Crown compounds for anions. The nature of chemical bonds in the complexes of halide anions with cyclic trimeric perfluoro-*o*-phenylenemercury and some of its analogs

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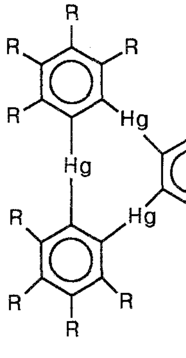
Geometries and electronic structures of the complexes of halide anions with cyclic trimeric *o*-phenylenemercury, $(o\text{-}C_6H_4Hg)_3$, perfluoro-*o*-phenylenemercury, $(o\text{-}C_6F_4Hg)_3$, vinylenemercury, $(C_2H_2Hg)_3$, and perfluorovinylenemercury, $(C_2F_2Hg)_3$, were modelled by the MNDO method. Calculations were performed for $[\mathbf{L}—X]^-$ semisandwich complexes, $[X—\mathbf{L}—X]^{2-}$ bipyramidal complexes, and $[\mathbf{L}—X—\mathbf{L}]^-$ sandwich complexes (where X = Hal, **L** is a mercury-containing macrocycle). Based on the results of calculations, we concluded that it was advantageous to describe the chemical bonding between halide anions and mercury-containing macrocycles in terms of generalized chemical bonds, which were successfully used for π-complexes of transition metals. In the $[\mathbf{L}—X]^-$ semisandwich complexes, the halide anion and the metallacycle are involved in the formation of three generalized chemical bonds: one headlight-shaped σ-bond and two two-lobe π-bonds. In the $[X—\mathbf{L}—X]^{2-}$ bipyramidal complexes, each halide anion forms three generalized chemical bonds with the macrocycle. It is possible because the macrocycle **L** has unoccupied molecular orbitals suitable for the formation of such bonds; these MOs consist mainly of the orbitals of mercury atoms directed toward both the upper and lower halogen atoms. In the $[\mathbf{L}—X—\mathbf{L}]^-$ sandwich complexes, the halide anion cannot be bonded to each ring *via* three bonds, and, hence, an unsymmetrical structure is formed, in which the rings are located at different distances from the central atom: the $[\mathbf{L}—X]^-$ semisandwich complex solvated by macrocycle **L**.

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

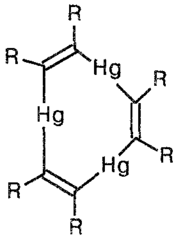
As part of our program aimed at the development of crown compounds efficiently binding anions, we have previously studied[1—4] the reactions of halide anions with cyclic trimeric *o*-phenylenemercury $(o\text{-}C_6H_4Hg)_3$ (**L1**) and perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**L2**), containing three mercury atoms in the planar nine-membered cycle.[5—7]

It was found that both compounds react readily with $[PPh_3Me]^+I^-$, $[PPh_4]^+Br^-$, and $[PPh_4]^+Cl^-$ to form complexes. In the case of **L2**, complexes of the composition $[(o\text{-}C_6F_4Hg)_3X]^-[PR'_3R'']^+$, where X = I, R′ = Ph, R′′ = Me (**I**); X = Br, R′ = R′′ = Ph (**II**), and $\{[(o\text{-}C_6F_4Hg)_3]_3Cl_2\}^{2-}[PPh_4]_2^+$ were isolated from the reaction mixture in a pure form.

X-ray structural study of complexes **I** and **II** demonstrated that these complexes have the structure of polydecker bent sandwiches, $[(\cdots\mathbf{L2}\cdots X\cdots)_n]^{n-}$, in which each halide anion is coordinated with six mercury atoms of two neighbouring **L2** molecules.[2—4]



L1: R = H
L2: R = F



L3: R = H
L4: R = F

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

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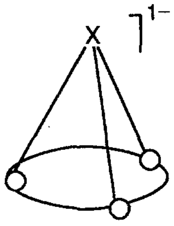
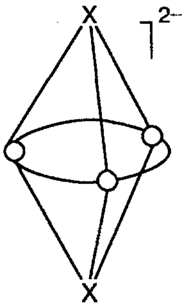
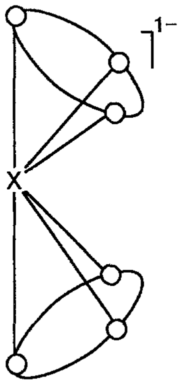


A



B



C

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

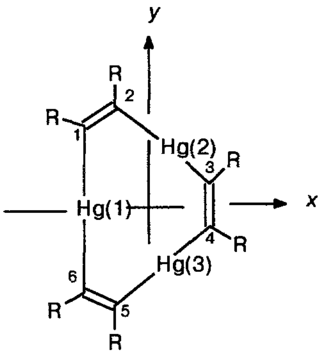
Bipyramidal complexes of type **B** with two halide anions per **L2** molecule have the shape of a spinning top, the equatorial girdle of which is the mercury-containing metallacycle, while the axis direction is fixed by halide anions located above and below the metallacycle plane at approximately equal distances from the mercury atoms. Similar complexes, $\{[(CF_3)_2CHg]_5Cl_2\}^{2-}[PPh_4]^+{}_2$ and $\{[(CF_3)_2CHg]_5Br_2\}^{2-}[PPh_4]^+{}_2$, have been obtained recently by the reaction of cyclic pentameric perfluoroisopropylidenemercury $[(CF_3)_2CHg]_5$ with $[PPh_4]^+Cl^-$ and $[PPh_4]^+Br^-$.[8,9]

The complexes of type **C** contain one halide anion per two molecules of **L2**; these complexes are shaped as double-decker bent sandwiches, in which, unlike ordinary sandwich compounds, a halogen anion rather than a cation or an atom of metal is the complex-forming center. Complexes of this type are unknown so far.

The present work is devoted to the theoretical study of the nature of chemical bonds between mercury-containing macrocycles and halide anions. For this purpose, we modeled the fragments of the potential energy surface for hypothetical complexes of halide anions of types **A**, **B**, and **C** with macrocycles **L1** and **L2** and with their simpler analogs **L3** and **L4**. Local minima were found on the potential energy surface of these complexes, and the electronic structures of the systems corresponding to these minima were studied. Calculations were performed by the MNDO method[10] (the parameters for the mercury atom were taken from Ref. 11). Calculations were performed also for macrocycles **L1**—**L4**.

Results and Discussion

Calculations were carried out on a PC AT/386 computer using the MOPAC program[12] adapted to this computer for basis sets containing up to 144 atomic orbitals. The atomic numbering scheme for the macrocycle framework of the **L1**—**L4** molecules and coordinate axes are shown below:



Mercury-containing macrocycles L1—L4. In the calculations for molecules **L1**—**L4**, the geometries were optimized with retention of C_{3v} symmetry. As follows from the results of calculations, these molecules are planar and have D_{3h} symmetry. In all of the cases, except for **L3**, the C—Hg—C angle (Table 1) differs little from 180°, which is in good agreement with the experimental data for molecules **L1** [5] and **L2**.[7] Therefore, each mercury atom in the **L1**—**L4** systems is in the state corresponding to sp hybridization and, hence, has two mutually orthogonal unoccupied p-orbitals: p_z-AO and p_ρ-AO (the symmetry axis of this AO passes through the center of the macrocycle and, in the case of the Hg(1) atom, coincides with the x axis). This conclusion is confirmed by the values of the populations of AOs of Hg atoms. It is seen from Table 2 that, for example, the populations of the p_x- and p_z-AOs of the Hg(1) atom 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** are small.

From the values of the effective charges of atoms in molecules **L1**—**L4** given in Table 1, it follows that a substantial positive charge is located on Hg atoms (the maximum value in **L4** and the minimum value in **L3**). When passing from molecules **L1** and **L3** to the perfluorinated analogs **L2** and **L4**, the positive charges on 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**. Among these orbitals, there are MOs of two types: (1) MOs belonging to the $a_1{}'$ and $a_2{}''$ irreducible representations of the D_{3h} group (they can interact with the s- and p_z-AOs of halide anions) and (2) MOs belonging to the e' and e'' irreducible representations of the D_{3h} group (they can interact with the p_x- and p_y-AOs of halide anions).

The semisandwich complexes (the type A). The structures of semisandwich complexes $[L-X]^-$ (where X = Hal and **L** = **L1**—**L4**) were modeled with partial geometrical optimization. We assumed that the structures of the C_6R_4 (when **L** = **L1** and **L2**) and C_2R_2 (when **L** = **L3** and **L4**) fragments remain unchanged on complex formation and the C(1)—C(6) carbon atoms are in the

Table 1. Heats of formation ($\Delta_f H°$), heats of reaction (1) (Δ_1), optimized geometric parameters, and effective charges on the atoms of macrocycles **L** and semisandwich complexes $[\mathbf{L}{-}X]^-$ (**L** = **L1**—**L4**, C_{3v} symmetry)* calculated by the MNDO method

System	Heat/kcal · mol^{-1}		Distance/Å			Angle/deg		Charge, q/au		
	$\Delta_f H°$	Δ_1	X—Hg	Hg—C	X—C	C—Hg—C	θ	C(1)	Hg	X
L1	255.3	—	—	2.002	—	174.3	0.0	−0.207	0.462	—
[**L1**—F]$^-$	132.2	106.0	2.067	2.043	3.112	156.4	13.1	−0.237	0.462	−0.314
[**L1**—Cl]$^-$	156.0	46.4	2.631	2.027	3.603	153.9	15.1	−0.215	0.451	−0.449
[**L1**—Br]$^-$	175.5	42.3	2.747	2.025	3.701	154.0	15.6	−0.211	0.448	−0.471
[**L1**—I]$^-$	174.4	74.5	2.785	2.029	3.754	152.2	16.6	−0.217	0.421	−0.363
L2	−220.8	—	—	2.024	—	178.2	0.0	−0.196	0.500	—
[**L2**—F]$^-$	−396.3	158.4	2.041	2.084	3.153	155.7	11.9	−0.229	0.510	−0.284
[**L2**—Cl]$^-$	−366.3	90.6	2.580	2.069	3.638	152.8	13.9	−0.212	0.486	−0.358
[**L2**—Br]$^-$	−345.6	87.3	2.691	2.071	3.643	152.7	14.0	−0.209	0.479	−0.361
[**L2**—I]$^-$	−346.6	119.4	2.745	2.097	3.686	151.1	15.1	−0.213	0.452	−0.265
L3	158.4	—	—	1.977	—	168.4	0.0	−0.231	0.432	—
[**L3**—F]$^-$	61.2	80.1	2.085	2.011	3.080	159.6	15.7	−0.292	0.413	−0.338
[**L3**—Cl]$^-$	78.4	25.1	2.670	1.996	3.565	155.2	16.2	−0.265	0.409	−0.510
[**L3**—Br]$^-$	96.8	24.3	2.788	1.994	3.660	155.6	16.1	−0.260	0.408	−0.538
[**L3**—I]$^-$	96.6	55.4	2.822	2.000	3.722	155.7	18.7	−0.267	0.380	−0.427
L4	−16.4	—	—	2.054	—	173.0	0.0	−0.077	0.526	—
[**L4**—F]$^-$	−175.9	142.4	2.057	2.082	3.116	157.2	12.8	−0.154	0.517	−0.295
[**L4**—Cl]$^-$	−146.6	75.3	2.597	2.071	3.596	154.4	14.8	−0.131	0.499	−0.393
[**L4**—Br]$^-$	−126.2	72.3	2.703	2.070	3.687	154.5	14.9	−0.127	0.494	−0.405
[**L4**—I]$^-$	−127.0	104.2	2.761	2.076	3.764	151.9	16.9	−0.132	0.468	−0.305

* The heats of formation of the halide anions (MNDO, kcal mol^{-1}) are: −17.1(F$^-$), −54.7(Cl$^-$), −37.5(Br$^-$), and −6.4(I).

same plane. Besides, because the calculations of complexes [**L4**—F]$^-$ and [**L4**—I]$^-$ demonstrated that the position of the halide anion on the symmetry axis of the semisandwich complex is stable with respect to transverse displacements, it was assumed that all semisandwich complexes [**L**—X]$^-$ have C_{3v} symmetry.

When calculations were performed for the complexes of the type **A**, 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 are 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 of the **L1** and **L2** systems and the (x,y) plane; and (6) the dihedral angles θ between the plane of each C_2R_2 fragment in **L3** and **L4** and the (x,y) plane. The results of the calculations of the type **A** complexes are given in Tables 1 and 2.

Analysis of the results demonstrates that the macrocyclic ligand is no longer planar because of the formation of the bond with the halide anion. The Hg atoms deviate from the (x,y) plane, in which the C(1)—C(6) atoms are located, and are displaced toward the z axis. The C—Hg—C angles in the semisandwich complexes deviate from 180° (by ~20—30°, see Table 1). The HgC_6R_4Hg (in [**L1**—X]$^-$ and [**L2**—X]$^-$) and HgC_2R_2Hg (in [**L3**—X]$^-$ and [**L4**—X]$^-$) fragments remain planar but are bent away from the (x,y) plane by the angle θ. This angle increases in the order F < Cl < Br < I.

The results of calculations indicate that in all of the cases under consideration, the reaction of complex formation

$$\mathrm{L} + \mathrm{X}^- \longrightarrow [\mathrm{L{-}X}]^- + \Delta_1 \qquad (1)$$

is exothermal. The heat of this reaction Δ_1 characterizing the stability of the complex [**L**—X]$^-$ for molecules **L1**—**L4** increases in the order Br < Cl < I < F (see Table 1) and is very high, being substantially higher for the perfluorinated systems than for the nonfluorinated systems. Note that the transition from macrocycle **L2** to **L4**, in which the positive charges on Hg atoms are larger, is not accompanied by enhanced stability of the [**L4**—X]$^-$ complexes compared to [**L2**—X]$^-$ complexes.

The bonding of a halide anion to three mercury atoms in [**L**—X]$^-$ complexes can be described by three equivalent donor—acceptor bonds. Each of these bonds is formed by the lone electron pair of a halide anion (occupying its sp^3 hybridized AO directed toward the corresponding mercury atom) and the unoccupied AO of the mercury atom directed toward the halide anion. However, this description with two-center bonds is no longer appropriate when the macrocycle contains more than three mercury atoms. Because of this, the bonding of the iodide anion to four mercury atoms of the carboranylmercury macrocycle $(HgC_2B_{10}H_{10})_4$ was described by 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

Table 2. Wiberg indices (*W*), valences of atoms (V), and atomic orbital populations (*Q*) of macrocycles **L** and semisandwich complexes $[L^{-}—X]^{-}$ (**L** = **L1**—**L4**, C_{3v} symmetry) calculated by the MNDO method

System	*W*/au		V/au			*Q*(Hg(1))/au			*Q*(X)/au		
	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	—	—	—
$[$**L1**$—F]^{-}$	0.370	0.805	2.125	1.215	0.832	0.154	0.455	0.097	1.743	1.829	1.913
$[$**L1**$—Cl]^{-}$	0.293	0.821	2.098	0.981	0.865	0.109	0.461	0.115	1.976	1.875	1.723
$[$**L1**$—Br]^{-}$	0.280	0.824	2.094	0.941	0.871	0.104	0.462	0.115	1.984	1.888	1.711
$[$**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	—	—	—
$[$**L2**$—F]^{-}$	0.384	0.786	2.095	1.259	0.797	0.152	0.446	0.095	1.730	1.823	1.908
$[$**L2**$—Cl]^{-}$	0.331	0.797	2.091	1.113	0.833	0.116	0.449	0.116	1.973	1.863	1.661
$[$**L2**$—Br]^{-}$	0.326	0.799	2.093	1.099	0.840	0.114	0.449	0.114	1.982	1.873	1.634
$[$**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	—	—	—
$[$**L3**$—F]^{-}$	0.357	0.818	2.128	1.174	0.868	0.152	0.461	0.106	1.754	1.836	1.912
$[$**L3**$—Cl]^{-}$	0.264	0.837	2.111	0.884	0.900	0.104	0.470	0.116	1.979	1.888	1.755
$[$**L3**$—Br]^{-}$	0.248	0.840	2.104	0.836	0.906	0.099	0.472	0.115	1.986	1.900	1.751
$[$**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	—	—	—
$[$**L4**$—F]^{-}$	0.381	0.788	2.093	1.245	0.790	0.154	0.447	0.095	1.736	1.820	1.918
$[$**L4**$—Cl]^{-}$	0.320	0.799	2.075	1.071	0.827	0.105	0.452	0.117	1.973	1.858	1.703
$[$**L4**$—Br]^{-}$	0.311	0.802	2.074	1.046	0.834	0.101	0.453	0.118	1.982	1.869	1.685
$[$**L4**$—I]^{-}$	0.357	0.796	2.111	1.197	0.841	0.108	0.449	0.134	1.929	1.846	1.683

and the doubly occupied p_x-(p_y-)AO of this anion, respectively.[13]

However, this interpretation is also inappropriate for complexes with macrocycles containing five and more mercury atoms, for example, for $[(CF_3)_2CHg]_5$.[8,9] The general description of the bond between halide anions and polymetallacycles, which is independent of the number of mercury atoms contained in these cycles, can be provided by the model of generalized chemical bonds, which was successfully applied to π-complexes of transition metals.[14]

Within this model, the interaction of a halide anion with metallamacrocycle **L** can be described in terms of three *generalized chemical bonds* (Fig. 1). The orbital of one of these bonds, the *headlight-shaped* σ-bond, 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'' representation of the D_{3h} group) of the initial macrocycle and corresponds to the a_1 irreducible representation of the C_{3v} group. The orbitals of two other bonds, *two-lobe* π-bonds (belonging to the *e* representation of the C_{3v} symmetry group) 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} group (Fig. 2). The

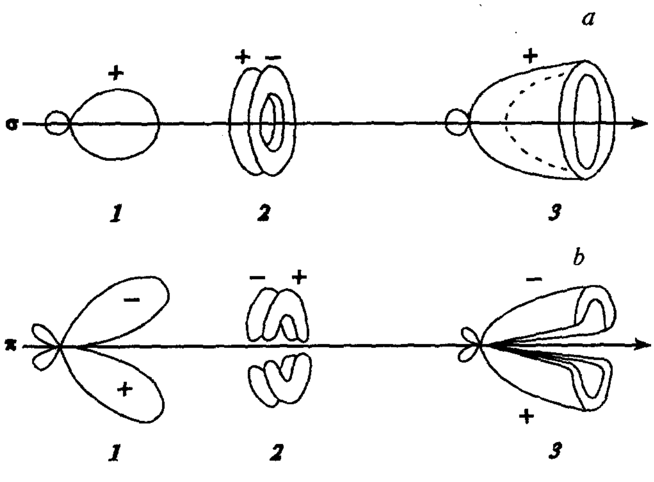


Fig. 1. Generalized chemical bonds in the π-complexes of transition metals: (*a*) headlight-shaped σ-bond and (*b*) one of two two-lobe π-bonds: hybrid metal orbital (*1*), MO of the ring (*2*), and generalized chemical bond (*3*).

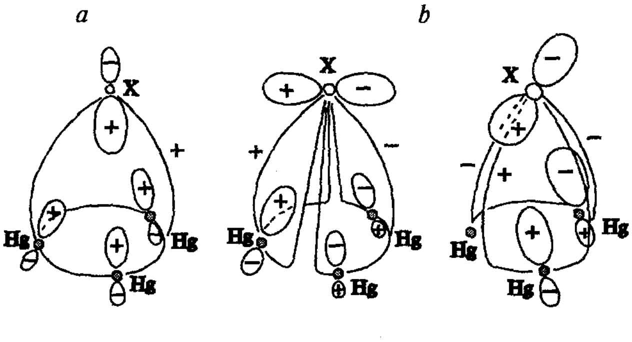


Fig. 2. Schematic representation of the orbitals of generalized chemical bonds between the halide anion and the mercury atoms of the macrocycle: headlight-shaped σ-bond (*a*) and two two-lobe π-bonds (*b*).

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.

The charge transfer from the anion to the metallamacrocycle occurs mainly along the σ-bond. For X = Cl, Br, and I, the p_z lone electron pair of the halide anion makes the major contribution, and for X = F, the shift of the electron density of the lone electron pair occupying the s-AO predominates. This difference is caused by the small size of the F atom, which allows this atom to be located closer to the plane through the Hg atoms. As a result, the axis of the p_z-AO of the fluorine atom is deflected from the Hg—X direction by a larger angle, and this orbital overlaps with the orbitals of the mercury atom to a lesser degree than the s-AO. Note that the electron density transfer from the atomic orbitals of the F^- anion to the p_ρ orbitals of mercury atoms is greater than that to the p_z orbitals, while for X = Cl, Br, and I, the reverse situation is observed (see in Table 2 the electron populations of the AOs of the Hg(1) atom, whose radial p_ρ-AO coincides with the p_x-AO). The total electron density transfer along the π-bonds from two lone electron pairs occupying the p_x- and p_y-AOs of the X^- anion is slightly less than the transfer along the σ bond (see Table 2).

The total electron density transfer from the halide anion to the metallamacrocycle generally correlates with the value of Δ_1 characterizing the stability of the complex, *i.e.*, the transfer increases in the order Br < Cl < I < F (see Table 1). The exception is the anion [**L2**—F]$^-$. The orders of the Hg—X bonds (the Wiberg indices W(Hg,X)[15]) are close to $^1/_3$, and the valence of the X atom determined in terms of Wiberg indices by the equation $V(X) = \Sigma_A W(X,A)$[16] is approximately equal to unity and increases in the order Br < Cl < I < F (see Table 2), *i.e.*, with the change in the value of Δ_1 characterizing the L—X bond strength.

The bipyramidal complexes (the type B, spinning tops). Calculations for bipyramidal complexes $[X—L—X]^{2-}$ of type **B** were performed only for macrocycles **L2** and **L4** with partial geometrical optimization: the structural parameters of the C_6F_4 and C_2F_2 fragments were the same as those for isolated macrocycles **L2** and **L4**, respectively. In this case, it was assumed that the complexes have C_{3v} symmetry. In the optimized $[X—$**L4**$—X]^{2-}$ structures (X = F and I), the macrocycles are planar and the distances to both halide anions are the same. Therefore, we chose D_{3h} symmetry also for all other $[X—L—X]^{2-}$ complexes. The results of calculations are given in Tables 3 and 4.

In all of the cases studied, the reactions of the formation of $[X—L—X]^{2-}$ complexes from molecule L and two X^- anions are exothermal (see Δ_2 in Table 3).

$$2X^- + L \longrightarrow [X—L—X]^{2-} + \Delta_2 \qquad (2)$$

From the values of Δ_3, the heats of the reactions of the addition of the second halide anion to semisandwich complex $[L—X]^-$ given in Table 3

$$[L—X]^- + X^- \longrightarrow [X—L—X]^{2-} + \Delta_3 \qquad (3)$$

it follows that these reactions are energetically favorable only for anions [**L2**—F]$^-$, [**L4**—F]$^-$, and [**L2**—I]$^-$, while for X = Cl and Br, these reactions are endothermal. The possibility of the occurrence of bipyramidal complexes of the spinning-top type in the case of Cl and Br is provided by high energy barriers to the removal of the halide anion from the $[X—L—X]^{2-}$ complex. These barriers are 37.4 and 24.3 kcal mol^{-1} for the chloride complexes and 10.4 and 21.6 kcal mol^{-1} for the bromide complexes with macrocycles **L2** and **L4**, respectively.

As in the case of semisandwich complexes, the bipyramidal complexes of halide anions with macrocycle **L2** are more stable than those with **L4**: the heats of complex

Table 3. Heats of formation ($\Delta_f H°$), heats of reactions (2) and (3) (Δ_2 and Δ_3, respectively), optimized geometric parameters, and effective charges on atoms of bipyramidal complexes $[X–L–X]^{2-}$ (L = **L2** and **L4**) and symmetrical sandwich complexes [**L4**—X—**L4**]$^-$ (L = **L2** and **L4**, D_{3h} symmetry)

Complex	Heat/kcal mol^{-1}			Distance/Å			Angle/deg		Charge, q/au		
	$\Delta_f H°$	Δ_2	Δ_3	X–Hg	Hg–C	X–C	C–Hg–C	θ	C(1)	Hg	X
[F—**L2**—F]$^{2-}$	−440.9	185.9	27.5	2.111	2.123	3.189	160.5	0.0	−0.226	0.516	−0.379
[Cl—**L2**—Cl]$^{2-}$	−409.9	79.3	−11.3	2.644	2.099	3.524	163.5	0.0	−0.196	0.486	−0.473
[Br—**L2**—Br]$^{2-}$	−371.9	76.1	−11.2	2.767	2.098	3.617	163.8	0.0	−0.190	0.476	−0.488
[I—**L2**—I]$^{2-}$	−368.6	135.0	15.6	2.829	2.109	3.676	163.3	0.0	−0.199	0.427	−0.403
[F—**L4**—F]$^{2-}$	−193.4	142.8	0.4	2.121	2.117	3.170	162.9	0.0	−0.202	0.512	−0.387
[Cl—**L4**—Cl]$^{2-}$	−166.5	40.3	−35.0	2.672	2.099	3.516	168.0	0.0	−0.158	0.491	−0.507
[Br—**L4**—Br]$^{2-}$	−129.1	37.7	−34.6	2.790	2.097	3.600	168.1	0.0	−0.148	0.484	−0.527
[I—**L4**—I]$^{2-}$	−124.6	95.4	−8.8	2.845	2.110	3.659	168.1	0.0	−0.234	0.436	−0.442
[**L4**—F—**L4**]$^-$	−79.8	—	—	4.641	2.047	5.155	166.0	8.2	−0.074	0.551	−0.999
[**L4**—I—**L4**]$^-$	−138.1	—	—	3.037	2.064	3.917	157.9	14.6	−0.100	0.491	−0.335

Table 4. Wiberg indices (W), valences of atoms (V), and atomic orbital populations (Q) of bipyramidal complexes $[X–L–X]^{2-}$ (**L** = **L2** and **L4**) and symmetrical sandwich complexes $[\mathbf{L4}–X–\mathbf{L4}]^-$ (**L** = **L2** and **L4**, D_{3h} symmetry) calculated by the MNDO method

Complex	W/au		V/au		Q(Hg(1))/au				Q(X)/au		
	Hg—X	Hg—C	Hg	X	s	p_x	p_y	p_z	s	$p_x = p_y$	p_z
$[F–\mathbf{L2}–F]^{2-}$	0.330	0.710	2.212	1.104	0.722	0.212	0.407	0.144	1.777	1.847	1.907
$[Cl–\mathbf{L2}–Cl]^{2-}$	0.270	0.744	2.194	0.927	0.778	0.167	0.423	0.146	1.978	1.901	1.693
$[Br–\mathbf{L2}–Br]^{2-}$	0.259	0.751	2.195	0.894	0.790	0.163	0.426	0.145	1.986	1.914	1.673
$[I–\mathbf{L2}–I]^{2-}$	0.295	0.745	2.260	1.015	0.805	0.174	0.421	0.172	1.939	1.904	1.656
$[F–\mathbf{L4}–F]^{2-}$	0.327	0.718	2.219	1.092	0.720	0.215	0.409	0.144	1.783	1.847	1.912
$[Cl–\mathbf{L4}–Cl]^{2-}$	0.258	0.754	2.182	0.889	0.777	0.159	0.428	0.144	1.979	1.901	1.723
$[Br–\mathbf{L4}–Br]^{2-}$	0.245	0.761	2.178	0.840	0.790	0.153	0.432	0.142	1.986	1.915	1.713
$[I–\mathbf{L4}–I]^{2-}$	0.283	0.753	2.246	0.967	0.882	0.166	0.426	0.169	1.940	1.904	1.694
$[\mathbf{L4}–F–\mathbf{L4}]^-$	0.000	0.851	1.861	0.002	0.882	0.025	0.495	0.047	2.000	2.000	1.999
$[\mathbf{L4}–I–\mathbf{L4}]^-$	0.179	0.828	2.007	1.189	0.841	0.108	0.449	0.134	1.909	1.870	1.686

formation Δ_2 for **L** = **L2** exceed the corresponding values for **L** = **L4** by 39—43 kcal mol^{-1}, and the Δ_3 values, by 24—27 kcal mol^{-1}. The Δ_2 values for bipyramidal complexes increase in the order Br < Cl <I < F. The electron density transfer from the X^- anion increases in the same order, being substantially larger for **L2** than for **L4** (see q(X) in Table 3). As in of semisandwich complexes, the largest electron density transfer occurs from the s-AO of the halide anion for X = F and from the p_z-AO in the other cases.

In complexes of type **B**, the Hg atoms are four-coordinated; the Hg—X bond lengths in these complexes are larger than those in the semisandwich complexes: by 0.20 Å for **L** = **L2** and by 0.09 Å for **L** = **L4**. The Hg—C bonds are also slightly longer. The Wiberg indices W(Hg—X) are only slightly smaller than those in the semisandwich complexes. Therefore, the valence of the X atom is lower, while the valence of the mercury atoms is correspondingly higher (Table 4).

The nature of the bond between the halide anion and mercury atoms in bipyramidal complexes is qualitatively the same as that in semisandwich complexes. Each halide anion is bonded to the mercury atoms *via* three generalized chemical bonds: one headlight-shaped σ bond and two two-lobe π bonds.

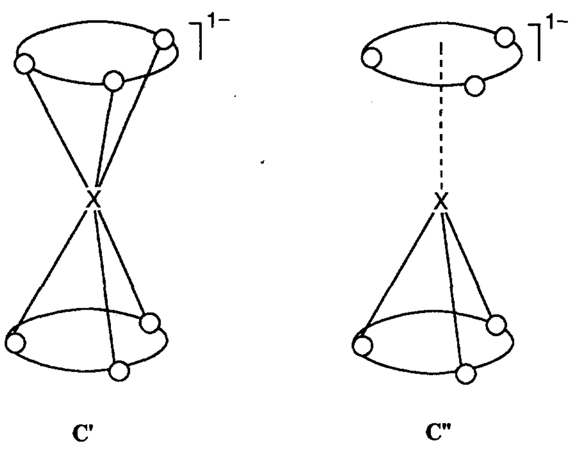


Fig. 3. Complexes of the sandwich type: symmetrical (**C**′) and unsymmetrical (**C**′′).

The sandwich complexes (the type C). Calculations of the **C** type sandwich complexes were carried out only for the **L4** model macrocycle. Calculations were performed with partial geometrical optimization: the C=C and C—F bond lengths as well as the C—C—F angle remained fixed and were taken to be equal to the corresponding parameters in the semisandwich complexes.

By varying the angle ϕ between the semiaxes of $[\mathbf{L4}–X–\mathbf{L4}]^-$ sandwich complexes , it was established that the energy minimum was attained at ϕ = 180° (Fig. 3). Therefore, as in the case of sandwich complexes of a number of transition metals, both cycles in the systems under consideration have a common rotation axis of symmetry passing through the central halogen atom.

Calculations for complexes with retention of C_{3v} symmetry demonstrate (Table 5) that unsymmetrical $[\mathbf{L4}–X\cdots\mathbf{L4}]^-$ sandwich complexes, in which molecules **L4** are located at different distances from the halide anion (see Fig. 3, **C**″), correspond to the energy minimum. The distances from the halide anion to mercury atoms in the macrocycle closest to the X^- anion are only slightly larger and the Wiberg indices W(Hg—X) are only slightly smaller than the corresponding parameters in semisandwich structures. The distances between the halide anion and the mercury atoms of another macrocyclic ligand 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 semisandwich complexes $[\mathbf{L4}–X]^-$ with macrocycle **L4**. The heats of formation of these complexes (Δ_4) from the corresponding semisandwich complex $[\mathbf{L4}–X]^-$ and macrocycle **L4** can serve as the criterion of stability of these complexes.

$$[\mathbf{L4}–X]^- + \mathbf{L4} \longrightarrow [\mathbf{L4}–X\cdots\mathbf{L4}]^- + \Delta_4. \qquad (4)$$

Table 5. Results of calculations of unsymmetrical sandwich complexes [**L4**—X···**L4**]$^-$ (C_{3v} symmetry) by the MNDO method

Complex	Heat/kcal mol^{-1}		Distance/Å		V/au	W/au	Charge, q/au		
	Δ_fH^o	Δ_4	X—Hg(1)	X—Hg(4)	X	X—Hg(1)	X	Hg(1)	Hg(4)
[**L4**—F···**L4**]$^-$	−193.4	1.1	2.061	7.309	1.237	0.378	−0.300	0.515	0.530
[**L4**—Cl···**L4**]$^-$	−165.3	2.3	2.607	6.499	1.042	0.311	−0.411	0.498	0.532
L4—Br···**L4**]$^-$	−145.1	2.5	2.713	6.356	1.014	0.301	−0.426	0.493	0.532
L4—I···**L4**]$^-$	−146.1	2.7	2.767	6.308	1.167	0.348	−0.325	0.467	0.533

As is evident from Table 5, the Δ_4 values are very small and increase in the order F < Cl < Br < I.

Note that for X = F and I, unlike X = Cl and Br, local energy minima were also found for symmetrical sandwich [**L4**—X—**L4**]$^-$ complexes with D_{3h} symmetry (see Fig. 3, **C'**); however, these minima are located higher than the energy minima corresponding to the unsymmetrical sandwich complexes by 8.0 and 113.6 kcal mol^{-1} for X = I and F, respectively (see Tables 3 and 5). The symmetrical complex with the F$^-$ anion is purely ionic (no electron density transfer from the F$^-$ anion to the rings, zero order of the Hg—F bond, and the larger Hg—F bond length), *i.e.*, in this complex, the F$^-$ ion may be considered as solvated by two macrocycles **L4**. In the case of iodine, the ordinary generalized chemical bonds between the anion and the macrocycles make the dominant contribution to the formation of the symmetrical sandwich complex. 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 semisandwich 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}.

Therefore, it is appropriate to describe the formation of the complex of halide anions with mercury-containing macrocycles in terms of generalized chemical bonds.

Actually, whereas for the studied macrocycles containing three mercury atoms, an alternative description using two-electron two-center donor-acceptor bonds is possible, and for the systems containing four mercury atoms, a description using two-electron three-center bonds is acceptable, for the macrocycles containing five and more mercury atoms, a description in terms of localized bonds is impossible. The halide anion lacks orbitals for the formation of these bonds. A general description of the bonding between halide anions and a polymetallamacrocycle regardless of the number of mercury atoms in the macrocycle can be realized only within the model 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 semisandwich complexes [L—X]$^-$, the macrocyclic ligand is bonded to the halide anion through the triple generalized chemical bond: one headlight-shaped σ-bond and two two-lobe π-bonds. In bipyramidal complexes [X—**L**—X]$^{2-}$, each halide anion is bonded to the macrocycle through three generalized chemical bonds; this is possible because in this case, there are suitable combinations of unoccupied orbitals of mercury atoms directed both toward the upper and lower halogen atoms.

A quite different situation occurs in sandwich complexes. The calculations performed revealed substantial differences in the character of chemical bonding in sandwich structures, depending on the nature of the central atom. In ordinary sandwich complexes, the central atom is the transition metal atom with nine valence AOs, and, therefore, full-value bonding to each ring through generalized chemical bonds is possible. On formation the above-discussed sandwich complexes with mercury-containing macrocycles, the central atom is the halide anion, which has only four valence AOs, and, therefore, the bonding of this atom to each ring through three generalized chemical bonds is no longer possible. As a result, the structure with the rings equidistant from the central atom, which is typical of sandwich complexes of transition metals, becomes less favorable than the unsymmetrical structure, in which the rings are at different distances from the central atom. The unsymmetrical sandwich complex contains semisandwich ion [L—X]$^-$ with a triple generalized chemical bond between the halide anion and the mercury-containing macrocycle. The weakly bonded complex of this semisandwich anion with the second **L** molecule (**L** = **L4**) is actually the ion [L—X]$^-$ solvated by this molecule.

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