of complex I [5]. The F atoms of the phenylene rings are omitted for clarity.

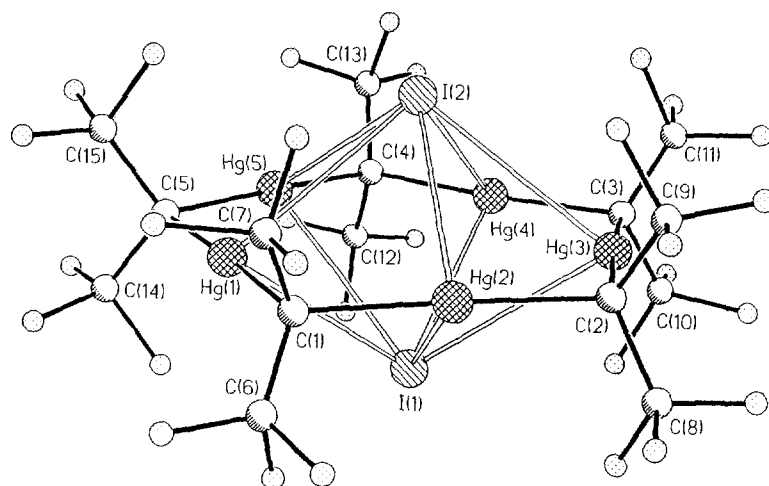


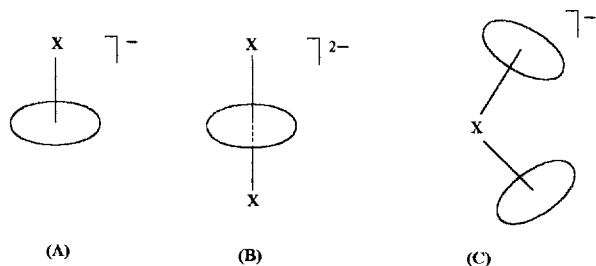
Fig. 2. Structure of the $\{[(\text{CF}_3)_2\text{CHg}_5\text{I}_2]^{2-}\}$ anion [7].

Elemental analysis of the complexes of **L2** with iodide and bromide anions has shown that they have the composition $[\text{L2-X}]^-$ ($X = \text{I}, \text{Br}$), i.e. contain one halide anion per macrocycle molecule. According to X-ray photoelectron spectra, the mercury atoms in the complexes proved to be equivalent. This fact enabled one to suggest that the complexes had unusual half-sandwich structures in which the halide anion was symmetrically coordinated to all three Hg atoms of the cycle. The corresponding polymeric structures of polydecker sandwiches $\{[\text{L2-X}]_n\}^{n-}$ with halide anions as coordinating centers were also drawn, but these seemed too fantastic and so were not discussed seriously. Nevertheless, it then turned out that just these polydecker structures were realized for both complexes (at least in the solid state) and the establishment of this remarkable fact was entirely the merit of Struchkov and coworkers [5]. It is a great pity that Yuri Timofeevich Struchkov left us so early, but the fond memory of him will remain forever in our hearts.

Fig. 1 shows the structure of the complex of macrocycle **L2** with iodide anion $\{[\text{L2-I}]_n\}^{n-}$ (**I**) [5]. The complex is indeed polymeric and contains an infinite zigzag chain which is made up of alternating **L2** molecules and I^- anions. Each iodide anion in **I** is symmetrically bonded to six mercury atoms of the two neighboring molecules of the macrocycle. The mean planes of the central nine-membered rings Hg_3C_6 of the neighboring **L2** molecules are non-parallel (dihedral angle 36.1°), i.e. the complex has a structure of a bent polydecker sandwich. A similar structure has been established for the complex of **L2** with bromide anion $\{[\text{L2-Br}]_n\}^{n-}$ (**II**) [5].

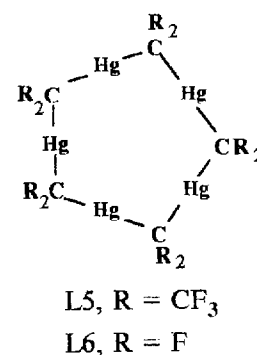
The polymeric chains of **I** and **II** contain three simple fragments (A, B and C) which might, in principle, correspond to individual complexes.

In the half-sandwich complexes of type A, which are monomeric units of polymer structures **I** and **II**, there is one halide anion per molecule of the initial macrocycle.



Bipyramidal complexes of type B with two halide anions per **L2** molecule have the shape of a spinning top, the equatorial girdle of which is the mercury-con-

taining macrocycle, whilst the axis direction is fixed by halide anions located above and below the metallacycle plane at approximately equal distances from the mercury atoms. Similar complexes $\{[(\text{CF}_3)_2\text{CHg}]_5\text{Cl}_2\}^{2-}[\text{PPh}_4]_2^+$ (**III**) $\{[(\text{CF}_3)_2\text{CHg}]_5\text{Br}_2\}^{2-}[\text{PPh}_4]_2^+$ (**IV**) and $\{[(\text{CF}_3)_2\text{CHg}]_5\text{I}_2\}^{2-}[\text{PPh}_3\text{Me}]_2^+$ (**V**) have previously been obtained in our studies [6,7] by the interaction of cyclic pentameric perfluoroisopropylidenemercury $(\text{CF}_3)_2\text{CHg}$ (**L5**) [17] with $[\text{PPh}_4]^+\text{Cl}^-$, $[\text{PPh}_4]^+\text{Br}^-$ and $[\text{PPh}_3\text{Me}]^+\text{I}^-$ in ethanol: the structures of these compounds have also been determined by Struchkov and coworkers (see Fig. 2 and Refs. [6,7]).



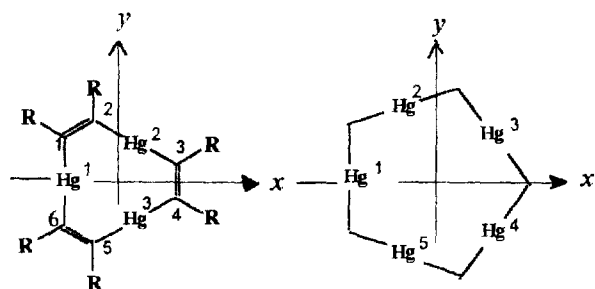
The complexes of type C contain one halide anion per two molecules of **L2** and represent double-decker bent sandwiches, in which the role of the coordinating center is played not by the metal atom or cation, as in the case of normal sandwich complexes, but by the anion of the halogen. Such complexes are so far unknown.

The present work is devoted to the theoretical study of the nature of chemical bonds between polymercury-containing macrocycles and halide anions [10]. For this purpose we modeled the fragments of the potential energy surface (PES) of the complexes of halide anions of types A, B, and C with macrocycles **L1**, **L2**, **L5** and their simpler hypothetical analogs **L3**, **L4** and **L6**. Local minima were found on the PES of these complexes and the electronic structures of the systems corresponding to these minima were studied. Calculations were performed by the MNDO method [18] (the parameters for the mercury atom were taken from Ref. [19]). Free macrocycles **L1**–**L6** were calculated as well.

2. Results and discussion

Calculations were carried out on a PC AT/486 computer and Workstation DEC Alpha AXP 3000-400 using the MOPAC program [20]. The atomic numbering

schemes for the macrocyclic frameworks of the **L1–L6** molecules and the coordinate axes are shown below:



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^1 -C bonds coincides with the p_y -AO.

2.1. Mercury-containing macrocycles **L1–L4** and **L6**

Calculations with the full optimization of geometric parameters of the mercury-containing macrocycles showed that macrocycles **L1–L4** were planar and had

D_{3h} symmetry. In the molecule **L6** having D_{5h} symmetry, the macrocyclic framework is planar too. In all the macrocycles, excepting **L3**, the C–Hg–C bond angles (Table 1) differ only slightly from 180° , which is in good agreement with the data of X-ray structural analysis for **L1**, **L2** and **L5** [14,16,17]. Hence, each mercury atom in the **L1–L4** and **L6** molecules is in the state corresponding to sp hybridization and, consequently, has two mutually orthogonal unoccupied p orbitals: p_z -AO and p_ρ -AO. This conclusion is confirmed by the values of the populations of AOs of Hg^1 atoms. As seen from Table 2, the populations of the p_x - and p_z -AOs of these atoms are close to zero. The contributions of the p_ρ - and p_z -AOs of all Hg atoms to the occupied MOs of molecules **L1–L4** and **L6** are small.

From the values of the effective charges of atoms in macrocycles **L1–L4** and **L6** (see Table 1) it follows that a substantial positive charge is located on the Hg atoms (the maximum value in **L4** and the minimum value in **L6**). When passing from molecules **L1** and **L3** to their perfluorinated analogs **L2** and **L4**, the positive charge on the mercury atoms increases.

The p_z - and p_ρ -AOs of Hg atoms make substantial contributions only to the unoccupied MOs of molecules **L1–L4** and **L6**. Among these orbitals, there are MOs of two types:

- (1) MOs belonging to the a_1' and a_2'' irreducible

Table 1

Heats of formation ΔH_f° , ^a heats of the reaction in Eq. (1) Δ_1 , optimized geometric parameters, and effective charges on the atoms of macrocycles **L** and their half-sandwich complexes $[\text{L-X}]^-$ calculated by the MNDO method

System	Symmetry	Heat/kcal mol ⁻¹		Distance/Å		Angle/deg		Charge/a.u.		
		ΔH_f°	Δ_1	X–Hg	Hg–C	C–Hg–C	θ	C(1)	Hg	X
L1	D_{3h}	255.3	—	—	2.002	174.3	0.0	–0.207	0.462	—
$[\text{L1-F}]^-$	C_{3v}	132.2	106.0	2.067	2.043	156.4	13.1	–0.237	0.462	–0.314
$[\text{L1-Cl}]^-$	C_{3v}	156.0	46.4	2.631	2.027	153.9	15.1	–0.215	0.451	–0.449
$[\text{L1-Br}]^-$	C_{3v}	175.5	42.3	2.747	2.025	154.0	15.6	–0.211	0.448	–0.471
$[\text{L1-I}]^-$	C_{3v}	174.4	74.5	2.785	2.029	152.2	16.6	–0.217	0.421	–0.363
L2	D_{3h}	–220.8	—	—	2.024	178.2	0.0	–0.196	0.500	—
$[\text{L2-F}]^-$	C_{3v}	–396.3	158.4	2.041	2.084	155.7	11.9	–0.229	0.510	–0.284
$[\text{L2-Cl}]^-$	C_{3v}	–366.3	90.6	2.580	2.069	152.8	13.9	–0.212	0.486	–0.358
$[\text{L2-Br}]^-$	C_{3v}	–345.6	87.3	2.691	2.071	152.7	14.0	–0.209	0.479	–0.361
$[\text{L2-I}]^-$	C_{3v}	–346.6	119.4	2.745	2.097	151.1	15.1	–0.213	0.452	–0.265
L3	D_{3h}	158.4	—	—	1.977	168.4	0.0	–0.231	0.432	—
$[\text{L3-F}]^-$	C_{3v}	61.2	80.1	2.085	2.011	159.6	15.7	–0.292	0.413	–0.338
$[\text{L3-Cl}]^-$	C_{3v}	78.4	25.1	2.670	1.996	155.2	16.2	–0.265	0.409	–0.510
$[\text{L3-Br}]^-$	C_{3v}	96.8	24.3	2.788	1.994	155.6	16.1	–0.260	0.408	–0.538
$[\text{L3-I}]^-$	C_{3v}	96.6	55.4	2.822	2.000	155.7	18.7	–0.267	0.380	–0.427
L4	D_{3h}	–16.4	—	—	2.054	173.0	0.0	–0.077	0.526	—
$[\text{L4-F}]^-$	C_{3v}	–175.9	142.4	2.057	2.082	157.2	12.8	–0.154	0.517	–0.295
$[\text{L4-Cl}]^-$	C_{3v}	–146.6	75.3	2.597	2.071	154.4	14.8	–0.131	0.499	–0.393
$[\text{L4-Br}]^-$	C_{3v}	–126.2	72.3	2.703	2.070	154.5	14.9	–0.127	0.494	–0.405
$[\text{L4-I}]^-$	C_{3v}	–127.0	104.2	2.761	2.076	151.9	16.9	–0.132	0.468	–0.305
L6	D_{5h}	–38.3	—	—	2.197	174.8	—	0.139	0.338	—
$[\text{L6-F}]^-$	D_{5h}	–149.0	93.6	2.383	2.173	152.3	—	0.408	0.317	–0.307
$[\text{L6-Cl}]^-$	C_{5v}	–174.7	81.7	2.798	2.196	163.7	—	0.066	0.343	–0.434
$[\text{L6-Br}]^-$	C_{5v}	–159.4	83.8	2.884	2.198	163.6	—	0.068	0.337	–0.420
$[\text{L6-I}]^-$	C_{5v}	–183.0	138.3	2.849	2.211	162.1	—	0.065	0.301	–0.227

^a The heats of formation of the halide anions (MNDO), ΔH_f° /kcal mol⁻¹, are: –17.1 (F⁻), –54.7 (Cl⁻), –37.5 (Br⁻), and –6.4 (I⁻).

representations of the D_{3h} and D_{5h} groups. These orbitals can interact with the s- and p_z -AOs of halide anions;

(2) MOs belonging to the e' and e'' irreducible representations of the D_{3h} and D_{5h} groups. These orbitals can interact with the p_x - and p_y -AOs of halide anions.

2.2. The half-sandwich complexes (type A)

The structures of half-sandwich complexes $[\text{L-X}]^-$ (where $X = \text{Hal}$ and $\text{L} = \text{L1-L4}$) were modeled with partial geometry optimization. It was assumed that the structures of the C_{6v} (when $\text{L} = \text{L1, L2}$) and C_{2v} (when $\text{L} = \text{L3, L4}$) fragments remain unchanged on complex formation and the C^1-C^6 carbon atoms are located in one and the same plane. Furthermore, as the calculations of complexes $[\text{L4-F}]^-$ and $[\text{L4-I}]^-$ demonstrated that the position of the halide anions on the symmetry axis of the half-sandwich complex was stable with respect to transverse displacements, the assumption was made that all half-sandwich complexes $[\text{L-X}]^-$ have C_{3v} (for $\text{L} = \text{L1-L4}$) and C_{5v} (for $\text{L} = \text{L6}$) symmetry.

In calculations of the half-sandwich complexes $[\text{L-X}]^-$ ($\text{L} = \text{L1-L4}$), the following parameters were optimized: (1) the distance from the halide anion to the

(x, y) plane, in which the C^1-C^6 atoms were located; (2) the distances from the Hg atoms to the C_3 symmetry axis; (3) the deviations of the Hg atoms from the (x, y) plane; (4) the distances from the middle of each C-C bond of the macrocycle to the C_3 symmetry axis; (5) the dihedral angles θ between the plane of each six-membered cycle in **L1** and **L2** systems and the (x, y) plane; (6) the dihedral angles θ between the plane of each C_2R_2 fragment in **L3** and **L4** and the (x, y) plane. Calculations of the half-sandwiches $[\text{L6-X}]^-$ ($X = \text{Hal}$) were carried out with full optimization of geometric parameters on retention of C_{5v} symmetry.

The results of the calculations have shown that, in all cases, the reaction (Eq. (1)) of complexation of macrocycles **L1-L4** and **L6** with halide anions to form half-sandwiches is exothermic (Table 1). The heat Δ_1 of this reaction characterizing the stability of the complex $[\text{L-X}]^-$ is very high, being substantially higher for the perfluorinated macrocycles than for the corresponding nonfluorinated systems.



As a result of complexation with halide anion the macrocyclic ligand becomes nonplanar. The Hg atoms deviate from the (x, y) plane, in which the C atoms are located, and are displaced toward the z axis. The C-Hg-C bond angles deviate markedly from 180° (see

Table 2

Wiberg indices W , valences of atoms V , and atomic orbital populations Q of macrocycles **L** and half-sandwich complexes $[\text{L-X}]^-$ calculated by the MNDO method

System	$W/\text{a.u.}$		$V/\text{a.u.}$		$Q(\text{Hg}^1)/\text{a.u.}$				$Q(X)/\text{a.u.}$		
	Hg-X	Hg-C	Hg	X	s	p_x	p_y	p_z	s	$p_x = p_y$	p_z
L1	—	0.877	1.926	—	0.942	0.042	0.505	0.049	—	—	—
$[\text{L1-F}]^-$	0.370	0.805	2.125	1.215	0.832	0.154	0.455	0.097	1.743	1.829	1.913
$[\text{L1-Cl}]^-$	0.293	0.821	2.098	0.981	0.865	0.109	0.461	0.115	1.976	1.875	1.723
$[\text{L1-Br}]^-$	0.280	0.824	2.094	0.941	0.871	0.104	0.462	0.115	1.984	1.888	1.711
$[\text{L1-I}]^-$	0.330	0.819	2.135	1.107	0.877	0.112	0.458	0.132	1.931	1.865	1.701
L2	—	0.854	1.902	—	0.917	0.039	0.501	0.042	—	—	—
$[\text{L2-F}]^-$	0.384	0.786	2.095	1.259	0.797	0.152	0.446	0.095	1.730	1.823	1.908
$[\text{L2-Cl}]^-$	0.331	0.797	2.091	1.113	0.833	0.116	0.449	0.116	1.973	1.863	1.661
$[\text{L2-Br}]^-$	0.326	0.799	2.093	1.099	0.840	0.114	0.449	0.114	1.982	1.873	1.634
$[\text{L2-I}]^-$	0.368	0.794	2.128	1.238	0.850	0.119	0.446	0.133	1.929	1.853	1.630
L3	—	0.882	1.936	—	0.964	0.045	0.509	0.049	—	—	—
$[\text{L3-F}]^-$	0.357	0.818	2.128	1.174	0.868	0.152	0.461	0.106	1.754	1.836	1.912
$[\text{L3-Cl}]^-$	0.264	0.837	2.111	0.884	0.900	0.104	0.470	0.116	1.979	1.888	1.755
$[\text{L3-Br}]^-$	0.248	0.840	2.104	0.836	0.906	0.099	0.472	0.115	1.986	1.900	1.751
$[\text{L3-I}]^-$	0.303	0.834	2.147	1.010	0.917	0.108	0.467	0.133	1.935	1.879	1.734
L4	—	0.855	1.870	—	0.901	0.026	0.500	0.044	—	—	—
$[\text{L4-F}]^-$	0.381	0.788	2.093	1.245	0.790	0.154	0.447	0.095	1.736	1.820	1.918
$[\text{L4-Cl}]^-$	0.320	0.799	2.075	1.071	0.827	0.105	0.452	0.117	1.973	1.8585	1.703
$[\text{L4-Br}]^-$	0.311	0.802	2.074	1.046	0.834	0.101	0.453	0.118	1.982	1.869	1.685
$[\text{L4-I}]^-$	0.357	0.796	2.111	1.197	0.841	0.108	0.449	0.134	1.929	1.846	1.683
L6	—	0.771	1.774	—	1.151	0.026	0.474	0.011	—	—	—
$[\text{L6-F}]^-$	0.225	0.737	1.939	1.236	1.090	0.132	0.444	0.015	1.777	1.778	1.975
$[\text{L6-Cl}]^-$	0.182	0.758	1.917	1.018	1.084	0.104	0.450	0.019	1.973	1.773	1.916
$[\text{L6-Br}]^-$	0.186	0.757	1.919	1.044	1.089	0.102	0.449	0.022	1.981	1.781	1.877
$[\text{L6-I}]^-$	0.243	0.741	1.954	1.354	1.109	0.123	0.442	0.026	1.890	1.727	1.882

Table 1). Among the $[L6-X]^-$ complexes, the complex with the fluoride anion stands out. In this complex, the anionic species is located in the center of the ring, which is a result of the small size of the F^- anion and the large size of the macrocycle. Test calculations have shown that the location of the F^- within the assumption of C_{5v} symmetry does not change on relaxation of this symmetry restriction.

The data of Tables 1 and 2 indicate the general similarity in characteristics of the bonds between halide anions and the macrocycles L1–L4 on the one hand and the macrocycle L6 on the other hand. Analysis of the values of the energy of the bond between the anion and the cycle, of the valence of the halide anion, and of the total electron density transfer from the halide anion to the macrocycle has demonstrated that, in the complexes with macrocycle L6 containing five Hg atoms, these parameters are within the range of analogous values for the complexes with macrocycles L1–L4 containing three Hg atoms (for $X = F, Cl$ or Br ; the complexes with the iodide anion are considered below). This suggests that the nature of bonds of halide anions with the macrocycles L1–L4 and the macrocycle L6 is of the same kind.

The bonding of a halide anion to three mercury atoms in complexes $[L-X]^-$ ($L = L1-L4$) can be described by three equivalent donor–acceptor bonds. Each of these bonds is formed due to the lone electron pair of a halide anion (occupying its sp^3 -hybridized AO directed toward the corresponding Hg atom) and the unoccupied AO of the mercury atom directed toward the halide anion. However, such a description by means of two-center bonds is no longer appropriate when the macrocycle contains more than three mercury atoms. For this reason, the bonding of the iodide anion to four mercury atoms of the carboranylmercury macrocycle $(HgC_2B_{10}H_{10})_4$ was described by Hawthorne and coworkers with the help of two three-center two-electron bonds constructed from unoccupied orbitals of the first and third (second and fourth) mercury atoms directed toward the iodide anion and the doubly occupied p_x -(p_y -)AO of this anion respectively [12].

However, this interpretation also becomes inappropriate on transition to macrocycles containing five and more mercury atoms, e.g. L5 and L6. When the description in terms of two- or three-center localized bonds fails the mesomeric description can be used. Another general approach to the description of the bonding between halide anions and polymetallamacrocycles, which is independent of the number of mercury atoms contained in the cycle, can be provided by the model of generalized chemical bonds (Fig. 3), which was successfully applied previously to π -complexes of transition metals [21].

Within the framework of this model, the interaction of a halide anion with metallamacrocycles L1–L6 is described in terms of three generalized chemical bonds.

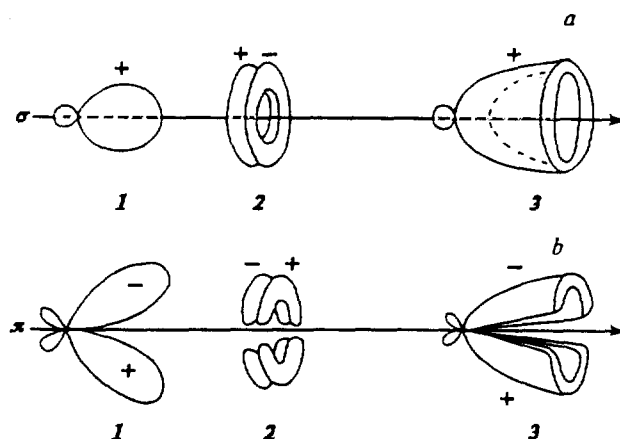


Fig. 3. Generalized chemical bonds in the π -complexes of transition metals: (a) headlight-shaped σ -bond and (b) one of the two-lobe π -bonds; hybrid metal orbital (1), MO of the ring (2) and generalized chemical bond (3).

The orbital of one of them, the headlight-shaped bond of σ -type, is constructed from s - and p_z -AOs of the X atom and a combination of MOs (belonging to the a_1 and a_2' representations of the D_{3h} and D_{5h} groups) of the initial macrocycle and corresponds to the a_1 irreducible representation of the C_{3v} and C_{5v} groups. The orbitals of two other bonds, two-lobe bonds of π -type (belonging to the e representation of the C_{3v} and C_{5v} groups) are constructed from the p_x - and p_y -AOs of the X atom and the corresponding combinations of MOs of the macrocycle corresponding to the e' and e'' representations of the D_{3h} and D_{5h} groups. The unoccupied p_ρ - and p_z -AOs of mercury atoms make the major contribution to the orbitals of the generalized chemical bonds of the metallamacrocycle, while the AOs of carbon and fluorine atoms are involved in these bonds with small coefficients.

Thus, in the half-sandwich complexes of polymercury-containing macrocycles the halide anion is bonded to the metallacycle through three generalized chemical bonds: one bond of σ -type and two bonds of π -type.

Despite the general similarity in the nature of bonding between halide anions and metallacycles regardless of the number of Hg atoms in the cycle, the complexes with macrocycle L6 have some specific peculiarities. First, because macrocycle L6 contains a greater number of Hg atoms than L1–L4, it is quite natural that in complexes with L6, the bonding of halide anions with 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 [22]) in complexes with macrocycle L6 (Tables 1 and 2).

Second, whereas the stability of the half-sandwich complexes of halide anions with macrocycles L1–L4 increases in the order $Br < Cl < I < F$, the stability of analogous complexes with L6 increases in a different series: $Cl < Br < F < I$. For F^- and I^- anions such a

permutation is quite understandable 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 cyclic pentameric difluoromethylidene mercury **L6**, leads to the fact that in the $[\mathbf{L6-I}]^-$ 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 half-sandwich complexes of the iodide anion with molecules **L1–L4**.

In the half-sandwich complexes of halide anions with metallacycles **L1–L4**, 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 is observed on going from Cl^- , Br^- and I^- to F^- . This transfer is even less pronounced in the planar $[\mathbf{L6-F}]^-$ complex. Here, the electron transfer from the p_z orbital of the F^- anion becomes quite insignificant. This can be explained by the fact that, in the $[\mathbf{L6-F}]^-$ 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 mercury atoms of the macrocycle is possible for this orbital. A rapid decrease in the π overlap with increasing Hg–F 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 of its unoccupied orbitals with the p_x and p_y orbitals of halide anions (occupied by the lone electron pairs) compared with the s and p_z orbitals, because the highest electron density of the p_x and p_y orbitals is localized in the region which is far from the axis of the complex, whereas the s and p_z orbitals of the lone electron pairs of X^- are localized near this axis. Indeed, the characteristic feature of the complexes with macrocycle **L6** 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, i.e. in other words, an increase in the donation of electron density from the p_x and p_y

orbitals of halide anions. As a result, in $[\mathbf{L6-X}]^-$ complexes, the total electron density transfer from the halide anion to the macrocycle along two two-lobe generalized chemical π -bonds exceeds the transfer along the generalized σ -bond. In analogous complexes with metallacycles **L1–L4**, the electron transfer along the σ -bond is, in all cases, greater than the total transfer along the π -bonds (Table 2).

2.3. The bipyramidal complexes (type B, spinning tops)

Calculations of bipyramidal complexes $[X-L-X]^{2-}$ of type **B** were performed for perfluorinated macrocycles **L2**, **L4** and **L6** with partial geometry optimization. In the case of complexes with **L2** and **L4** the structural parameters of the C_6F_4 and C_2F_2 fragments were taken to be the same as those for free macrocycles **L2** and **L4** respectively. It was assumed that these complexes have C_{3v} symmetry. In the optimized $[X-L4-X]^{2-}$ structures ($X = F, I$), the macrocycle turned out to be planar, with the distances to both halide anions being equal. So we also chose D_{3h} symmetry for all other $[X-L-X]^{2-}$ complexes ($L = \mathbf{L2}, \mathbf{L4}, X = Cl, Br$). Optimization of geometric parameters of $[X-L6-X]^{2-}$ bipyramidal complexes ($X = F, Cl, Br, I$) was carried out under the assumption that C_{5v} symmetry of the nuclear framework is retained.

The calculations demonstrated that, in all cases, local minima occur on the PES. The lengths of both **L6–X** semiaxes are equal and, in conformity with the data of X-ray structural analysis [6,7] of the $[X-L5-X]^{2-}$ complexes ($X = Cl, Br, I$), these systems have D_{5h} symmetry. The structures of the real $[X-L5-X]^{2-}$ complexes are also characterized by abnormally short $X \cdots X$ distances, substantially shorter than twice the van der Waals radius of the halogen atom. An analogous, although more substantial, shortening of the $X \cdots X$ distances was also observed in our calculations of $[X-L5-X]^{2-}$ complexes (see Table 3). Wiberg $X \cdots X$ indices ($X = Cl, Br, I$) in the bipyramidal $[X-L-X]^{2-}$ complexes ($L = \mathbf{L5}, \mathbf{L6}$) are equal to zero. Therefore, we suppose that the short $X \cdots X$ distances in these complexes are a consequence of strong attractive interactions of halide anions with the Hg atoms of the macrocycles and of the large size of these cycles.

Table 3

Hg–X bond lengths, C–Hg–C bond angles and $X \cdots X$ distances in the bipyramidal complexes of halide anions X^- with macrocycle **L5** according to the data of X-ray structural analysis (average values) [6,7] and the results of MNDO calculations

Complex	Hg–X/Å		C–Hg–C/deg		X \cdots X/Å		$2r_B(X)/\text{Å}^a$
	X-ray	MNDO	X-ray	MNDO	X-ray	MNDO	
$[Cl-L5-Cl]^{2-}$ (IV)	3.25	2.72	174.4	147.2	3.25	3.07	3.6
$[Br-L5-Br]^{2-}$ (V)	3.34	2.82	172.9	148.0	3.62	3.26	3.8
$[I-L5-I]^{2-}$ (VI)	3.48	2.80	175.4	147.3	4.04	3.37	4.2

^a Twice the van der Waals radius of the X atoms.

Table 4

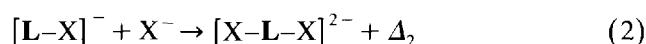
Heats of formation ΔH_f° and heats of the reaction in Eq. (2) Δ_2 , optimized geometric parameters, and effective charges on atoms of bipyramidal complexes $[X-L-X]^{2-}$ ($L = L2$ and $L4$, D_{3h} symmetry, and $L = L6$, D_{5h} symmetry)

Complex	Heat/kcal mol ⁻¹		Distance/Å			Angle/deg		Charge/a.u.			
	ΔH_f°	Δ_2	X-Hg	Hg-C	X...X	C-Hg-C	C ¹	Hg	X	F	
[F-L2-F] ²⁻	-440.9	27.5	2.111	2.123	2.571	160.5	-0.226	0.516	-0.379	—	
[Cl-L2-Cl] ²⁻	-409.9	-11.3	2.644	2.099	4.024	163.5	-0.196	0.486	-0.473	—	
[Br-L2-Br] ²⁻	-371.9	-11.2	2.767	2.098	4.320	163.8	-0.190	0.476	-0.488	—	
[I-L2-I] ²⁻	-368.6	15.6	2.829	2.109	4.487	163.3	-0.199	0.427	-0.403	—	
[F-L4-F] ²⁻	-193.4	0.4	2.121	2.117	2.522	162.9	-0.202	0.512	-0.387	—	
[Cl-L4-Cl] ²⁻	-166.5	-35.0	2.672	2.099	3.976	168.0	-0.158	0.491	-0.507	—	
[Br-L4-Br] ²⁻	-129.1	-34.6	2.790	2.097	4.271	168.1	-0.148	0.484	-0.527	—	
[I-L4-I] ²⁻	-124.6	-8.8	2.845	2.110	4.432	168.1	-0.234	0.436	-0.442	—	
[F-L6-F] ²⁻	-116.6	-49.5	2.443	2.183	2.096	144.9	-0.031	0.343	-0.395	-0.277	
[Cl-L6-Cl] ²⁻	-205.7	-23.9	2.917	2.191	3.052	155.7	-0.001	0.356	-0.488	-0.280	
[Br-L6-Br] ²⁻	-180.0	-16.9	2.995	2.195	3.232	156.9	0.004	0.350	-0.482	-0.280	
[I-L6-I] ²⁻	-206.7	17.3	2.989	2.207	3.305	155.1	-0.003	0.298	-0.342	-0.279	

On going from half-sandwich to bipyramidal complexes, the general characteristics of the bonds between the halide anions and the Hg atoms of metallacycles change only slightly (cf. Tables 4 and 5 with 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 the analogous values in the half-sandwich complexes. The changes in the valences of the Hg and X atoms are also reasonable: in the bipyramidal dianions, the valence of the four-coordinated Hg atoms is higher, while the valence of the halide anion is slightly lower than the corresponding values in the half-sandwich 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, namely one bond of σ -type and two bonds of π -type. As in the case of the $[L6-X]^-$ half-sandwich structures, the electron density transfer in the $[X-L6-X]^{2-}$ complexes occurs predominantly along

the π -bonds rather than along the σ -bond, unlike the case for the bipyramidal complexes of halide anions with metallacycles **L1-L4**.

At the same time, it should be pointed out that electrostatic destabilization of double-charged anions does not allow a direct comparison of the energy characteristics of the half-sandwich and the bipyramidal complexes. Addition reactions (Eq. (2)) of the second halide anion to the half-sandwich complexes are energetically favorable only for addition of F⁻ to $[L2-F]^-$ and $[L4-F]^-$ anions, and I⁻ to $[L2-I]^-$ and $[L6-I]^-$ anions. In all other cases these reactions are endothermal.



Nevertheless, the bipyramidal complexes here are kinetically feasible since the high energy barriers should be overcome for the removal of the halide anion from $[X-L-X]^{2-}$. The values of the barriers are 37.4 kcal mol⁻¹ and 24.3 kcal mol⁻¹ for the chloride

Table 5

Wiberg indices W , valences of atoms V , and atomic orbital populations Q of bipyramidal complexes $[X-L-X]^{2-}$ ($L = L2, L4, L6$) calculated by the MNDO method

Complex	$W/a.u.$		$V/a.u.$		$Q(Hg^1)/a.u.$				$Q(X)/a.u.$		
	Hg-X	Hg-C	Hg	X	s	P _x	P _y	P _z	s	P _x = P _y	P _z
[F-L2-F] ²⁻	0.330	0.710	2.212	1.104	0.722	0.212	0.407	0.144	1.777	1.847	1.907
[Cl-L2-Cl] ²⁻	0.270	0.744	2.194	0.927	0.778	0.167	0.423	0.146	1.978	1.901	1.693
[Br-L2-Br] ²⁻	0.259	0.751	2.915	0.894	0.790	0.163	0.426	0.145	1.986	1.914	1.673
[I-L2-I] ²⁻	0.295	0.745	2.260	1.015	0.805	0.174	0.421	0.172	1.939	1.904	1.656
[F-L4-F] ²⁻	0.327	0.718	2.219	1.092	0.720	0.215	0.409	0.144	1.783	1.847	1.912
[Cl-L4-Cl] ²⁻	0.258	0.754	2.182	0.889	0.777	0.159	0.428	0.144	1.979	1.901	1.723
[Br-L4-Br] ²⁻	0.245	0.761	2.178	0.840	0.790	0.153	0.432	0.142	1.986	1.915	1.713
[I-L4-I] ²⁻	0.283	0.753	2.246	0.967	0.882	0.166	0.426	0.169	1.940	1.904	1.694
[F-L6-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-L6-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-L6-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-L6-I] ²⁻	0.206	0.728	2.093	1.172	1.048	0.164	0.417	0.072	1.928	1.792	1.830

complexes with macrocycles **L2** and **L4** respectively, and $10.4 \text{ kcal mol}^{-1}$ and $21.6 \text{ kcal mol}^{-1}$ for the corresponding bromide complexes. For the complexes of macrocycle **L6** with F^- , Cl^- and Br^- the barriers are $10.8 \text{ kcal mol}^{-1}$, $16.5 \text{ kcal mol}^{-1}$ and $20.8 \text{ kcal mol}^{-1}$ respectively.

Note, further, that macrocycle **L5**, for which, as mentioned above, bipyramidal complexes **IV**, **V** and **VI** have been obtained, has substantially greater possibilities for delocalization of the electron density than the macrocycle **L6**, and just in this case the reaction in Eq. (2), according to the results of our calculations, is exothermal for all halide anions.

Thus, the MNDO calculations describe correctly the principal features of the geometric and electronic structures of the bipyramidal complexes of halide anions with mercury-containing macrocycles, correlate with natural changes in the character of the bonding between halide anions and macrocycles on going from the half-sandwich to bipyramidal complexes, and adequately reflect characteristic features of the bipyramidal complexes that are associated with the size of the cycle. At the same time, it should be noted that the degree of interaction between halide anions and mercury-containing macrocycles is substantially overestimated by calculations. This leads to peculiarities in the results of the calculations which are believed to be artifacts. Among them the Hg–X and X···X distances are too short and the C–Hg–C bond angles decrease too strongly in the calculated structures of $[\text{X–L–X}]^{2-}$ complexes compared with the corresponding data of X-ray structural analysis (Table 3). In turn, values of the calculated C–Hg–C bond angles that are too small result in an unreasonable character of the charge redistribution in the metallacycle. Indeed, as is evident from Table 4, the electron density on the C and F atoms increases so significantly upon complexation of **L6** with X^- that the electron density transfer from the halide anions to the metallacycle leads to an increase rather than a decrease in the positive charges on the Hg atoms (except for the case when $\text{X} = \text{I}$, where 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 changes in the populations in the series

$\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ (see Table 5) 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 forming the Hg–C bonds (see the populations of the s and p_y orbitals of the Hg^1 atom in Table 5). A decrease in the populations of these AOs is a result of a change of the hybridization of Hg atoms in the bipyramidal dianion from the sp-type 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 **L5** with bromide anions using the last version of the MNDO/PM3 method [23] have shown that in this case the Hg–Br bond lengths, the $\text{Br} \cdots \text{Br}$ distance and the C–Hg–C bond angles are also substantially smaller than those observed experimentally [6] for the $[\text{Br–L5–Br}]^{2-}$ complex.

2.4. The sandwich complexes (C type)

Calculations of the C type sandwich complexes were carried out for the model macrocycle **L4**. Calculations were performed with partial geometry optimization: the C=C and C–F bond lengths, as well as the C–C–F bond angles, remained fixed and were taken to be equal to the corresponding parameters in the half-sandwich complexes.

By varying the angle ϕ between the semiaxes of $[\text{L4–X–L4}]^-$ sandwiches, it was established that the energy minimum is attained at $\phi = 180^\circ$. Therefore, as in the case of classical sandwich complexes of transition metals, both cycles in the sandwiches $[\text{L4–X–L4}]^-$ have a common rotation symmetry axis passing through the central halogen atom.

Calculations of complexes with retention of C_{3v} symmetry demonstrated that unsymmetrical $[\text{L4–X} \cdots \text{L4}]^-$ sandwich complexes (Table 6), in which molecules **L4** are located at different distances from the halide anion, correspond to the energy minimum. The

Table 6

Heats of formation ΔH_f° , heats of reaction in Eq. (3) Δ_3 , optimized geometric parameters, and effective charges on atoms of unsymmetrical sandwich complexes $[\text{X–L} \cdots \text{X}]^-$ ($\text{X} = \text{Hal}$, $\text{L} = \text{L2}$ and **L4**)

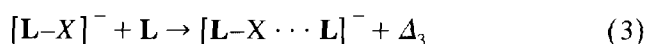
Complex	Heat/ kcal mol^{-1}		Distance/ \AA		V/a.u. X	W/a.u. X–Hg(1)	Charge/a.u.		
	ΔH_f°	Δ_3	X–Hg(1)	X–Hg(1')			X	Hg(1)	Hg(1')
$[\text{L2–I} \cdots \text{L2}]^-$	–568.8	1.4	2.758	6.250	1.192	0.354	–0.297	0.453	0.511
$[\text{L4–F} \cdots \text{L4}]^-$	–193.4	1.1	2.061	7.309	1.237	0.378	–0.300	0.515	0.530
$[\text{L4–Cl} \cdots \text{L4}]^-$	–165.3	2.3	2.607	6.499	1.042	0.311	–0.411	0.498	0.532
$[\text{L4–Br} \cdots \text{L4}]^-$	–145.1	2.5	2.713	6.356	1.014	0.301	–0.426	0.493	0.532
$[\text{L4–I} \cdots \text{L4}]^-$	–146.1	2.7	2.767	6.308	1.167	0.348	–0.325	0.467	0.533

Table 7

Heats of formation ΔH_f° , heats of reaction in Eq. (3) Δ_3 , optimized geometric parameters, and effective charges on atoms of symmetrical sandwich complexes $[X-L-X]^-$ (X = Hal, L = L2 and L4)

Complex	Heat/kcal mol ⁻¹		Distance/Å		Angle/deg		Charge/a.u.		
	ΔH_f°	Δ_3	X-Hg	Hg-C	C-Hg-C	θ	C ^I	Hg	X
[L2-I-L2] ⁻	-563.2	-4.2	3.010	2.058	156.3	12.7	-0.206	0.473	-0.303
[L4-F-L4] ⁻	-79.8	-112.5	4.641	2.047	166.0	8.2	-0.074	0.551	-0.999
[L4-I-L4] ⁻	-138.1	-5.3	3.037	2.064	157.9	14.6	-0.100	0.491	-0.335

distances from the halide anion to mercury atoms of the macrocycle closest to the X⁻ anion are only slightly larger and the Wiberg indices $W(\text{Hg-X})$ are only slightly smaller than the corresponding parameters in half-sandwich structures. The distances between the halide anion and the mercury atoms of another molecule of the macrocycle are much larger than the sum of the van der Waals radii of the Hg and X atoms and attain values of 6.3–7.3 Å. The Wiberg indices for the corresponding Hg-X bonds are very small. Therefore, these systems can be considered as weakly bonded complexes of half-sandwiches $[\text{L4-X}]^-$ with macrocycle L4. The heats of formation of these complexes (Δ_3) from the corresponding half-sandwich and macrocycle can serve as the criterion of their stability.



As is evident from Table 6, the Δ_3 values are very small and increase in the order F < Cl < Br < I.

Thus, the sandwich complexes of halide anions differ essentially from the transition metal sandwiches wherein the cycles are located at equal distances from the central atom. This difference is due to the fact that transition metal atoms have nine valence orbitals and, therefore, can be bonded to each ring of the sandwich through three generalized bonds: one bond of σ -type and two bonds of π -type. In contrast to the transition metal atoms, the halide anions have only four valence orbitals and so they are not able to form three bonds with each of two cycles. As a result, the sandwich complexes of halide anions lose the symmetry typical of transition metal sandwiches. In fact, the halide anions form a complex (of half-sandwich type) only with one molecule of the metallacycle while it is as if the other cycle solvates this half-sandwich complex.

It should be pointed out that for X = F and I, unlike X = Cl and Br, local energy minima were also found for symmetrical sandwich complexes $[\text{L-X-L}]^-$ with D_{3h} symmetry; however, these minima are located higher than the energy minima corresponding to the unsymmetrical sandwich complexes by 8.0 kcal mol⁻¹ and 113.6 kcal mol⁻¹ for X = I and F respectively (see Tables 6 and 7). Note that whereas the symmetrical complex of L4 with the F⁻ anion is purely ionic (no electron density transfer from F⁻ anion to the rings, zero order of the Hg-F bonds, very large Hg-F distances), the corresponding complex with iodide anion is of a covalent nature (see Tables 7 and 8). In this complex the predominant contribution in the bonding of I⁻ anion with the two macrocycle molecules is made by the single generalized chemical bonds. These headlight-shaped σ -bonds are formed through the interaction of the occupied sp-hybridized AOs of the I⁻ anion with the corresponding unoccupied orbitals of each macrocycle. The electron density transfer from the p_x- and p_y-AOs of the I⁻ anion to each ring is substantially smaller than in the case of the half-sandwich complex (0.130 and 0.308 respectively). The barrier to conversion from symmetrical to unsymmetrical complex is no more than 3.5 kcal mol⁻¹. Analogous results have been obtained for the sandwich complex of iodide anion with macrocycle L2. Thus, in the competition between two sandwich complex structures, the preference is on the part of that complex in which the iodide anion is triply bonded with one cycle and not on the part of the complex with two single bonds between iodide anion and each of the two cycles.

It is interesting that we found systems in which the preference is on the part of the structure with two single bonds. Such systems are sandwich complexes of sulfide

Table 8

Wiberg indices W , valences of atoms V , and atomic orbital populations Q of symmetrical sandwich complexes $[\text{L-X-L}]^-$ (X = Hal, L = L2 and L4, D_{3h} symmetry) calculated by the MNDO method

Complex	$W/\text{a.u.}$		$V/\text{a.u.}$		$Q(\text{Hg}^1)/\text{a.u.}$				$Q(\text{X})/\text{a.u.}$		
	Hg-X	Hg-C	Hg	X	s	P _x	P _y	P _z	s	P _x = P _y	P _z
[L2-I-L2] ⁻	0.184	0.833	2.028	1.228	0.882	0.075	0.473	0.096	1.901	1.879	1.645
[L4-F-L4] ⁻	0.000	0.851	1.861	0.002	0.882	0.025	0.495	0.047	2.000	2.000	1.999
[L4-I-L4] ⁻	0.179	0.828	2.007	1.189	0.841	0.108	0.449	0.134	1.909	1.870	1.686

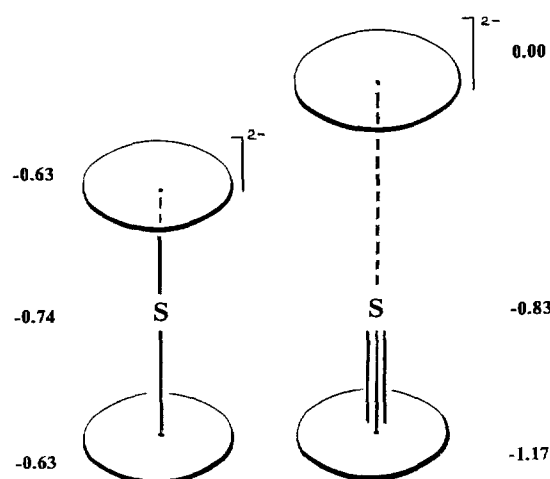


Fig. 4. The charge distribution in the symmetrical ($\Delta H_f = -165.2 \text{ kcal mol}^{-1}$) and unsymmetrical ($\Delta H_f = -157.9 \text{ kcal mol}^{-1}$) sandwich complexes of sulfide anion with macrocycle L4.

anion with macrocycles L2 and L4. Here, the symmetrical sandwiches $[\text{L-S-L}]^{2-}$ ($\text{L} = \text{L2}, \text{L4}$) are more stable than the unsymmetrical $[\text{L-S} \cdots \text{L}]^{2-}$ ones. This is explained by the fact that in the unsymmetrical structures there is no chemical bond between half-sandwich and the second molecule of the metallacycle. Therefore, the electron density cannot flow from the S^{2-} anion to this latter cycle, and the whole negative charge of two electrons remains on the half-sandwich. As a consequence, the unsymmetrical sandwiches are destabilized by electrostatic repulsion. By contrast, in the symmetrical sandwiches the negative charge can be delocalized on two macrocycle molecules and this delocalization reduces the electrostatic repulsion (see Fig. 4). The results of these calculations will be considered in detail in the next publication.

3. Conclusion

It has been established that a uniform description of the bonding between halide anions and polymercury-containing macrocycles, not depending on the number of metal atoms in the cycle, can be reached within the framework of the concept of generalized chemical bonds.

The orbitals of generalized chemical bonds are constructed from the AOs of a halide anion and the symmetrically appropriate combinations of the unoccupied orbitals of mercury atoms directed toward the halide anion. In half-sandwich complexes $[\text{L-X}]^-$, the halide anion is bonded to the macrocyclic ligand by a triple generalized chemical bond: one headlight-shaped bond of σ -type and two two-lobe bonds of π -type. In bipyramidal complexes $[\text{X-L-X}]^{2-}$, each halide anion forms a triple generalized chemical bond with the macrocycle. This is possible because in the metallacycle there are

suitable combinations of unoccupied orbitals of the mercury atoms directed toward both the upper and lower halogen atoms, and the fact that such bonds are formed by halide anions rather than by transition metal atoms puts no specific features in their description.

A quite different situation occurs in sandwich complexes. Here the character of chemical bonding depends strongly on the nature of the central atom. When the role of the central atom in the sandwich is played by the halide anion, having only four valence AOs, its full-value bonding to each ring by three bonds is impossible. As a result, the sandwich structures with the rings equidistant from the central atom (which is typical of transition metal sandwiches) turn out to be less favorable than the unsymmetrical structures in which the rings are located at different distances from the central atom. The unsymmetrical sandwiches $[\text{L-X} \cdots \text{L}]^-$ contain half-sandwich complex $[\text{L-X}]^-$ with a triple generalized chemical bond between the halide anion and the mercury-containing macrocycle. With regard to the second molecule of the macrocycle, it is as if it solvates this half-sandwich.

Thus, the results obtained extend the scope of the model of generalized chemical bonds. Now it is clear that not only the transition metal atoms but the halide anions too are capable of forming such bonds.

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References

- [1] (a) M. Newcomb, J.H. Horner and M.T. Blanda, *J. Am. Chem. Soc.*, 109 (1987) 7878. (b) M. Newcomb, A.M. Madonic, M.T. Blanda and J.K. Judice, *Organometallics*, 6 (1987) 145. (c) M. Newcomb and M.T. Blanda, *Tetrahedron Lett.*, 29 (1988) 4261. (d) M. Newcomb, J.H. Horner, M.T. Blanda and P.J. Squatrit, *J. Am. Chem. Soc.*, 111 (1989) 6294.
- [2] M.E. Jung and Y. Xia, *Tetrahedron Lett.*, 29 (1988) 297.
- [3] (a) K. Jurkschat, H.G. Kuivila, S. Liu and J.A. Zubieta, *Organometallics*, 8 (1989) 2755. (b) K. Jurkschat, A. Ruhlemann and A. Tzschach, *J. Organomet. Chem.*, 381 (1990) C53.
- [4] V.B. Shur, I.A. Tikhonova, P.V. Petrovskii and M.E. Vol'pin, *Metalloorg. Khim.*, 2 (1989) 1431; *Organomet. Chem USSR*, 2 (1989) 759.
- [5] V.B. Shur, I.A. Tikhonova, A.I. Yanovsky, Yu.T. Struchkov, P.V. Petrovskii, S.Yu. Panov, G.G. Furin and M.E. Vol'pin, *J. Organomet. Chem.*, 418 (1991) C29; *Dokl. Akad. Nauk SSSR*, 321 (1991) 1002.
- [6] V.B. Shur, I.A. Tikhonova, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, A.Yu. Volkonsky, E.V. Solodova, S.Yu. Panov, P.V. Petrovskii and M.E. Vol'pin, *J. Organomet. Chem.*, 443 (1993) C19; *Dokl. Akad. Nauk*, 328 (1993) 339.

- [7] I.A. Tikhonova, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, A.Yu. Volkonsky and V.B. Shur, in preparation.
- [8] A.P. Zaraisky, O.L. Kachurin, L.I. Velichko, I.A. Tikhonova, G.G. Furin, V.B. Shur and M.E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, (1994) 547.
- [9] A.P. Zaraisky, O.L. Kachurin, L.I. Velichko, I.A. Tikhonova, A.Yu. Volkonsky and V.B. Shur, *Izv. Akad. Nauk, Ser. Khim.*, (1994) 2047.
- [10] A.L. Chistyakov, I.V. Stankevich, N.P. Gambaryan, I.A. Tikhonova and V.B. Shur, *Izv. Akad. Nauk, Ser. Khim.*, (1995) 1035; *Izvest. Akad. Nauk, Ser. Khim.*, (1996) 44.
- [11] I.A. Tikhonova, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, A.N. Gavrilova, L.N. Saitkulova, E.S. Shubina, L.M. Epstein, G.G. Furin and V.B. Shur, *J. Organomet. Chem.*, 508 (1996) 271.
- [12] X. Yang, C.B. Knobler and M.F. Hawthorne, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 1507; *J. Am. Chem. Soc.*, 114 (1992) 380; *J. Am. Chem. Soc.*, 115 (1993) 4904.
- [13] (a) X. Yang, S.E. Johnson, S.I. Khan and M.F. Hawthorne, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 893. (b) X. Yang, Z. Zheng, C.B. Knobler and M.F. Hawthorne, *J. Am. Chem. Soc.*, 115 (1993) 193. (c) X. Yang, C.B. Knobler, Z. Zheng and M.F. Hawthorne, *J. Am. Chem. Soc.*, 116 (1994) 7142. (d) Z. Zheng, C.B. Knobler and M.F. Hawthorne, *J. Am. Chem. Soc.*, 117 (1995) 5105. (e) Z. Zheng, C.B. Knobler, C.E. Curtis and M.F. Hawthorne, *Inorg. Chem.*, 34 (1995) 432.
- [14] D.S. Brown, A.G. Massey and D.A. Wickens, *Acta Crystallogr. Sect. B*, 34 (1978) 1695.
- [15] P. Sartori and A. Golloch, *Chem. Ber.*, 101 (1968) 2004.
- [16] M.C. Ball, D.S. Brown, A.G. Massey and D.A. Wickens, *J. Organomet. Chem.*, 206 (1981) 265.
- [17] M.Yu. Antipin, Yu.T. Struchkov, A.Yu. Volkonsky and E.M. Rokhlin, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1983) 452.
- [18] M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 99 (1977) 4899.
- [19] M.J.S. Dewar, G.G. Grady, K.M. Merz, Jr. and J.J.P. Stewart, *Organometallics*, 4 (1985) 1964.
- [20] T. Clark, *A Handbook of Computational Chemistry*, Wiley, New York, 1985.
- [21] (a) D.A. Bochvar, N.P. Gambaryan, E.M. Brainina and R.H. Freidlina, *Dokl. Akad. Nauk SSSR*, 183 (1968) 1324. (b) D.A. Bochvar and N.P. Gambaryan, in A.N. Nesmeyanov (ed.), *Methods of Organoelement Chemistry. Types of Organometallic Compounds of Transition Metals*, Vol. 1, Nauka, Moscow, 1975, p. 9. (c) N.P. Gambaryan and I.V. Stankevich, *Usp. Khim.*, 58 (1989) 1945; *Russ. Chem. Rev.*, 58 (1989) 1103.
- [22] K.B. Wiberg, *Tetrahedron*, 24 (1968) 1083.
- [23] J.J.P. Stewart, *J. Comput. Chem.*, 10 (1989) 209.