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# Reviews

## Perfluorinated polymercuramacrocycles as anticrowns. Applications in catalysis*

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The catalytic and complexing properties of two perfluorinated polymercuramacrocycles, *viz.*, cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ and cyclic pentameric perfluoroisopropylidenemercury $[(CF_3)_2CHg]_5$, are analyzed. These macrocycles contain several Lewis acidic centers in the ring and can be considered as peculiar antipodes of crown ethers and their thia and aza analogs. Both macrocycles can efficiently bind various anions to form unique complexes, in which the anionic species is simultaneously coordinated to all Lewis acidic atoms of the ring. For the $(o\text{-}C_6F_4Hg)_3$ macrocycle, unusual complexes with various neutral Lewis bases, such as nitriles, carbonyl compounds, aromatic hydrocarbons, *etc.*, were also described. Data on the activity of polymercury-containing macrocycles in phase transfer catalysis of electrophilic reactions and proton transfer from an aqueous to an organic phase are surveyed and discussed.

**Key words:** anticrowns, macrocyclic multidentate Lewis acids, polymercuramacrocycles, anions, neutral Lewis bases, supramolecular complexes, X-ray diffraction analysis.

### Introduction

In the last decade, the problem of the design of highly efficient chemical systems, which can perform molecular recognition of anions, has attracted growing interest of researchers. One of promising approaches to the solution of this important problem is based on the use of macrocyclic multidentate Lewis acids as anion receptors.

Macrocyclic multidentate Lewis acids can be considered as peculiar antipodes of crown ethers and their thia and aza analogs, which have been extensively studied over many years.[1—3] A great interest in crown ethers and related macrocycles results from their ability to form stable complexes with metal cations due to the presence of several Lewis basic centers in the chain. High affinity of these unique reagents for metal cations and the lipophilic properties of the resulting complexes are widely used for

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selective extraction of cations, in cation-selective electrodes, in phase transfer catalysis of nucleophilic reactions, and for many other purposes.

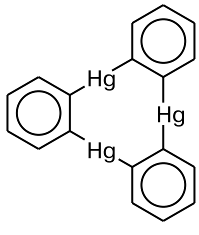
In contrast to crown ethers and their analogs, macrocyclic multidentate Lewis acids contain several atoms exhibiting Lewis acidity and, hence, can efficiently bind various anions to form unusual complexes in which the anionic species is simultaneously coordinated to all Lewis centers of the macrocycle.* Due to this remarkable feature, macrocyclic multidentate Lewis acids hold considerable promise for the highly efficient and selective extraction of anions, the design of anion-selective electrodes, and application in analytical chemistry, organic synthesis, and catalysis.

First reports on the successful use of macrocyclic multidentate Lewis acids as anion receptors emerged in the late 1980s—early 1990s. Since that time, considerable amount of data (see, for examples, the reviews[4—6]) were accumulated on various aspects of the chemistry of these new reagents called anticrowns. The data on the complexing properties of macrocycles containing from two to five Lewis acidic centers in the ring were published in the literature. However, only macrocycles containing three or more atoms exhibiting Lewis acidity can be considered as true anticrowns. Particularly efficient anticrowns were found in the series of polymercuramacrocycles. Polytin- and polysilicon-containing macrocycles were also tested as anticrowns.

The present review is devoted to the coordination chemistry and catalytic properties of perfluorinated polymercuramacrocycles, which have been first used as receptors of anionic species at our laboratory. These macrocycles have two important advantages. First, the presence of a large number of electron-withdrawing fluorine atoms in the ring sharply increases the Lewis acidity of the mercury centers and, correspondingly, their efficiency in the complex formation with anions. Second, the introduction of fluorine atoms into the macrocycle should lead to a sharp increase in stability of the mercury—carbon bonds toward protons and other electrophilic reagents, which is of considerable importance from the viewpoint of the possible application of such macrocycles in catalysis of electrophilic reactions. Actually, investigation of the complexing ability of perfluorinated polymercuramacrocycles demonstrated that these compounds exhibit extremely high activity in binding of various anions and neutral Lewis bases to give complexes with unique structures. Later on, it was found that macrocycles of this type hold also considerable promise in catalysis, for example, as phase transfer catalysts for electrophilic reactions.

## Complexing properties of perfluorinated polymercuramacrocycles

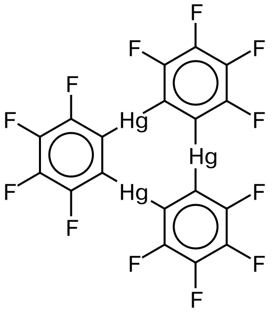
When we started our studies on the use of macrocyclic multidentate Lewis acids for anion binding in 1987, we chose cyclic trimeric *o*-phenylenemercury $(o\text{-}C_6H_4Hg)_3$ (**1**) containing three Hg atoms in the planar nine-membered ring as a potential receptor of anionic species,[7,8] and even the first experiments clearly demonstrated that this macrocycle can form complexes with anions.[9]



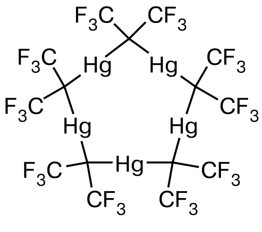
**1**

The experiments were very simple. Macrocycle **1** is virtually insoluble in $CH_2Cl_2$. However, it appeared that the addition of quaternary ammonium or phosphonium halide (for example, $[NEt_3(CH_2Ph)]^+Cl^-$, $[PPh_4]^+Br^-$, or $[PPh_3Me]^+I^-$) to a suspension of compound **1** leads to its immediate dissolution, thus indicating on the complex formation. Subsequent $^{199}$Hg NMR spectroscopic studies confirmed this conclusion. However, all attempts to isolate the resulting complexes from solutions in the analytically pure state failed. In all cases, only complex mixtures of the reaction products and the starting reagents were obtained.

A different situation was observed, when we used the perfluorinated analog of macrocycle **1**, *viz*., cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**2**), which also contains three Hg atoms in the planar nine-membered ring.[10,11] In this case, the complexes with halide anions were isolated in individual form.[12—14] Later on, yet another perfluorinated polymercuramacrocycle, *viz*., cyclic pentameric perfluoroisopropylidenemercury $[(CF_3)_2CHg]_5$ (**3**), containing five Hg atoms in the planar ten-membered ring was successfully used for anion binding.[15] The complexing properties of these macrocycles are considered below.



**2**



**3**

**Complexation with anions.** Macrocycle **2** exhibits high affinity for various anions and binds them at room temperature to form complexes, whose composition and struc-

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* For complexation of anions with protonated cryptands and other macrocycles containing several onium centers, see, for example, the monographs.[1—3]

ture depend strongly on the nature of the anionic species and the reagent ratio.

In the case of the bromide, iodide, and thiocyanate ions, the isolated $[(o\text{-}C_6F_4Hg)_3X]^-$ complexes (X = Br, I, or SCN) contain one anion per molecule of the macrocycle.[12–14,16] The reaction of compound **2** with chloride ions affords the $\{[(o\text{-}C_6F_4Hg)_3]_3Cl_2\}^{2-}$ complex, which contains two anions per three molecules of the macrocycle.[12,13]

X-ray diffraction study of the complexes of macrocycle **2** with bromide and iodide anions revealed (Fig. 1) that in the solid state these compounds exist as the $\{[(o\text{-}C_6F_4Hg)_3X]_n\}^{n-}$ polymers (X = Br or I) and have an unusual wedge-shaped multidecker sandwich structure, in which each halide anion is coordinated to six Hg atoms of two adjacent molecules of the macrocycle.[12–14] The unique feature of the complexes is that, in contrast to normal sandwhich complexes, the halide anions rather than metal atoms or cations serve as the coordinating centers in their molecules. The halogen atoms in both complexes have a coordination number of six.

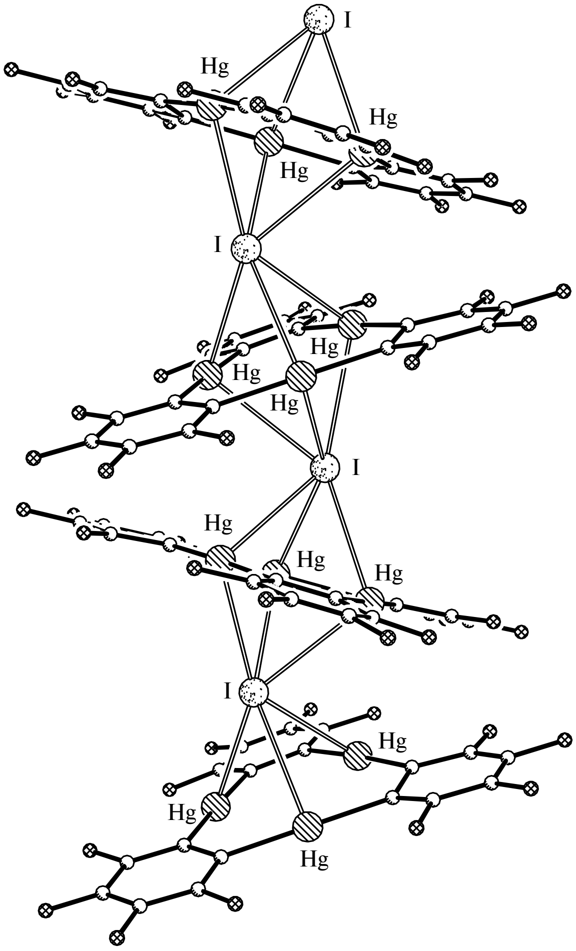


**Fig. 1.** Fragment of the polyanionic chain in the structure of the $\{[(o\text{-}C_6F_4Hg)_3I]_n\}^{n-}$ complex.[14]

An analogous multidecker sandwich structure was found for the complex of macrocycle **2** with the thiocyanate ion, *viz.*, $\{[(o\text{-}C_6F_4Hg)_3(SCN)]_n\}^{n-}$.[16] The anionic species in this complex is bound to the Hg centers of the anticrown through the S atom. However, the coordination of the anion to the macrocycle in this complex is less symmetrical: each $SCN^-$ ion is involved in two rather short and one substantially longer Hg—S bonds with each molecule **2**. Apparently, the observed asymmetry arises from steric repulsions between the CN group of the coordinated $SCN^-$ ion and the C and F atoms of the macrocycle, which lead to the displacement of the thiocyanate guest from the space between the anticrown molecules. The complexation with the macrocycle results in a weakening of the S—C bond of the thiocyanate anion and a strengthening of its C—N bond.

The above-mentioned complex of macrocycle **2** with the chloride anions, *viz.*, $\{[(o\text{-}C_6F_4Hg)_3]_3Cl_2\}^{2-}$, could not be obtained as crystals suitable for X-ray diffraction study. Presumably, this complex has the triple-decker sandwich structure $[\mathbf{2}\cdot Cl\cdot \mathbf{2}\cdot Cl\cdot \mathbf{2}]^{2-}$.

The reaction of macrocycle **2** with potassium *p*-nitrothiophenoxide in THF affords complexes with three different compositions: $\{[(o\text{-}C_6F_4Hg)_3](p\text{-}O_2NC_6H_4S)\}^-$ (**4**), $\{[(o\text{-}C_6F_4Hg)_3](p\text{-}O_2NC_6H_4S)_2\}^{2-}$ (**5**), or $\{[(o\text{-}C_6F_4Hg)_3]_2(p\text{-}O_2NC_6H_4S)\}^-$ (**6**) depending on the reagent ratio.[17] Complexes **4** and **5** contain one and two anionic species, respectively, per molecule of the mercury anticrown, whereas there is only one anion per two anticrown molecules in complex **6**. The formation of the complexes was judged from the high-frequency shifts of the $\nu_s$(NO) band at 1298 $cm^{-1}$ in the IR spectrum and the absorption band at $\lambda = 500$ nm of the starting anion in the electronic spectrum. The largest shifts (by 34 $cm^{-1}$ and 95 nm, respectively) are observed for complex **6**. The compositions of the complexes were determined by spectrophotometry using the continuos variation method. Complex **4** was isolated in the analytically pure state from the reaction of macrocycle **2** with an equimolar amount of $p\text{-}O_2NC_6H_4S^-K^+$ in ethanol. All three complexes are very stable, as evidenced by their stability constants (Table 1), which were calculated from the spectroscopic data. Complex **6** is particularly stable. At 20 °C, the constant of its formation in THF is $5\cdot 10^8$ $L^2$ $mol^{-2}$.

In contrast to the *p*-nitrothiophenoxide anion, the *p*-nitrophenoxide anion reacts with macrocycle **2** in THF to form the only complex $\{[(o\text{-}C_6F_4Hg)_3](p\text{-}O_2NC_6H_4O)_2\}^{2-}$ (**7**) independently of the reagent ratio.[18] The stability constant of this complex, which contains two anionic species per anticrown molecule, is somewhat smaller than the corresponding constant for compositionally similar complex **5** (see Table 1).

According to the IR and NMR spectroscopic data, the reaction of macrocycle **2** with borohydride anions in THF also gives rise to three complexes:

**Table 1.** Stability constants of the complexes at 20 °C

| Complex | Solvent | Stability constant |
|---|---|---|
| $\{[(o\text{-}C_6F_4Hg)_3](p\text{-}O_2NC_6H_4S)\}^-$ (**4**) | THF | $2 \cdot 10^7$ L mol$^{-1}$ |
| $\{[(o\text{-}C_6F_4Hg)_3](p\text{-}O_2NC_6H_4S)_2\}^{2-}$ (**5**) | THF | $10^6$ L$^2$ mol$^{-2}$ |
| $\{[(o\text{-}C_6F_4Hg)_3]_2(p\text{-}O_2NC_6H_4S)\}^-$ (**6**) | THF | $5 \cdot 10^8$ L$^2$ mol$^{-2}$ |
| $\{[(o\text{-}C_6F_4Hg)_3](p\text{-}O_2NC_6H_4O)_2\}^{2-}$ (**7**) | THF | $6 \cdot 10^5$ L$^2$ mol$^{-2}$ |
| $\{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-}$ (**9**) | THF | $10^4$ L$^2$ mol$^{-2}$ |
| $\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$ (**10**) | THF | $10^7$ L$^2$ mol$^{-2}$ |
| $\{[(C_6F_5)_2Hg](BH_4)\}^-$ | THF | $10^2$ L mol$^{-1}$ |
| $\{[(o\text{-}C_6F_4Hg)_3](B_{10}H_{10})\}^{2-}$ (**11**) | THF—acetone (1 : 1) | $10^2$ L mol$^{-1}$ |
| $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{10}H_{10})\}^{2-}$ (**12**) | THF | $2.6 \cdot 10^3$ L$^2$ mol$^{-2}$ |
| $\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{12})\}^{2-}$ (**13**) | THF—acetone (1 : 1) | $0.7 \cdot 10^2$ L mol$^{-1}$ |
| $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{12})\}^{2-}$ (**14**) | THF | $9.8 \cdot 10^2$ L$^2$ mol$^{-2}$ |
| $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}^{2-}$ (**15**) | THF | $9.9 \cdot 10^2$ L$^2$ mol$^{-2}$ |
| $\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{11}SCN)\}^{2-}$ (**16**) | THF | $0.16 \cdot 10^2$ L mol$^{-1}$ |

$\{[(o\text{-}C_6F_4Hg)_3](BH_4)\}^-$ (**8**), $\{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-}$ (**9**), and $\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$ (**10**).[19] In these complexes, the anionic species is bound to the Hg atoms through the B—H—Hg bridges. According to the IR spectroscopic data, complex **9** contains both the bridging and terminal B—H bonds. In complex **10**, all four B—H bonds of the starting $BH_4^-$ anion are involved in coordination with the macrocycle, *i.e.*, serve as bridges. Complex **8** was not detected by IR spectroscopy due, apparently, to overlapping of its ν(BH) bands with the bands of compound **9**. However, the formation of this complex is clearly evidenced by the $^{199}$Hg NMR spectra. The compositions of complexes **9** and **10** were determined from the IR spectroscopic data by the molar ratio and continuos variation methods. Both complexes are very stable (see Table 1). For example, the stability constant of complex **10** in THF at 20 °C is $10^7$ L$^2$ mol$^{-2}$. According to the results of quantum-chemical calculations,[19] complexes **8—10** should have unusual pyramidal (half-sandwich), bipyramidal, and sandwich structures, respectively (Fig. 2). The results of these calculations agree well with the spectroscopic data. Apparently, the above-mentioned *p*-nitrothiophenoxide complex **6**, which is similar in composition to compound **10**, also has a double-decker sandwich structure, whereas complexes **5** and **7** have bipyramidal structures.

To reveal the cooperative effect of the Hg atoms in the binding of $BH_4^-$ anions by macrocycle **2**, the complexation of its monomeric acyclic analog, *viz.*, perfluorodiphenylmercury $(C_6F_5)_2Hg$, with $BH_4^-$ ions was examined. Study by IR spectroscopy demonstrated[19] that, regardless of the reagent ratio, the reaction of $(C_6F_5)_2Hg$ with $[Bu_4N]^+(BH_4)^-$ in THF affords the only complex with composition $\{[(C_6F_5)_2Hg](BH_4)\}^-$ containing both the bridging and terminal B—H bonds. The stability constant of this complex in THF (see Table 1) appeared to be much smaller than the corresponding constants of compounds **9** and **10**.

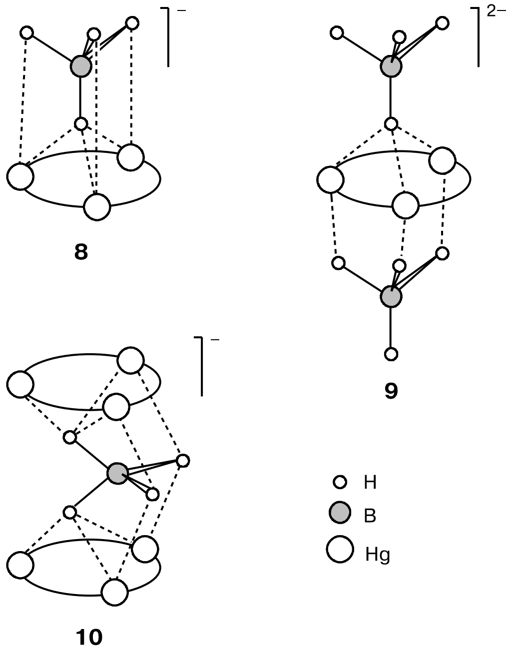


**Fig. 2.** Structures of the $\{[(o\text{-}C_6F_4Hg)_3](BH_4)\}^-$ (**8**), $\{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-}$ (**9**), and $\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$ (**10**) complexes based on the results of calculations by the AM1 method.[19]

Macrocycle **2** readily reacts with the polyhedral dianions *closo*-$[B_{10}H_{10}]^{2-}$ and *closo*-$[B_{12}H_{12}]^{2-}$ to give the
$\{[(o\text{-}C_6F_4Hg)_3](B_{10}H_{10})\}^{2-}$ (**11**),
$\{[(o\text{-}C_6F_4Hg)_3]_2(B_{10}H_{10})\}^{2-}$ (**12**),
$\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{12})\}^{2-}$ (**13**),
and $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{12})\}^{2-}$ (**14**)
complexes containing respectively one and two molecules of the mercury anticrown per anionic species.[20] The reactions with the use of a twofold molar excess of the macrocycle with respect to the dianion afford complexes **12** and **14**. According to the X-ray diffraction data, these complexes have wedge-shaped double-decker sandwich

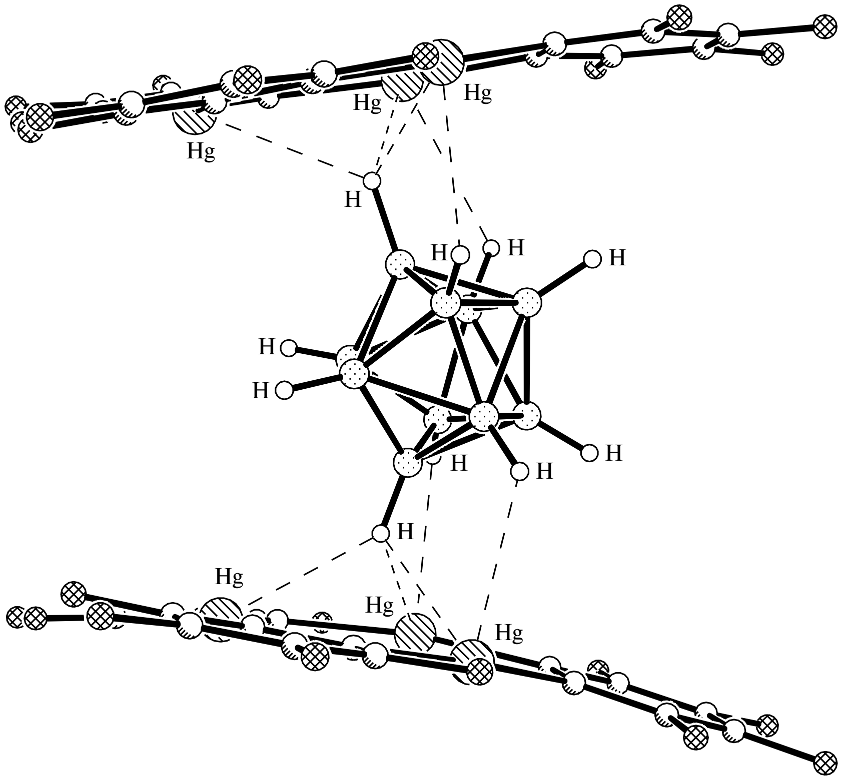


**Fig. 3.** Molecular structure of the $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{10}H_{10})\}^{2-}$ (**12**) complex.[20]

structures. In these unique sandwiches, anionic borane is located between the planes of two molecules of the macrocycle and is bound to each of them by the bridging B—H—Hg bonds of two types (Fig. 3). One type of the bridges is characterized by the simultaneous coordination of the BH group to all three Hg atoms of the macrocycle, whereas the BH group in a bridge of another type is coordinated only to one Hg center of the anticrown molecule. In complex **12**, the dihedral angle between the mean planes of the central nine-membered rings of the macrocycles is 19°. In complex **14**, this angle is much larger (59°).

The reactions of equimolar amounts of compound **2** and the $[B_{10}H_{10}]^{2-}$ or $[B_{12}H_{12}]^{2-}$ anions give complexes **11** or **13**, respectively, with half-sandwich structures (Fig. 4).

The stability constants of the above-mentioned four complexes were measured at 20 °C. As can be seen from Table 1, sandwich complex **12** is noticeably more stable than its analog **14**. This fact is, apparently, associated with a larger degree of delocalization of the negative charge in the $[B_{12}H_{12}]^{2-}$ anion compared to that in the smaller $[B_{10}H_{10}]^{2-}$ anion. However, complex **12** is much less stable compared to the above-considered complexes **6** and **10**, which, presumably, also have sandwich structures. The stability constant decreases on going from sandwiches to half-sandwiches (see Table 1).

The analogous wedge-shaped double-decker sandwich complex $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}^{2-}$ (**15**) was isolated from the products of the reaction of the thiocyanate-substituted polyhedral dianion $[B_{12}H_{11}SCN]^{2-}$ with a twofold molar excess of macrocycle **2**.[21] In this sandwich, both the S atom of the thiocyanate group and the BH groups are involved in the bonding to the Hg centers of the anticrown molecule. Sandwich complex **15** is similar in stability to its unsubstituted analog **14** (see Table 1). The reaction of equimolar amounts of macrocycle **2** and $[B_{12}H_{11}SCN]^{2-}$ ion affords the $\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{11}SCN)\}^{2-}$ complex (**16**) with 1 : 1 composition, as evidenced by the results of spectroscopic study.[21] Attempts to isolate this complex in individual form failed. Apparently, complex **16** has a half-sandwich structure. According to the IR spectroscopic data, the thiocyanate group in compound **16** is weakly coordinated, if at all, to the Hg atoms of the macrocycle. Complex **16** is considerably less stable than half-sandwich **13** (see Table 1).

Macrocycle **2** is also able to bind the hexacyanoferrate(III) and nitroprusside anions.[22] These reactions afford the unusual double-decker sandwiches $\{[(o\text{-}C_6F_4Hg)_3]_2[Fe(CN)_6]\}^{3-}$ (**17**) and $\{[(o\text{-}C_6F_4Hg)_3]_2[Fe(CN)_5NO]\}^{2-}$ (**18**), respectively, in which the complex anion is coordinated to the Hg atoms of both molecules of the macrocycle through the Fe—C—N—Hg bridges of two types. One type is characterized by the cooperative binding of the cyanide group by all three Hg centers of the anticrown, whereas another type of the bridges corresponds to coordination of the

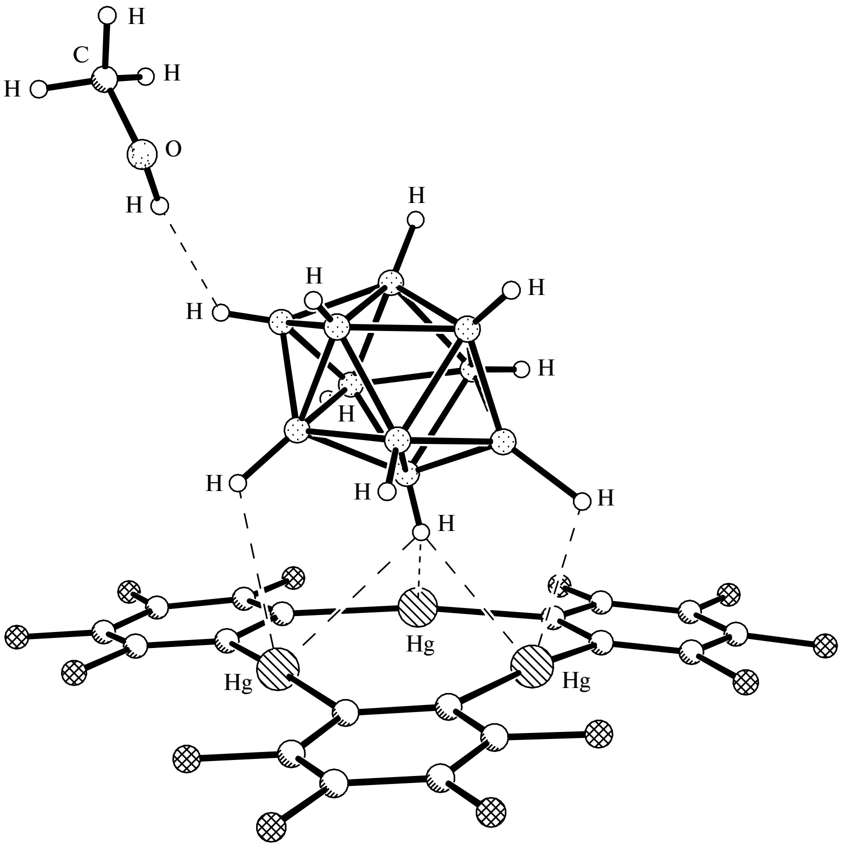


**Fig. 4.** Molecular structure of the $\{[(o\text{-}C_6F_4Hg)_3](B_{10}H_{10})\}^{2-}$ (**11**) complex as a solvate with methanol.[20]

cyanide group to only one Hg atom. It should be noted that in both complexes, the π electrons of the cyanide ligands are involved in the bonding to the macrocycle.

In complex **17**, the dihedral angle between the planes of the central nine-membered rings of the macrocycles is 11.1°, *i.e.*, the complex has a wedge-shaped sandwich structure. In complex **18**, the rings are coplanar. According to the X-ray diffraction data, the bonding of the anionic species to the anticrown molecules in complex **18** is weaker than that in complex **17**, which is, apparently, associated with a decrease in the negative charge of the anion on going from $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_5NO]^{2-}$.

In the crystals, the both compounds form extended stacks, in which the outer sides of the mercuracarbon rings of the complexes face each other. The stacks are characterized by the presence of shortened intermolecular Hg···Hg and Hg···C contacts. The magnetic susceptibility measurement demonstrated that complex **17** is ferromagnetic. This result is attributable to the ferromagnetic exchange interaction between the $Fe^{III}$ atoms, which becomes possible upon the formation of stacks in the crystal packing of complex **17**.

For macrocycle **3**, complexes with the halide, acetate, trifluoroacetate, and sulfate anions were prepared.

In the case of halides anions, the resulting $\{[(CF_3)_2CHHg]_5X_2\}^{2-}$ complexes (X = Cl, Br, or I) contain two anionic species per molecule of the macrocycle and have pyramidal structures (Fig. 5).[23–25] In these adducts, the halide anions are located above and below the plane of the metallacycle and each of them is symmetrically bound to all Hg centers of the anticrown, as a result of which the halogen atoms have a coordination number of five. Another interesting feature of the complexes is the presence of abnormally short distances between the halide anions, which are substantially shorter than twice the van der Waals radius of the corresponding halogen atom. Such an energetically unfavorable shortening of the distance between the anionic species in the complexes can, evidently, occur only due to very strong attractive mercury—halogen interactions.

The complexes of macrocycle **3** with the acetate and trifluoroacetate anions have the composition $\{[(CF_3)_2CHHg]_5(RCOO)_2\}^{2-}$ (R = $CH_3$ or $CF_3$), *i.e.*, also contain two anions per anticrown molecule.[26] These complexes were synthesized by the reactions of $\{[(CF_3)_2CHHg]_5Br_2\}^{2-}$ with 2 equiv. of $CH_3COOAg$ or $CF_3COOAg$, respectively. Like in the dihalide complexes, the anionic species in $\{[(CF_3)_2CHHg]_5(RCOO)_2\}^{2-}$ are located on opposite sides of the plane of the macrocycle

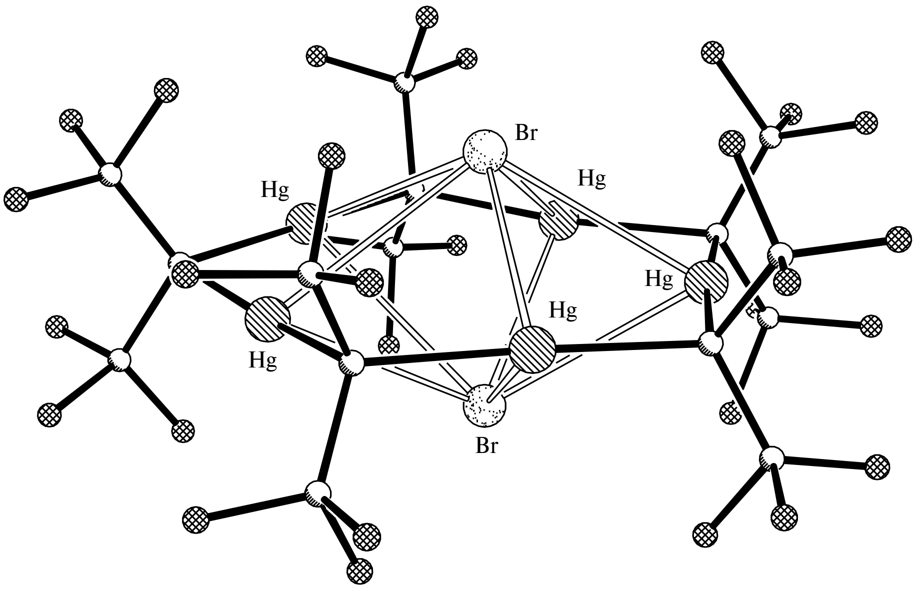


**Fig. 5.** Molecular structure of the $\{[(CF_3)_2CHg]_5Br_2\}^{2-}$ complex.[24]

and are coordinated to it in the same fashion. However, the dihalide and bis-carboxylate complexes differ substantially from each other in the character of coordination of the anions. In the bis-carboxylate complexes, one of the O atoms of each anionic species is bound to three Hg atoms of the anticrown, whereas another O atom is bound only to two Hg atoms. On going from the bis-acetate to the bis-trifluoroacetate complex, the Hg—O bonds are substantially elongated due to the much higher Lewis basicity of the acetate ion compared to its trifluoroacetate analog.

The complex of macrocycle **3** with the sulfate anion, *viz.*, $\{[(CF_3)_2CHg]_5(SO_4)\}^{2-}$, which was synthesized by the reaction of $\{[(CF_3)_2CHg]_5Br_2\}^{2-}$ with an equimolar amount of $Ag_2SO_4$ in acetone, has an even more unusual structure.[26] In this 1 : 1 complex, the sulfate anion serves as the tetradentate ligand and, in addition, is involved in three different types of Hg—O bonds with the macrocycle (Fig. 6). One of the O atoms of the $SO_4^{2-}$ ion in the complex is simultaneously coordinated to all five Hg centers of the macrocycle. This O atom with a coordination number of six lies virtually in the plane of the ten-mem-

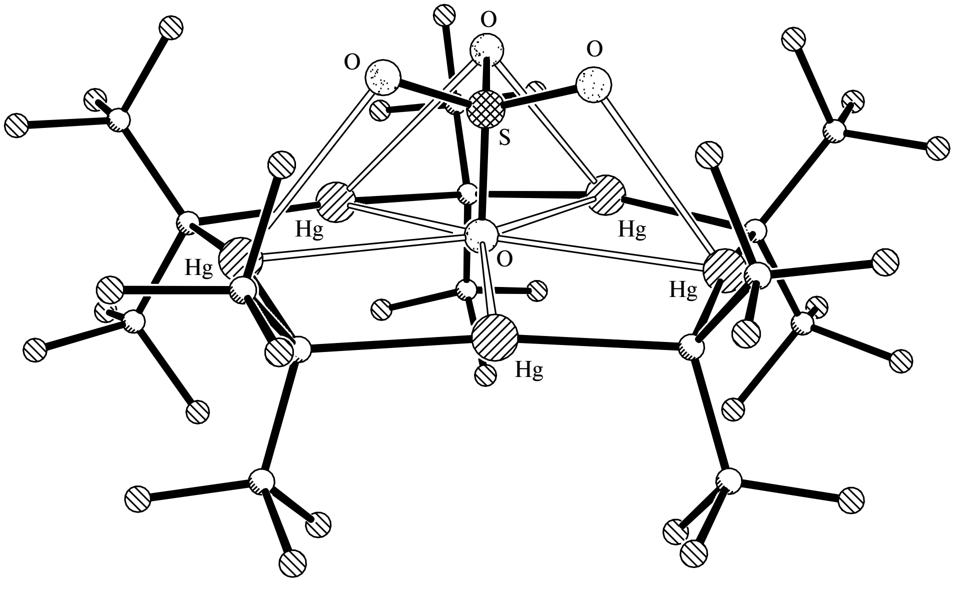


**Fig. 6.** Molecular structure of the $\{[(CF_3)_2CHg]_5(SO_4)\}^{2-}$ complex.[26]

bered mercuracarbon ring. Two other O atoms of the sulfate ligand are each coordinated only to one Hg center of the anticrown. Finally, the fourth O atom in the complex is coordinated to two Hg atoms.

To elucidate the nature of the bonds between the halide anions and polymercury-containing anticrowns, quantum-chemical calculations (by the MNDO method) were carried out for various complexes of macrocycles **1—3** and some of their analogs with fluoride, chloride, bromide, and iodide anions.[25,27,28] The bipyramidal complexes $[X \cdot M \cdot X]^{2-}$ as well as the hypothetical pyramidal (half-sandwich) structures $[M \cdot X]^-$ and the double-decker sandwiches $[M \cdot X \cdot M]^-$ (M is the macrocycle and X = F, Cl, Br, or I) were calculated. There are minima on the potential energy surfaces of all bipyramidal and pyramidal complexes, whereas the potential energy surfaces of the corresponding sandwich complexes (calculated for the analog of macrocycle **2**, *viz*., cyclic trimeric difluorovinylenemercury $[C_2F_2Hg]_3$) have such minima only in the case of the iodide and fluoride anions, the iodide complex being considerably more stable than its fluoride analog. It was also shown that the sulfide anion forms the particularly stable double-decker sandwich complex with macrocycle **2**.[25] According to the results of calculations,[25,28] the fluoride anion in the hypothetical monofluoride complex of macrocycle **3**, *viz*., $\{[(CF_3)_2CHg]_5F\}^-$, lies in the center of the planar ten-membered mercuracarbon ring and is coordinated to all five Hg atoms.

An important conclusion, which was made based on the results of calculations, is that it is appropriate to describe the chemical bonds between the halide anions and polymercuramacrocycles in terms of the generalized chemical bonds, which are successfully used in considering transition metal π-complexes. It was found that the halide anions in the pyramidal and bipyramidal complexes are bound to the Hg atoms by three generalized chemical bonds: one headlight-shaped σ bond and two two-lobe π bonds. In the sandwich complexes with the iodide and sulfide anions, headlight-shaped σ bonds make the major contribution to the bonding with the macrocycle, whereas the sandwich complex with the fluoride anion is purely ionic in character.

**Complexation with neutral Lewis bases.** Macrocycle **2** can efficiently bind not only anions but also various neutral Lewis bases, such as nitriles,[29,30] carbonyl compounds,[30—34] dimethyl sulfide,[35] aromatic hydrocarbons,[36—38] *etc*.[31,39,40]

In the case of nitriles, the composition and structure of the complexes depend on the nature of the nitrile used. For example, the reactions of compound **2** with acrylonitrile[29] and *n*-butyronitrile[30] afford the $\{[(o\text{-}C_6F_4Hg)_3](CH_2CHCN)\}$ (**19**) and $\{[(o\text{-}C_6F_4Hg)_3](Pr^nCN)\}$ (**20**) complexes, respectively, which contain one molecule of the Lewis base per molecule of the macrocycle and have pyramidal structures (Fig. 7). The nitrile ligand in these complexes is symmetrically coordinated to all Hg centers of the anticrown through the N atom. The $\{[(o\text{-}C_6F_4Hg)_3](MeCN)_2\}$ complex (**21**) was isolated from the products of the reaction of macrocycle **2** with acetonitrile.[29] This complex contains two molecules of the Lewis base per molecule of the mercury anticrown and has the corresponding bipyramidal structure (Fig. 8). The reaction of macrocycle **2** with benzonitrile[29] gives rise to the $\{[(o\text{-}C_6F_4Hg)_3](PhCN)_3\}$ complex (**22**) containing three molecules of the Lewis base per anticrown molecule. The remarkable feature of this complex is that all nitrile ligands are located on one side of the plane of the macrocycle and, in addition, differ

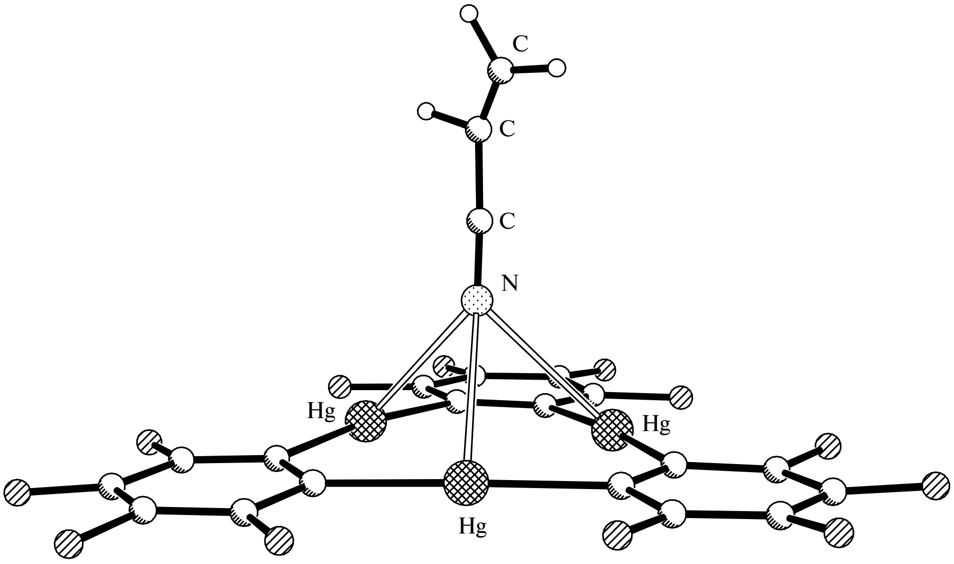


**Fig. 7.** Molecular structure of the $\{[(o\text{-}C_6F_4Hg)_3](CH_2CHCN)\}$ (**19**) complex.[29]

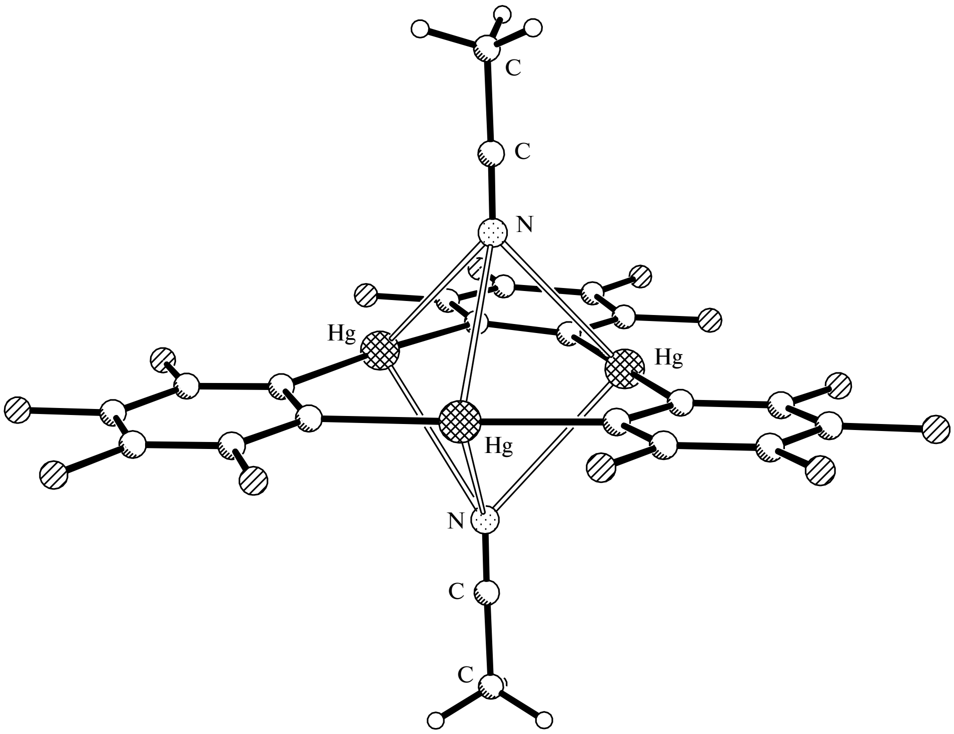


**Fig. 8.** Molecular structure of the $\{[(o\text{-}C_6F_4Hg)_3](MeCN)_2\}$ (**21**) complex in the crystal.[29]

from each other by the mode of coordination to the Hg atoms (Fig. 9). One of the nitrile ligands in compound **22** is coordinated to all Hg atoms of the ring and forms a pyramidal fragment. Two other nitrile ligands are coordinated only to one Hg center each, but they differ in the arrangement with respect to the plane of the anticrown. The $p_\pi$ electrons of the N atoms are involved in the bonding of these nitrile ligands to the macrocycle.

Complex **21** is thermally less stable than adducts **19**, **20**, and **22**. Upon drying *in vacuo* at 20 °C, **21** loses one acetonitrile molecule to give the $\{[(o\text{-}C_6F_4Hg)_3](MeCN)\}$ complex (**23**) with 1 : 1 composition. Presumably, this complex, like compounds **19** and **20**, has a pyramidal structure. Complexes **19**, **20**, and **22** remain unchanged upon storage *in vacuo* at 20 °C.

In the IR spectra of nitrile complexes **19**, **20**, and **23** in Nujol mulls, the ν(CN) band is shifted to the high-frequency region, which is characteristic of nitrile complexes with Lewis acids. The IR spectrum of complex **22** shows two ν(CN) bands, which are shifted to the high- and low-frequency regions relative to the corresponding band of the free nitrile. The $^{199}$Hg NMR spectra of the nitrile complexes in THF differ only slightly from the spectrum of the starting macrocycle, which indicates that the nitrile ligands are displaced from the coordination spheres of the Hg atoms by the solvent molecules. This result is quite reasonable taking into account considerably lower basicity of nitriles compared to THF[41] and the presence of a large excess of THF with respect to the nitrile complex. Correspondingly, the addition of an excess of nitrile to solutions of the complexes in THF leads to an essential downfield shift of the $^{199}$Hg NMR signal. Therefore, the nitrile complexes of macrocycle **2** are labile in THF and can exist in solution only in the presence of an excess of a nitrile ligand.

Neutral oxygeneous Lewis bases (aldehydes, ketones, esters, amides, *etc.*) also form three types of complexes with macrocycle **2**. For example, the reactions with acetaldehyde[33] and benzophenone[33] afford the $\{[(o\text{-}C_6F_4Hg)_3](MeCHO)\}$ (**24**) and $\{[(o\text{-}C_6F_4Hg)_3](Ph_2CO)\}$ (**25**) complexes, respectively, which contain one molecule of the Lewis base per molecule of the mercury anticrown. According to the X-ray diffraction data, both complexes have pyramidal structures. The reactions of macrocycle **2** with *N*,*N*-dimethylacetamide (DMA),[30] dimethylformamide (DMF),[31,32] *N*,*N*,*N*-hexamethylphosphoramide (HMPA),[31] and acetophenone[33] afford the

$\{[(o\text{-}C_6F_4Hg)_3](MeCONMe_2)_2\}$ (**26**),
$\{[(o\text{-}C_6F_4Hg)_3](HCONMe_2)_2\}$ (**27**),
$\{[(o\text{-}C_6F_4Hg)_3][(Me_2N)_3PO]_2\}$ (**28**),
and $\{[(o\text{-}C_6F_4Hg)_3](MeCOPh)_2\}$ (**29**)

complexes, respectively, which contain two molecules of the Lewis base per anticrown molecule and have bipyramidal structures. In all these complexes, the Lewis bases are bound to the Hg centers through the O atom. Finally, for ethyl acetate,[31] dimethyl sulfoxide,[31] and acetone,[33] the $\{[(o\text{-}C_6F_4Hg)_3](MeCOOEt)_3\}$

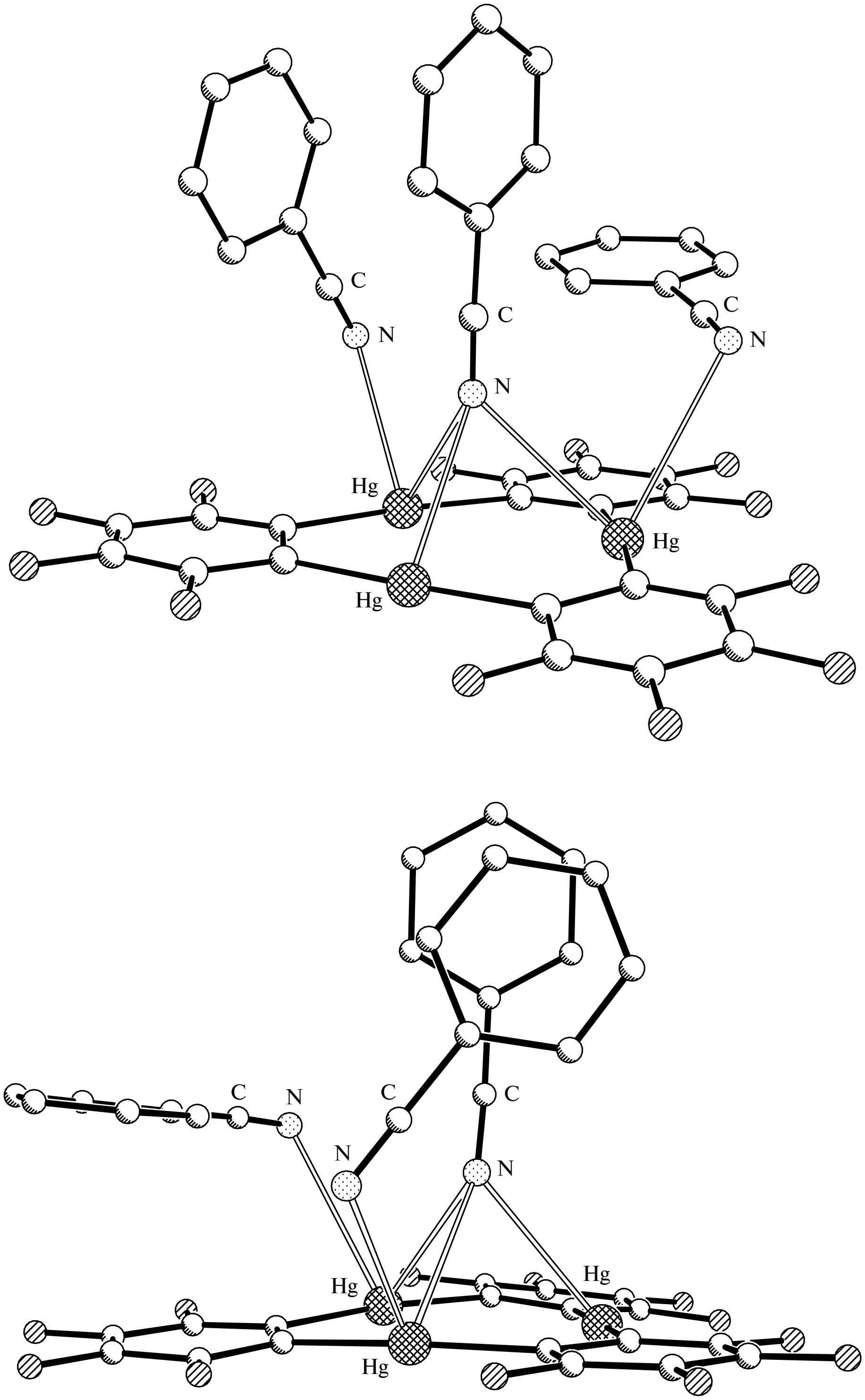


**Fig. 9.** Two views of the molecular structure of the $\{[(o\text{-}C_6F_4Hg)_3](PhCN)_3\}$ (**22**) complex.[29]

(**30**), $\{[(o\text{-}C_6F_4Hg)_3](Me_2SO)_3\}$ (**31**), and $\{[(o\text{-}C_6F_4Hg)_3](Me_2CO)_3\}$ (**32**) complexes containing one anticrown molecule and three molecules of the Lewis base were described. It should be noted that the structures of these complexes differ substantially from that of the above-described compositionally similar benzonitrile complex **22**. In contrast to compound **22**, two of three molecules of the Lewis base in complexes **30**—**32** are located on opposite sides of the plane of the macrocycle, each of them being coordinated to all Hg centers of the

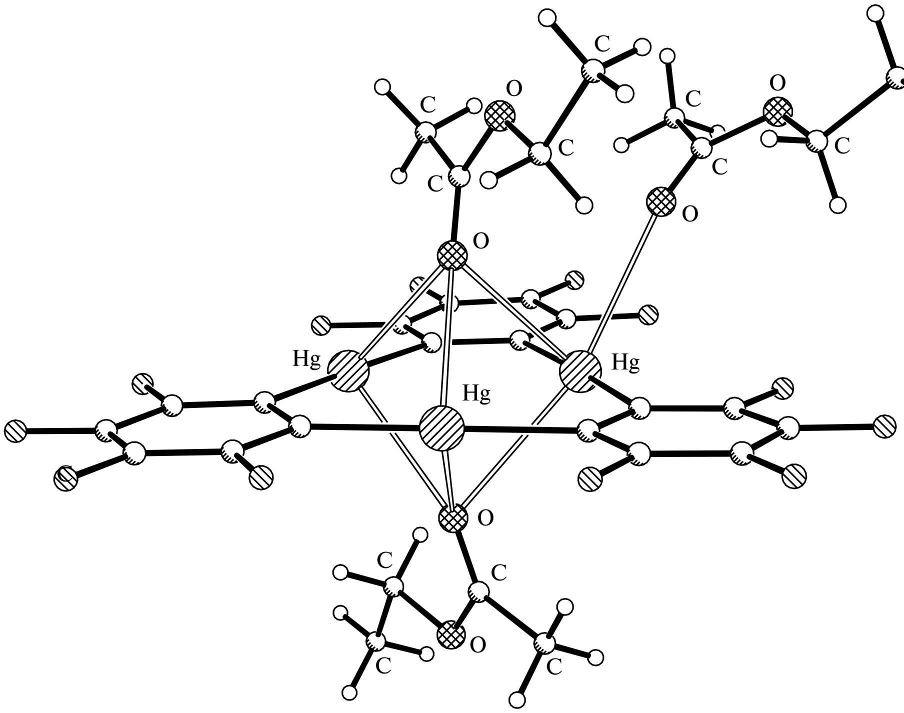


**Fig. 10.** Molecular structure of the $\{[(o\text{-}C_6F_4Hg)_3](MeCOOEt)_3\}$ (**30**) complex.[31]

anticrown to form a bipyramidal fragment (Fig. 10). The third molecule of the Lewis base in compounds **30—32** is bound only to one Hg atom.

Thermal stability of the complexes obtained depends on their composition and the nature of the oxygen-containing ligand. Complexes **29**, **30**, and **32** are the least stable. At 20 °C, they readily lose one or two molecules of the coordinated Lewis base to give the corresponding 1 : 1 adducts, *viz.*, $\{[(o\text{-}C_6F_4Hg)_3](MeCOPh)\}$ (**33**),[33] $\{[(o\text{-}C_6F_4Hg)_3](MeCOOEt)\}$ (**34**),[31] and $\{[(o\text{-}C_6F_4Hg)_3](Me_2CO)\}$ (**35**).[33,34] These adducts, like compositionally similar complexes **24** and **25**, are thermally considerably more stable. For example, according to the thermogravimetric data,[33] compound **24** decomposes with elimination of acetaldehyde only at 120 °C. Apparently, adducts **33** and **34**, like complexes **24** and **25**, also have pyramidal structures. The pyramidal structure of monoacetone adduct **35** was established[34] by X-ray diffraction analysis. This adduct can be synthesized not only from tris-acetone complex **32** but also by the direct reaction of macrocycle **2** with acetone in 1,2-dichloroethane.[34] Unlike compounds **29**, **30**, and **32**, complexes **26—28** and **31** are thermally stable.

In the IR spectra of the complexes, the ν(CO), ν(PO), or ν(SO) band of the coordinated Lewis base is shifted to the low-frequency region with respect to the corresponding band of the free Lewis base. In the series of complexes of the same type, the low-frequency shift increases with increasing Lewis basicity of the oxygen-containing nucleophile (Table 2). In the $^{199}$Hg NMR spectra of complexes **26—28** and **31** in THF, the Hg resonance is shifted downfield relative to the signal of the starting macrocycle.[30,31] In this case, the downfield shift also increases with increasing strength of a Lewis base. However, the $^{199}$Hg NMR spectrum of complex **34** in THF, like the spectra of nitrile complexes **19—23**, differs only slightly from the spectrum of the free macrocycle due, apparently, to the displacement of the ethyl acetate ligand from the complex by more basic THF molecules.[31,41] The addition of an excess of ethyl acetate to a solution of complex **34** leads to a downfield shift of the Hg resonance in the $^{199}$Hg NMR spectrum. Consequently, this complex, like the above-considered nitrile adducts, can exist in THF only in the presence of an excess of the ligand. It is known[41] that the DMA, DMF, HMPA, and DMSO molecules possess considerably higher Lewis basicities compared to THF. Therefore, their complexes with macrocycle **2** are much more stable in this solvent, and an excess of the ligand is not necessary for their existence in solution.

The reaction of macrocycle **2** with dimethyl sulfide affords the $\{[(o\text{-}C_6F_4Hg)_3](Me_2S)_4\}$ complex (**36**) containing four molecules of the Lewis base per anticrown molecule.[35] In this compound, the dimethyl sulfide ligands are located in pairs above and below the plane of the metallacycle. In each pair, one dimethyl sulfide molecule is coordinated to all Hg centers of the anticrown giving rise to a bipyramidal structure, whereas another dimethyl sulfide molecule is coordinated only to one Hg atom.

**Table 2.** IR spectroscopic data for complexes of macrocycle **2** with neutral oxygeneous Lewis bases (Nujol mulls)*

| Complex | ν(EO) | Δν(EO) | DN /kcal mol$^{-1}$ | References |
|---|---|---|---|---|
| | cm$^{-1}$ | | | |
| $\{[(o\text{-}C_6F_4Hg)_3](MeCOPh)\}$ (**33**) | 1680 | 6 | — | 33 |
| $\{[(o\text{-}C_6F_4Hg)_3](MeCHO)\}$ (**24**) | 1706 | 20 | — | 33 |
| $\{[(o\text{-}C_6F_4Hg)_3](Me_2CO)\}$ (**35**) | 1683 | 33 | 17.0 | 33, 34 |
| $\{[(o\text{-}C_6F_4Hg)_3](MeCOOEt)\}$ (**34**) | 1678 | 64 | 17.1 | 31 |
| $\{[(o\text{-}C_6F_4Hg)_3](HCONMe_2)_2\}$ (**27**) | 1646 | 29 | 26.6 | 31 |
| $\{[(o\text{-}C_6F_4Hg)_3](MeCONMe_2)_2\}$ (**26**) | 1605 | 43 | 27.8 | 30 |
| $\{[(o\text{-}C_6F_4Hg)_3][(Me_2N)_3PO]_2\}$ (**28**) | 1138 | 71 | 38.8 | 31 |
| $\{[(o\text{-}C_6F_4Hg)_3](Me_2SO)_3\}$ (**31**) | 1001 | 49 | 29.8 | 31 |

* ν(EO) is the stretching frequency of the coordinated C—O, P—O, or S—O bond in the complex; Δν(EO) is the low-frequency shift of the ν(EO) band in the complex relative to the corresponding band of free Lewis base; DN is the donor number of the corresponding free Lewis base with respect to $SbCl_5$ (Gutmann's number).[41]

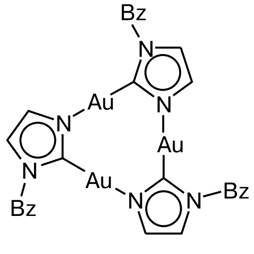
Compound **36** readily loses three dimethyl sulfide molecules at 20 °C to give the $\{[(o\text{-}C_6F_4Hg)_3](Me_2S)\}$ complex (**37**) with 1 : 1 composition. This complex was also prepared by the reaction of macrocycle **2** with an excess of dimethyl sulfide in 1,2-dichloroethane.[35] Compound **37** is thermally stable and decomposes with loss of dimethyl sulfide at a temperature higher than 100 °C. X-ray diffraction study of complex **37** demonstrated that it is structurally similar to the above-considered thiocyanate complex $\{[(o\text{-}C_6F_4Hg)_3](SCN)\}^-$.[16] Like the thiocyanate complex, adduct **37** exists in a solid state as the $\{[(o\text{-}C_6F_4Hg)_3](Me_2S)\}_n$ polymer and has a wedged-shaped multidecker sandwich structure. In this sandwich, each dimethyl sulfide ligand is located between the planes of two molecules **2** and forms three Hg—S bonds with each of these molecules, *i.e.*, the S atoms in compound **37** have a coordination number of eight. The Lewis base in molecule **37**, unlike that in the thiocyanate complex, is symmetrically bound to the Hg centers of the macrocycle.

Macrocycle **2** can coordinate also even weak Lewis bases, such as aromatic hydrocarbons: benzene,[36] biphenyl,[37] naphthalene,[37] triphenylene,[37] and pyrene.[38] The resulting complexes have the composition $\{[(o\text{-}C_6F_4Hg)_3](ArH)\}$, *i.e.*, contain one aromatic hydrocarbon molecule per molecule of the macrocycle. In the crystals, these complexes form polymeric stacked structures representing multidecker sandwiches with alternating molecules **2** and hydrocarbon molecules. Each aromatic hydrocarbon molecule in the stack is located between the planes of two anticrown molecules and is bound to each of them through donation of its π electrons to the unoccupied orbitals of the Hg atoms. In all complexes, except for the adduct with biphenyl, the planes of the macrocycles are approximately parallel to the planes of aromatic hydrocarbons.

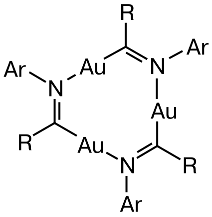
A particularly interesting multidecker structure is observed in the benzene complex $\{[(o\text{-}C_6F_4Hg)_3](C_6H_6)\}_n$ (**38**), in which each of the six carbon—carbon bonds of the benzene molecule interacts with one of the six Hg centers of the two adjacent molecules of the macrocycle. Such an unusual $\mu_6\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination of the benzene ligand in compound **38** becomes possible due to a staggered conformation of the anticrown molecules in the stacks and has not been known earlier. The complexation with the macrocycle leads to substantial changes in the spectroscopic characteristics of the benzene molecule. For example, the band of out-of plane C—H vibrations of the benzene ligand in complex **38** is shifted by 42 cm$^{-1}$ to the short-wave region with respect to the corresponding band in the IR spectrum of the free $C_6H_6$ molecule. Compound **38** is rather stable. Its thermal decomposition with elimination of benzene is observed at 70—110 °C.

Complexes of macrocycle **2** with biphenyl, naphthalene, and pyrene exhibit phosphorescence at room temperature,[37,38] the color of phosphorescence being dependent on the nature of aromatic hydrocarbon.

Unusual supramolecular complexes of compound **2** with polyauramacrocycles, *viz.*, $[Au(\mu\text{-}C(2),N(3)\text{-}bzim)]_3$ (**39**) (bzim is 1-benzylimidazolate) and $[AuC(R)=N(Ar)]_3$ (**40**) (R = EtO; Ar = $p\text{-}MeC_6H_4$), containing three $Au^I$ atoms in the planar nine-membered rings were also de-



**39**



**40**

scribed.[39,40] In these macrocycles, the electron-rich Au atoms serve as the basic centers.

It appeared that the addition of a solution of compound **39** or **40** in $CH_2Cl_2$ to a solution of macrocycle **2** in the same solvent leads to rapid precipitation of white powders of adducts **2**·**39** and **2**·**40** with 1 : 1 composition. However, recrystallization of these adducts from an acetone—hexane mixture results in their transformation into complexes with another composition, *viz.*, **2**·[**39**]$_2$ (**41**) and **2**·[**40**]$_2$ (**42**), respectively, which contain two molecules of the polyauramacrocycle per molecule of the mercury anticrown. According to the X-ray diffraction data,[39] macrocycle **2** in these complexes is located between the planes of two metallacycles **39** or **40**, *i.e.*, these compounds have sandwich structures. In the crystals, both complexes (**41** and **42**) form stacks through intermolecular aurophilic Au···Au interactions. Dissolution of complex **41** in THF is accompanied by its partial dissociation giving rise to the above-mentioned 1 : 1 adduct.[40] Solutions of complex **42** in THF contain only 1 : 1 adducts in a mixture with free macrocycles **2** and **40**.

Crystals of complexes **41** and **42** exhibit luminescence properties both at ambient and cryogenic temperatures, the intensity of their luminescence being much higher than that of the starting macrocycles.[39]

## Catalytic properties of perfluorinated polymercuramacrocycles

There are at least two types of reactions in which anticrowns could be successfully used as catalysts. The first type involves reactions catalyzed or promoted by ordinary monodentate Lewis acids. The use of anticrowns in such reactions could lead to an additional increase in the reaction rate due to the cooperative effect of several Lewis acidic centers.

Taking into account the ability of anticrowns to give lipophilic anionic species due to the complex formation with anions, one would expect that these compounds will efficiently transfer various organic and inorganic cations from an aqueous to an organic phase. Consequently, yet another area of synthetic organic chemistry in which anticrowns could be useful is the phase transfer catalysis of electrophilic reactions.

The first example of the successful application of anticrowns in phase transfer catalysis was reported in 1989[9] when it was shown that nonfluorinated polymercuramacrocycle **1** can catalyze the azo-coupling reaction of phenyldiazonium halides $PhN_2^+X^-$ (X = Cl or Br) with β-naphthol in a two-phase $H_2O$—$CH_2Br_2$ system at 20 °C. Under the optimum conditions, the yield of 1-phenylazo-2-naphthol in the presence of compound **1** after 5.5 h varied in the range of 35—50% with respect to β-naphthol ($[\mathbf{1}]_0$ = 0.013 mol $L^{-1}$, $[\beta\text{-naphthol}]_0$ = 0.039 mol $L^{-1}$, $[PhN_2X]_0$ = 0.17 mol $L^{-1}$). In the absence of the catalyst, the yield of the azo compound was no higher than 9—10%. Mercuric chloride appeared to be inactive in this reaction.

**Table 3.** Catalytic activity of macrocycles **1—3** in phase transfer catalysis of azo-coupling of β-naphthol with phenyldiazonium salts $PhN_2^+X^-$

| Catalyst | $X^-$ in $PhN_2^+X^-$ | Time/h | Yield (%) |
|---|---|---|---|
| — | $Cl^-$ | 3.5 | 15 |
| **3** | $Cl^-$ | 2.0 | 68 |
| **3** | $Cl^-$ | 3.5 | 96 |
| **2** | $Cl^-$ | 3.5 | 54 |
| $(C_6F_5)_2Hg$ | $Cl^-$ | 3.5 | 23 |
| $HgCl_2$ | $Cl^-$ | 3.5 | 16 |
| **1** | $Cl^-$ | 3.5 | 25 |
| — | $HSO_4^-$ | 5.5 | 0 |
| **3** | $HSO_4^-$ | 5.5 | 3 |
| **2** | $HSO_4^-$ | 5.5 | 0 |

*Note.* The aqueous phase: a 0.7 *M* $PhN_2X$ solution in water (1 mL). The organic phase: a 0.1 *M* solution of β-naphthol in a 100 : 15 benzene—nitrobenzene mixture (1.2 mL). The amount of the catalyst is 0.012 mmol, 20 °C.

Considerably greater catalytic accelerations of the azo-coupling reaction were observed in the presence of perfluorinated polymercuramacrocycles **2** and **3** as phase transfer catalysts (Table 3).* In these experiments, a 0.1 *M* solution of β-naphthol in a benzene—nitrobenzene mixture (100 : 11) was used as the organic phase, and a 0.7 *M* phenyldiazonium chloride or phenyldiazonium bisulfate solution served as the aqueous phase. As can be seen from Table 3, the highest efficiency in catalysis of azo-coupling is displayed by macrocycle **3**. In the presence of this macrocycle, the reaction of phenyldiazonium chloride with β-naphthol affords the azo product in virtually quantitative yield after 3.5 h. In the absence of the catalyst, the yield of the azo compound was only 15% under the same conditions. Perfluorinated macrocycle **2** is less active than its pentamercury analog **3**, whereas nonfluorinated compound **1** exhibits negligibly low activity. The use of perfluorodiphenylmercury $(C_6F_5)_2Hg$ instead of macrocycle **2** also leads to a substantial decrease in the reaction rate. Mercuric chloride was again inactive.

It should be noted that if phenyldiazonium bisulfate is used instead of phenyldiazonium chloride in the reaction with β-naphthol, macrocycle **2** completely loses its ability to catalyze the azo-coupling reaction, and if the reaction is carried out in the presence of macrocycle **3** at 20 °C, only traces of the azo product are produced even after 5.5 h (see Table 3). Apparently, this is associated with either the fact that bisulfate anions, unlike chloride anions, cannot efficiently be coordinated to the Hg atoms of

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* I. A. Tikhonova, V. S. Lenenko, A. P. Zaraisky, G. G. Furin, A. Yu. Volkonsky, and V. B. Shur, the data will be published elsewhere.

the macrocycles or with the fact that their complexes with the macrocycles are insufficiently lipophilic to provide the efficient transfer of the phenyldiazonium cation through the interface.

The particularly strong catalytic effects of perfluorinated polymercuramacrocycles were observed in the aromatic nitration reaction with dilute nitric acid in the presence of sodium nitrite as an initiator.[42,43] This well-known reaction is often used for the preparative synthesis of nitro derivatives of arylamines, phenols, and other highly active aromatic substrates. Generally, it is assumed that the nitration proceeds through a step of nitrosation of an aromatic compound followed by oxidation of the resulting nitroso derivative with nitric acid.[44]

$$\mathrm{ArH + HNO_2 \longrightarrow ArNO + H_2O}$$

$$\mathrm{ArNO + HNO_3 \longrightarrow ArNO_2 + HNO_2}$$

The nitrosonium cation ($NO^+$), protonated nitrous acid ($H_2NO_2^+$), and some other species can serve here as nitrosating agents.[44] In homogeneous media, nitration generally proceeds rather smoothly. However, in the case of solid aromatic compounds poorly soluble in water, one would have to use organic solvents and perform nitration in a two-phase system. Under these conditions, it is reasonable to use phase transfer catalysts (see, for example, Ref. 45).

In the first experiments on phase transfer catalysis of this reaction by anticrowns, acenaphthene was subjected to nitration in the presence of macrocycle **2** as the catalyst and sodium chloride as the promoter. A 0.5 *M* acenaphthene solution in a benzene—nitrobenzene mixture (100 : 15) was used as the organic phase, and 21.3% nitric acid containing $NaNO_2$ (0.13 mol $L^{-1}$) and NaCl (0.51 mol $L^{-1}$) served as the aqueous-acidic component of the system. The reaction was carried out at 21 °C with vigorous stirring.

The results of these experiments showed that nitration in the absence of a catalyst proceeds very slowly and acenaphthene remains virtually unconsumed (~99%) within 3 h. However, the starting aromatic substrate rapidly disappears upon the addition of macrocycle **2** (31 mg) to the system, and, after 40 min, the reaction mixture contains only traces of acenaphthene. As a result of the reaction, 5-nitro- and 3-nitroacenaphthenes in a ratio of (90—93) : (10—7) are formed in virtually quantitative yield (>95%).[42] According to the kinetic data, the addition of macrocycle **2** increases the initial rate of nitration of acenaphthene by more than three orders of magnitude.

The use of benzene instead of a benzene—nitrobenzene mixture as the organic phase leads to a decrease in the reaction rate due, apparently, to poor solubility of the mercury anticrown in benzene. Under such conditions, nitroacenaphthenes are obtained in 55% yield after 1 h, and it is necessary to carry out the reaction for 2.5—3 h to achieve the quantitative conversion of acenaphthene into the nitro products. It should be noted that the starting macrocycle is rather stable under the nitration conditions, and it can be recovered in 95% yield upon stirring with a mixture of benzene and 21.3% $HNO_3$ in the presence of $NaNO_2$ and NaCl for 1 h.

The chloride anions play an important role in nitration, like in the above-considered phase-transfer azo-coupling reaction. In the absence of chloride ions, macrocycle **2** does not exhibit activity in this process. Presumably, either nitrate anions, like bisulfate anions, do not form complexes with macrocycle **2** or these complexes are insufficiently lipophilic. Mercuric chloride and perfluorodiphenylmercury $(C_6F_5)_2Hg$, unlike compound **2**, do not catalyze aromatic nitration even in the presence of chloride ions.

Subsequently, it was found that not only acenaphthene but also some other aromatic substrates, such as 2-methylnaphthalene, 1,3- and 2,6-dimethylnaphthalenes, anthracene, and pyrene, can be involved in phase-transfer nitration under the action of macrocycle **2**.* Here, additives of the macrocycle also have a very strong accelerating effect.

Macrocycle **3** also exhibits[43] high catalytic activity in phase-transfer nitration with 21.3% nitric acid at 21 °C. This reaction is also initiated by nitrite and is accelerated in the presence of NaCl. Under the optimum conditions, the rate of the process is very high. For example, the addition of compound **3** (8 mg) to a system containing a 0.23 *M* acenaphthene solution in a benzene—nitrobenzene mixture (100 : 8.4) as the organic phase leads to the quantitative conversion of the aromatic substrate into 5-nitro- and 3-nitroacenaphthenes already within 10 min. According to the kinetic measurements, the initial rate of nitration of acenaphthene increases by a factor of 3300 in the presence of macrocycle **3**.

Since it is believed (see above) that nitrite-initiated nitration with dilute nitric acid proceeds through the intermediate formation of nitroso derivatives, it was attempted to perform phase-transfer nitrosation of aromatic substrates (naphthalene, acenaphthene, 1,3- and 2,6-dimethylnaphthalenes, phenanthrene, pyrene) under the action of sodium nitrite and sulfuric acid in the presence of perfluorinated polymercuramacrocycles as catalysts and NaCl. However, these reactions unexpectedly afforded only the corresponding nitro products, whereas nitroso derivatives were not obtained.[46] The reaction proceeds according to the following stoichiometric equation:

$$\mathrm{ArH + 3\,HNO_2 \longrightarrow ArNO_2 + 2\,NO + 2\,H_2O.}$$

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* A. P. Zaraisky, O. I. Kachurin, L. I. Velichko, I. A. Tikhonova, G. G. Furin, and V. B. Shur, the data will be published elsewhere.

The highest rate of this unusual nitration reaction with nitrous acid is observed for pyrene, which is quantitatively transformed into 1-nitropropene ($[\text{pyrene}]_0$ = 0.092 mol $L^{-1}$, $NaNO_2$ : pyrene = 4 : 1, 25.6% $H_2SO_4$, a mixture of benzene and nitrobenzene as the organic phase) in the presence of macrocycle **2** already after 9 min at 21 °C in a closed system under dinitrogen. In the absence of the catalyst, nitration does not occur within at least 4 h.

Perfluorinated polymercuramacrocycles also proved to be catalytically active in the proton transfer from an aqueous to an organic phase.[42,43] The proton transfer process can easily be monitored by adding triphenylcarbinol as an indicator to the organic phase. It is known that this colorless compound is rapidly transformed into the yellow triphenylmethyl cation in the presence of sufficiently strong acids:

$$Ph_3COH + H^+ \rightleftharpoons Ph_3C^+ + H_2O.$$

Using this indicator method, it was demonstrated that macrocycle **2** can catalyze the proton transfer to the benzene phase from aqueous solutions of mineral acids in the presence of chloride anions. It was found that macrocycle **3** can also perform the interphase proton transfer. These results open the way to the use of this type of macrocycles in phase transfer catalysis of reactions catalyzed by protic acids.

## Conclusion

Research into the coordination chemistry of perfluorinated polymercuramacrocycles revealed their ability to efficiently bind various anions giving rise to complexes with unique structures. In these complexes, the anionic species is simultaneously coordinated to all Lewis centers of the macrocycle, which resembles the behavior of crown ethers and their analogs in the metal-cation binding. Various neutral Lewis bases, such as nitriles, carbonyl compounds, aromatic hydrocarbons, *etc.*, also can be cooperatively bound by all Hg atoms of the anticrown molecule.

The complex formation with the macrocycle leads to substantial changes in the spectroscopic characteristics of both the mercury anticrown and the starting Lewis base. These spectroscopic changes as well as stability of the resulting complexes increase with increasing strength of Lewis base. The involvement of carbonyl compounds and nitriles in the coordination sphere of the macrocycle is accompanied by a weakening of the $C=O$ and $C\equiv N$ bonds, which is of interest for organic synthesis and catalysis.

The size of the cavity formed by the Hg and C atoms in macrocycle **3** and, particularly, in macrocycle **2** is rather small. Therefore, the atom of Lewis base involved in coordination is, generally, located outside this cavity giving rise to unusual pyramidal (half-sandwich), bipyramidal, and sandwich structures or fragments. Similar structures are realized also in complexes of crown ethers with metal cations if the size of the cation is substantially larger than the cavity size of the crown compound. However, in the above-considered complex of macrocycle **3** with the sulfate anion, one of the O atoms of the $SO_4^{2-}$ ion lies nearly in the plane of the ten-membered mercuracarbon ring, *i.e.*, virtually in the plane of the anticrown molecule. According to the results of quantum-chemical calculations (see above), the hypothetical complex of macrocycle **3** with the small fluoride anion should have an analogous structure

The use of perfluorinated polymercuramacrocycles holds promise for the organic synthesis, as illustrated by their high activity in phase transfer catalysis of electrophilic reactions. It was also found that perfluorinated polymercuramacrocycles can perform the proton transfer from an aqueous to an organic phase. The presence of chloride anions in the mixture is of importance in all these reactions. Apparently, the role of chloride anions is to form a lipophilic anionic complex with anticrown thus facilitating the interphase transfer of a cationic electrophile. One would expect that further investigations of the catalytic and complexing properties of perfluorinated polymercuramacrocycles will lead to the successful use of these remarkable compounds in various fields of chemistry.

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