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Coordination chemistry of polymercuramacrocycles. Complexation of cyclic trimeric perfluoro-*o*-phenylenemercury with neutral oxygeneous Lewis bases

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Abstract

Cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**I**) readily reacts with *N*,*N*-dimethylformamide and hexamethylphosphoramide to form complexes $\{[(o\text{-}C_6F_4Hg)_3](HCONMe_2)_2\}$ (**II**) and $\{[(o\text{-}C_6F_4Hg)_3][(Me_2N)_3PO]_2\}$ (**III**), respectively, which contain two amide ligands per one macrocycle molecule. An X-ray diffraction study of **II** and **III** has shown that they have bipyramidal structures wherein the molecules of an amide are located above and below the metallacycle plane and each of them is simultaneously bonded via the oxygen atom to all Hg atoms of the cycle. The reaction of **I** with dimethylsulfoxide affords complex $\{[(o\text{-}C_6F_4Hg)_3](Me_2SO)_3\}$ (**VI**) containing three Lewis basic species per molecule of **I**. According to X-ray diffraction data, two of three dimethylsulfoxide ligands in **VI** are also coordinated through the oxygen atom with all mercury centres of the macrocycle, forming a bipyramidal structure, while the third sulfoxide ligand is bonded only to one Hg atom of the cycle. The complex of similar composition and structure, $\{[(o\text{-}C_6F_4Hg)_3](MeCOOEt)_3\}$ (**IV**), is produced in the interaction of **I** with ethyl acetate but this complex is much less stable than **VI**. The latter correlates with a considerably lower Lewis basicity of ethyl acetate as compared to that of dimethylsulfoxide. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymercuramacrocycles; Neutral oxygeneous Lewis bases; Complexes; X-ray structure analysis; IR spectra; NMR spectra

1. Introduction

Coordination chemistry of polymercuramacrocycles has attracted increasing attention in the past decade due to their ability to bind effectively various anions and neutral Lewis bases with the formation of complexes wherein the Lewis basic species is simultaneously coordinated to all Hg centres of the macrocycle. Such an unusual type of bonding, being realized in a charge-reversed variant in host–guest complexes of crown ethers and their thia and aza analogues with metal cations, opens new promising prospects to the areas of molecular recognition, ion transport and catalysis. The first reports on complexing properties of polymercuramacrocycles emerged in 1989–91 [1–3]. Subsequently, a considerable amount of information on different aspects of the chemistry of these remarkable reagents has been accumulated (for recent studies, see Refs. [4–7]).

The ability of polymercury-containing macrocycles to form lipophilic anionic species in the interaction with anions allows the use of these mercuracycles as phase transfer catalysts for electrophilic reactions [1a,4d,8]. Another interesting aspect of practical application of polymercuramacrocycles is the activation of carbonyl and nitrile groups due to cooperative binding of their Lewis basic oxygen and nitrogen atoms by all Lewis acidic centres of the cycle. By the present time, the first indications on the possibility of complexation of polymercuramacrocycles with carbonyl compounds and

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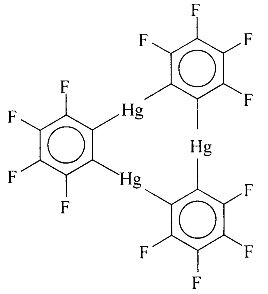
nitriles have been obtained [4b,6,9]. Recently, the accelerating effect of such macrocycles on the Diels–Alder reaction of a thionoester with cyclopentadiene has been reported [5f].

As part of our continuing research programme aimed at the development of new type of anion receptors and catalysts, we have previously described (see Refs. [4a,4b,4c] and the papers cited therein) the anion binding properties of cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**I**) [10] which contains three Hg atoms in a planar nine-membered cycle. The complexation of **I** with nitriles has also been studied and it has been shown that the composition and structure of the resulting complexes are dramatically dependent on the nature of a nitrile used [4b].



(**I**)

In the present paper, we wish to report the synthesis, spectral characterization and structures of the complexes of macrocycle **I** with carbonyl compounds such as ethyl acetate and *N*,*N*-dimethylformamide (DMF). The carbonyl C–O bonds in these complexes are notably weakened indeed as a result of the coordination with the mercury atoms. The complexes of **I** with hexamethylphosphoramide (HMPA) and dimethylsulfoxide (DMSO) are also reported.

2. Results and discussion

The complexes of macrocycle **I** with DMF, HMPA, ethyl acetate and DMSO can be readily prepared under conditions of recrystallization of **I** from the above Lewis bases as solvents. The isolated complexes are colourless crystalline solids stable to air. The structure of the complexes has been established by analytical and spectral means as well as by an X-ray single crystal diffraction study.

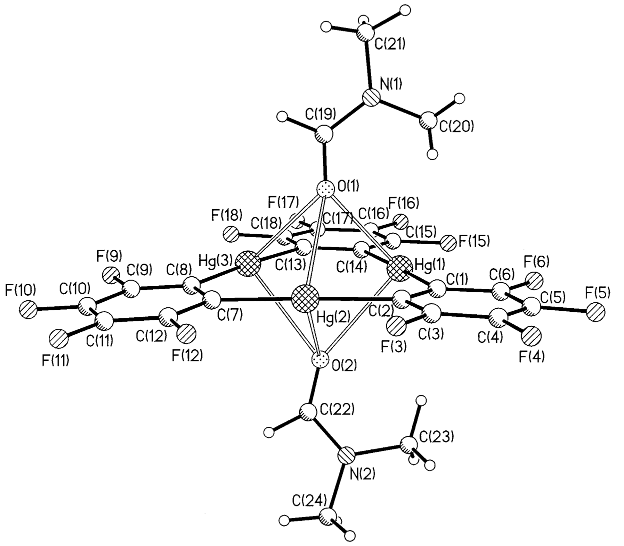


Fig. 1. Molecular structure of complex **II** in the crystal.

According to elemental analysis, the complex of **I** with DMF can be formulated as $\{[(o\text{-}C_6F_4Hg)_3](HCONMe_2)_2\}$ (**II**), i.e. contains two amide ligands per one macrocycle molecule. The complex has a bipyramidal structure wherein the molecules of DMF are located above and below the metallacycle plane and each of them is simultaneously bonded via the oxygen atom to all Hg centres of the cycle (Fig. 1). The Hg–O distances in **II** span the range of 2.799–3.024(5) Å (av. 2.87 Å; see Table 1). All these distances are considerably shorter than the sum of the van der Waals radii of Hg and O atoms (2.1 + 1.5 = 3.6 Å [11]). As a result of the coordination with the mercury atoms, the C–O bonds of the DMF ligands become slightly longer (C(19)–O(1) 1.241(8), C(22)–O(2) 1.239(9) Å), while the N–C(O) bonds become slightly shorter (N(1)–C(19) 1.334(8), N(2)–C(22) 1.330(9) Å) than the corresponding dis-

Table 1
Selected geometrical parameters for complex **II**

Bond lengths (Å)			
Hg(1)–O(l)	2.814(5)	C(1)–C(2)	1.403(10)
Hg(2)–O(1)	2.865(5)	C(7)–C(8)	1.393(10)
Hg(3)–O(1)	3.024(5)	C(13)–C(14)	1.424(9)
Hg(1)–O(2)	2.799(5)	C(19)–O(1)	1.241(8)
Hg(2)–O(2)	2.828(5)	N(1)–C(19)	1.334(8)
Hg(3)–O(2)	2.888(5)	N(1)–C(21)	1.450(9)
Hg(1)–C(14)	2.081(7)	N(1)–C(20)	1.464(8)
Hg(1)–C(1)	2.088(8)	C(22)–O(2)	1.239(9)
Hg(2)–C(7)	2.075(7)	N(2)–C(22)	1.330(9)
Hg(2)–C(2)	2.087(6)	N(2)–C(24)	1.451(9)
Hg(3)–C(8)	2.073(6)	N(2)–C(23)	1.460(10)
Hg(3)–C(13)	2.084(7)		
Bond angles (°)			
C(14)–Hg(1)–C(1)	176.8(3)	C(19)–N(1)–C(21)	121.6(5)
C(7)–Hg(2)–C(2)	176.3(3)	C(19)–N(1)–C(20)	120.6(6)
C(8)–Hg(3)–C(13)	176.7(3)	C(21)–N(1)–C(20)	116.9(6)
C(2)–C(1)–Hg(1)	122.8(5)	O(1)–C(19)–N(1)	124.4(6)
C(1)–C(2)–Hg(2)	120.2(5)	C(22)–N(2)–C(24)	121.1(6)
C(8)–C(7)–Hg(2)	121.4(5)	C(22)–N(2)–C(23)	122.2(6)
C(7)–C(8)–Hg(3)	122.1(5)	C(24)–N(2)–C(23)	116.7(6)
C(14)–C(13)–Hg(3)	120.2(5)	O(2)–C(22)–N(2)	125.4(6)
C(13)–C(14)–Hg(1)	121.6(5)		
Torsion angles (°)			
Hg(1)–C(1)–C(2)–Hg(2)	3.7(8)	Hg(3)–C(13)–C(14)–Hg(1)	−1.0(7)
Hg(2)–C(7)–C(8)–Hg(3)	0.3(8)		

tances (1.22 and 1.35 Å) in free tertiary amides [6b]. In the IR spectrum of **II** (in Nujol mull), the ν_{CO} band (1646 cm^{-1}) is shifted by 29 cm^{-1} to a low-frequency region relatively to the corresponding band (1675 cm^{-1}) in the spectrum of non-coordinated DMF. All these data indicate on a noticeable weakening of the C–O bond in both amide ligands due to their complexation with the macrocycle.

The room temperature ^{199}Hg-NMR spectrum of **II** in THF ($[\mathbf{II}]_o = 8 \times 10^{-2}$ M) exhibits triplet of triplets of triplets at −305.6 ppm (Table 2) shifted by 12.3 ppm downfield relatively to the analogous signal of free **I**. Such a splitting pattern could arise due to coupling of the ^{199}Hg nucleus (natural abundance 16.84%) with the *o*-fluorine atoms of two adjacent C_6F_4 moieties ($^3J_{Hg-F}$), one of two pairs of the *m*-fluorine atoms of the same moieties ($^4J_{Hg-F}$) and, at last, either with other pair of the *m*-fluorine atoms ($^4J_{Hg-F}$) or with two *p*-fluorine atoms ($^5J_{Hg-F}$). The forth ^{199}Hg–^{19}F triplet splitting whose appearance could be expected here is not manifested in the spectrum because of, apparently, very small value of the corresponding coupling constant and insufficient resolution.

An interesting structural feature of complex **II** is a considerable deviation (by 24.6°) of the C(22)–O(2) bond vector from the perpendicular to the mean plane of the central nine-membered ring of **I**. By contrast, the C(19)–O(1) vector in **II** is practically normal to this plane (the corresponding angle is 88.7°). In the previously described bipyramidal complex of macrocycle $[(o\text{-}C_6Me_4HgO(H)Hg)_2]^{2+}$ with two molecules of diethylformamide [6b], both C–O bonds deviate from the perpendicular to the plane of the central 10-membered cycle by ca. 17°. The ability of macrocyclic multidentate Lewis acids to form bipyramidal structures with Lewis bases has been demonstrated for the first time in Ref. [12] on the example of the complexes of macrocycle $[(CF_3)_2CHg]_5$ with halide anions. Similar bipyramidal structure has been established recently for the complex of **I** with acetonitrile [4b]. However, this complex is much less stable than **II** because of considerably lower Lewis basicity of nitriles as compared to that of DMF [13].

Table 2
^{199}Hg-NMR data for **I**–**III** and **VI** in THF [a]

Compound	δ (ppm) [b]	Coupling constants (Hz)		
		$^3J_{Hg-F}$	$^4J_{Hg-F}$	$^{4(5)}J_{Hg-F}$
I	−317.9	446	125	27
II	−305.6	467	132	22
III	−282.4	510	144	29
VI	−287.4	515	144	38

[a] The initial concentration of **I**–**III** and **VI** in THF is 8×10^{-2} M.
[b] Relatively to Ph_2Hg as an external standard.

As in free DMF, all atoms of each of the DMF ligands in **II** (excluding the hydrogen atoms of the methyl groups) are disposed approximately in one and the same plane. One of these planes, O(1)C(19)N(1)C(20)C(21), is again nearly perpendicular to the plane of the central nine-membered cycle of **II** (the dihedral angle is 87.4°) while the other one, O(2)C(22)N(2)C(23)C(24), significantly deviates from the normal to this plane (the dihedral angle is 71.0°). Thus, the DMF ligands in complex **II** noticeably differ from each other in their orientation towards the mercury-containing macrocycle.

The reaction of **I** with HMPA gives also complex, $\{[(o\text{-}C_6F_4Hg)_3][(Me_2N)_3PO]_2\}$ (**III**), which contains two Lewis basic species per one macrocycle molecule. The complex has an analogous bipyramidal structure, with the molecules of HMPA being coordinated via the oxygen atom to all Lewis acidic centres of **I** (see Fig. 2). The Hg–O distances in **III** vary within the range of 2.824–2.895(4) Å (av. 2.85 Å; see Table 3) and are close to those in **II**. The coordinated P(1)–O(1) bond (1.477(4) Å) of one of the HMPA ligands in **III** is slightly elongated as compared to the average P–O distance (1.46 Å [14]) in free hexaalkylphosphoramides. The angle (83.6°) between the P(1)–O(1) bond vector and the mean plane of the central nine-membered cycle of **I** is close to 90°. The $P(NMe_2)_3$ moiety in the other HMPA ligand in **III** is disordered over two positions with non-equivalent occupancies (0.7/0.3). In Fig. 2, only more occupied position is shown for this ligand. The P(2)–O(2) distance is equal to 1.494(4) Å and the P(2)–O(2) bond vector deviates from the perpendicular to the mean plane of the central nine-membered cycle of **I** by 17.6°.

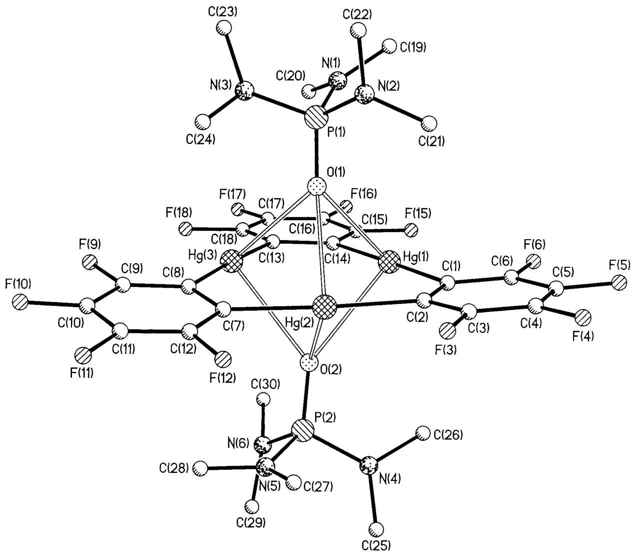


Fig. 2. Molecular structure of complex **III** in the crystal. The hydrogen atoms of methyl groups are omitted for clarity.

Table 3
Selected geometrical parameters for complex **III**

Bond lengths (Å)			
Hg(1)–O(1)	2.882(4)	C(1)–C(2)	1.416(7)
Hg(2)–O(1)	2.848(3)	C(7)–C(8)	1.394(7)
Hg(3)–O(1)	2.830(4)	C(13)–C(14)	1.402(7)
Hg(1)–O(2)	2.895(4)	P(1)–O(1)	1.477(4)
Hg(2)–O(2)	2.835(4)	P(1)–N(1)	1.616(5)
Hg(3)–O(2)	2.824(4)	P(1)–N(2)	1.637(5)
Hg(1)–C(1)	2.069(5)	P(1)–N(3)	1.637(5)
Hg(1)–C(14)	2.091(5)	P(2)–O(2)	1.494(4)
Hg(2)–C(2)	2.080(5)	P(2)–N(5)	1.636(8)
Hg(2)–C(7)	2.091(5)	P(2)–N(6)	1.641(8)
Hg(3)–C(8)	2.066(6)	P(2)–N(4)	1.651(12)
Hg(3)–C(13)	2.066(5)		
Bond angles (°)			
C(1)–Hg(1)–C(14)	178.0(2)	O(1)–P(1)–N(3)	111.3(2)
C(2)–Hg(2)–C(7)	177.2(2)	N(1)–P(1)–N(2)	107.3(3)
C(8)–Hg(3)–C(13)	177.1(2)	N(1)–P(1)–N(3)	105.0(3)
C(2)–C(1)–Hg(1)	121.3(4)	N(3)–P(1)–N(2)	108.3(3)
C(1)–C(2)–Hg(2)	120.2(4)	O(2)–P(2)–N(4)	112.0(5)
C(8)–C(7)–Hg(2)	120.0(4)	O(2)–P(2)–N(5)	117.1(3)
C(7)–C(8)–Hg(3)	122.1(4)	O(2)–P(2)–N(6)	108.3(4)
C(14)–C(13)–Hg(3)	120.8(4)	N(5)–P(2)–N(4)	98.1(5)
C(13)–C(14)–Hg(1)	120.9(4)	N(6)–P(2)–N(4)	117.9(5)
O(1)–P(1)–N(1)	114.2(3)	N(5)–P(2)–N(6)	103.3(5)
O(1)–P(1)–N(2)	110.4(2)		
Torsion angles (°)			
Hg(1)–C(1)–C(2)–Hg(2)	1.9(6)	Hg(3)–C(13)–C(14)–Hg(1)	−2.2(6)
Hg(2)–C(7)–C(8)–Hg(3)	6.5(7)		

Table 4
Selected geometrical parameters for complex **IV**

Bond lengths (Å)			
Hg(1)–O(1)	2.898(5)	C(1)–C(2)	1.406(9)
Hg(2)–O(1)	2.963(5)	C(7)–C(8)	1.425(10)
Hg(3)–O(1)	2.879(5)	C(13)–C(14)	1.425(10)
Hg(1)–O(3)	2.975(5)	C(19)–O(1)	1.204(8)
Hg(2)–O(3)	2.884(5)	C(19)–O(2)	1.340(8)
Hg(3)–O(3)	2.848(5)	C(21)–O(2)	1.448(8)
Hg(1)–O(5)	2.881(6)	C(23)–O(3)	1.218(8)
Hg(1)–C(1)	2.075(6)	C(23)–O(4)	1.325(8)
Hg(1)–C(14)	2.079(6)	C(25)–O(4)	1.478(10)
Hg(2)–C(7)	2.060(8)	C(27)–O(5)	1.207(9)
Hg(2)–C(2)	2.080(7)	C(27)–O(6)	1.327(9)
Hg(3)–C(13)	2.076(7)	C(29)–O(6)	1.457(10)
Hg(3)–C(8)	2.077(7)		
Bond angles (°)			
C(1)–Hg(1)–C(14)	176.7(3)	O(1)–C(19)–C(20)	125.7(6)
C(7)–Hg(2)–C(2)	175.5(3)	O(2)–C(19)–C(20)	111.4(6)
C(13)–Hg(3)–C(8)	176.5(3)	C(23)–O(4)–C(25)	114.6(6)
C(2)–C(1)–Hg(1)	123.0(5)	O(3)–C(23)–O(4)	123.4(7)
C(1)–C(2)–Hg(2)	120.9(5)	O(3)–C(23)–C(24)	123.1(6)
C(8)–C(7)–Hg(2)	123.2(5)	O(4)–C(23)–C(24)	113.5(6)
C(7)–C(8)–Hg(3)	120.9(5)	C(27)–O(6)–C(29)	116.5(6)
C(14)–C(13)–Hg(3)	122.0(5)	O(5)–C(27)–O(6)	123.0(8)
C(13)–C(14)–Hg(1)	120.9(5)	O(5)–C(27)–C(28)	124.4(8)
C(19)–O(2)–C(21)	115.5(5)	O(6)–C(27)–C(28)	112.6(6)
O(1)–C(19)–O(2)	122.9(6)		
Torsion angles (°)			
Hg(1)–C(1)–C(2)–Hg(2)	1.5(8)	Hg(3)–C(13)–C(14)–Hg(1)	3.1(8)
Hg(2)–C(7)–C(8)–Hg(3)	1.0(8)		

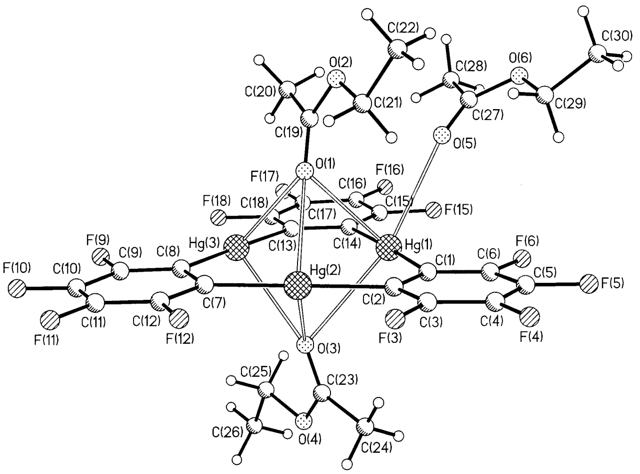


Fig. 3. Molecular structure of complex **IV** in the crystal.

The IR spectrum of **III** (Nujol mull) shows the ν_{PO} band at 1138 cm^{-1}, which is shifted by 71 cm^{-1} to lower wavenumbers in comparison to free HMPA ($\nu_{PO} = 1209$ cm^{-1}). The room temperature ^{199}Hg-NMR spectrum of **III** in THF ($[\mathbf{III}]_o = 8 \times 10^{-2}$ M) like that of **II** is also characterized by a triplet of triplets of triplets (Table 2) but the value of the downfield shift of this ^{199}Hg multiplet relatively to the analogous signal of non-coordinated **I** is considerably greater (35.5 ppm) than in the case of **II**, which is in a good accord with a higher Lewis basicity of HMPA compared to DMF [13]. The room temperature ^{31}P-NMR spectrum of **III** in THF ($[\mathbf{III}]_o = 8 \times 10^{-2}$ M) exhibits a sharp singlet at 27.94 ppm shifted by 3.26 ppm downfield as compared to free HMPA.

Unlike the reactions with DMF and HMPA, the interaction of macrocycle **I** with ethyl acetate affords complex $\{[(o\text{-}C_6F_4Hg)_3](MeCOOEt)_3\}$ (**IV**) containing three Lewis basic species per one molecule of **I**. As seen from Fig. 3, two of them (like the amide ligands in **II** and **III**) are arranged above and below the metallacycle plane and each of these is coordinated through the carbonyl oxygen atom with all Hg centres of the macrocycle. The third ester ligand in **IV** is bonded only to one mercury atom of **I**, viz. Hg(1), and because this Hg(1) atom is involved additionally in the bonding to two other ethyl acetate ligands its coordination number becomes equal to five.

The complex of similar composition, $\{[(o\text{-}C_6F_4Hg)_3](PhCN)_3\}$, has been isolated previously from the interaction of **I** with benzonitrile [4b] but in this complex, in contrast to **IV**, all three Lewis basic species are located on one side of the metallacycle plane.

The Hg–O distances in **IV** are close to each other (2.848–2.975 Å; av. 2.90 Å; see Table 4) and again are significantly shorter than the corresponding van der Waals distance (3.6 Å). But the C–O bond lengths of the carbonyl group of the ethyl acetate ligands (C(19)–O(1) 1.204(8), C(23)–O(3) 1.218(8), C(27)–O(5) 1.207(9) Å) change only insignificantly as a result of the coordination with the macrocycle (the average value of the carbonyl C–O bond distance for aliphatic esters is 1.196 Å [14]).

Unlike **II**, in complex **IV** the vectors of both carbonyl C–O bonds of the bipyramidal fragment deviate considerably from the perpendicular to the plane of the central nine-membered ring (by 24.2° for the C(19)–O(1) vector and by 18.5° for the C(23)–O(3) vector). The angle between the C(27)–O(5) vector and the mean plane of the nine-membered cycle of **I** is 34.0°. The O(3)–Hg(1)–O(5) and Hg(1)–O(5)–C(27) bond angles are equal to 156.7 and 141.2°, respectively. The coordination of the ethyl acetate molecules with **I** does not affect essentially their geometry.

Complex **IV** is less stable than **II** and **III**: on drying in vacuum at room temperature it loses two coordinated ethyl acetate molecules to afford monoester complex $\{[(o\text{-}C_6F_4Hg)_3](MeCOOEt)\}$ (**V**). The ν_{CO} band (1678 cm^{-1}) in the IR spectrum of **V** (Nujol mull) is shifted by 64 cm^{-1} to a low-frequency region relatively to the ν_{CO} band of free ethyl acetate (1742 cm^{-1}). However, the ^{199}Hg-NMR spectrum of **V** in THF at 20 °C ($[\mathbf{V}]_o = 8 \times 10^{-2}$ M) exhibits only negligible differences from the spectrum of starting macrocycle **I**, thus indicating on the displacement of the ethyl acetate ligand from complex **V** by the molecules of the solvent. The latter is not surprising if one takes into account a considerably lower Lewis basicity of ethyl acetate as compared to THF [13] as well as very large excess of THF (ca. 150:1) with respect to the ester complex. In accordance with this, the addition of an excess of ethyl acetate to a solution of **V** in THF causes a pronounced downfield shift of the ^{199}Hg-NMR resonance relatively to that of starting **I** (e.g. by 4.3 ppm at the MeCOOEt:**V** molar ratio of 40:1). Thus, the ^{199}Hg-NMR data show that

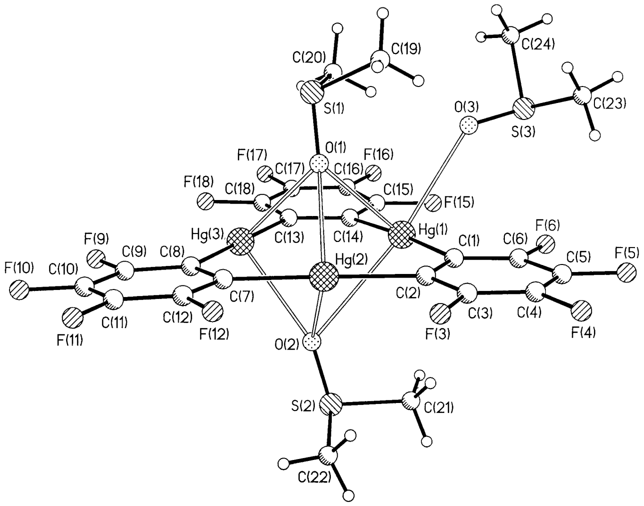


Fig. 4. Molecular structure of complex **VI** in the crystal.

Table 5
Selected geometrical parameters for complexes **VIA/VIB**

Bond lengths (Å)			
Hg(1)–O(1)	2.778(5)/2.783(5)	C(1)–C(2)	1.409(9)/1.400(9)
Hg(2)–O(1)	2.818(4)/2.793(5)	C(7)–C(8)	1.411(9)/1.398(10)
Hg(3)–O(1)	2.786(4)/2.808(5)	C(13)–C(14)	1.417(9)/1.435(9)
Hg(1)–O(2)	3.120(5)/2.947(4)	S(1)–O(1)	1.519(5)/1.515(5)
Hg(2)–O(2)	2.836(5)/2.842(6)	S(1)–C(20)	1.783(6)/1.763(7)
Hg(3)–O(2)	2.759(5)/2.823(5)	S(1)–C(19)	1.786(7)/1.781(7)
Hg(1)–O(3)	2.819(5)/2.991(6)	S(2)–O(2)	1.502(5)/1.503(5)
Hg(1)–C(1)	2.087(7)/2.102(7)	S(2)–C(21)	1.783(7)/1.791(7)
Hg(1)–C(14)	2.096(7)/2.077(7)	S(2)–C(22)	1.796(8)/1.786(7)
Hg(2)–C(7)	2.071(7)/2.086(7)	S(3)–O(3)	1.471(5)/1.499(6)
Hg(2)–C(2)	2.094(6)/2.087(7)	S(3)–C(23)	1.776(11)/1.742(10)
Hg(3)–C(13)	2.087(6)/2.074(7)	S(3)–C(24)	1.772(11)/1.763(14)
Hg(3)–C(8)	2.088(7)/2.081(7)		
Bond angles (°)			
C(1)–Hg(1)–C(14)	176.1(2)/175.9(2)	O(1)–S(1)–C(20)	105.8(3)/105.8(3)
C(7)–Hg(2)–C(2)	176.9(3)/177.2(3)	O(1)–S(1)–C(19)	105.6(4)/106.7(4)
C(13)–Hg(3)–C(8)	177.5(3)/177.2(3)	C(20)–S(1)–C(19)	98.5(4)/98.4(4)
C(2)–C(1)–Hg(1)	122.3(5)/120.8(5)	O(2)–S(2)–C(21)	105.3(3)/105.5(4)
C(1)–C(2)–Hg(2)	120.1(5)/122.1(5)	O(2)–S(2)–C(22)	106.4(4)/107.0(4)
C(8)–C(7)–Hg(2)	122.6(5)/120.8(5)	C(21)–S(2)–C(22)	97.6(4)/96.5(4)
C(7)–C(8)–Hg(3)	120.5(5)/121.9(5)	O(3)–S(3)–C(23)	105.9(4)/107.5(4)
C(14)–C(13)–Hg(3)	120.3(5)/120.9(5)	O(3)–S(3)–C(24)	104.2(5)/104.8(5)
C(13)–C(14)–Hg(1)	121.9(5)/121.6(5)	C(24)–S(3)–C(23)	100.7(6)/97.5(7)
Torsion angles (°)			
Hg(1)–C(1)–C(2)–Hg(2)	−0.7(8)/1.7(8)	Hg(3)–C(13)–C(14)–Hg(1)	−4.6(8)/−1.7(8)
Hg(2)–C(7)–C(8)–Hg(3)	−2.5(8)/5.4(9)		

complex **V**, in contrast to **II** and **III**, is labile in THF medium and can exist in the solution only in the presence of an excess of the ethyl acetate ligand. Such a difference in the behaviour of **II** and **III** on the one hand and **V** on the other is quite understandable as well because DMF and HMPA considerably exceed in their Lewis basicity not only ethyl acetate but also THF [13].

The interaction of **I** with DMSO results also in the formation of a complex, $\{[(o\text{-}C_6F_4Hg)_3][(Me_2SO)_3\}$ (**VI**), containing three Lewis basic species per one molecule of the macrocycle, however this complex is quite stable and, in contrast to **IV**, does not change its composition on drying at room temperature in vacuum.

The IR spectrum of **VI** (Nujol mull) is characterized by the ν_{SO}, band at 1001 cm^{-1} shifted by 49 cm^{-1} to lower wavenumbers in comparison to the ν_{SO} band of free DMSO (1050 cm^{-1}). The ^{199}Hg-NMR spectrum of **VI** in THF ($[\mathbf{VI}]_o = 8 \times 10^{-2}$ M) exhibits triplet of triplets of triplets at −287.4 ppm (Table 2) and thus the complexation of **I** with DMSO to form **VI** leads to the lowfield displacement of the ^{199}Hg resonance by 30.5 ppm. Much greater stability of **VI** compared to **IV** and **V** is well consistent with a considerably higher Lewis basity of DMSO in comparison with ethyl acetate [13]. According to Ref. [13], DMSO is also much stronger Lewis base than THF.

The structure of **VI** is shown in Fig. 4. The unit cell of **VI** contains two crystallographically independent molecules **VIA** and **VIB**. The selected bond distances and angles for **VIA** and **VIB** are presented in Table 5.

In its structural features, complex **VI** is very similar to **IV**. As in **IV**, two of three Lewis basic ligands in **VI** are coordinated via the oxygen atom with all Hg centres of the macrocycle, while the third one is bonded only to one Hg atom of the cycle. The coordination number of this mercury atom (as that of the Hg(1) atom in **IV**; see above) is equal to five.

The Hg–O bond distances in the bipyramidal fragment of **VI** range from 2.759(5) to 3.120(5) Å (av. 2.85 Å) for **VIA** and from 2.783(5) to 2.947(4) Å (av. 2.83 Å) for **VIB** and are close in general to one another with the exception of the Hg(1)–O(2) distance (3.120(5) Å in **VIA**; 2.947(4) Å in **VIB**) which is noticeably longer than the other Hg–O distances in this fragment (2.759–2.836(5) Å, av. 2.80 Å in **VIA**; 2.783(5)–2.842(6) Å, av. 2.81 Å in **VIB**). The Hg(1)–O(3) bond length in **VIA** and **VIB** is 2.819(5) and 2.991(6) Å, respectively.

The S(1)–O(1) and S(2)–O(2) vectors deviate from the perpendicular to the plane of the central nine-membered ring of **I** by 14.3 and 15.0°, respectively, in **VIA** and by 13.1 and 8.5° in **VIB**. The angle between the S(3)–O(3) vector and this plane is 8.5° in **VIA** and 16.7° in **VIB**, i.e. the S(3)–O(3) bond in complex **VI** is located almost parallel to the mercury-containing macrocycle. The other interesting peculiarity of **VI** is close to linear geometry of the O(2)–Hg(1)–O(3) fragment (the corre-

Table 6
Crystal data, data collection and structure refinement parameters for **II**, **III**, **IV** and **VI**

Complex	**II**	**III**	**IV**	**VI**
Formula	$C_{24}H_{14}F_{12}Hg_3N_2O_2$	$C_{30}H_{36}F_{12}Hg_3N_6O_2P_2$	$C_{30}H_{24}F_{12}Hg_3O_6$	$C_{24}H_{18}F_{12}Hg_3O_3S_3$
Molecular weight	1192.14	1404.36	1310.26	1280.33
Temperature (K)	100.0(2)	240.0(2)	110.0(2)	200.0(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$,	$P\bar{1}$	$P\bar{1}$
a (Å)	9.274(2)	15.578(2)	10.805(5)	11.009(2)
b (Å)	10.626(2)	11.389(1)	12.291(6)	11.137(3)
c (Å)	15.434(3)	23.280(3)	14.391(6)	26.223(7)
α (°)	86.37(3)		75.552(9)	79.62(1)
β (°)	79.40(3)	91.506(3)	69.310(8)	84.58(1)
γ (°)	64.57(3)		81.172(9)	81.46(1)
V (Å^3)	1349.9(5)	4128.7(8)	1727(1)	3120(2)
Z	2	4	2	4
D_{calc} (g cm^{-3})	2.933	2.259	2.520	2.726
Absorption coefficient μ (cm^{-1})	171.28	112.95	134.08	150.25
θ_{max} (°)	31	30	31	31
Observed reflections [$I > 2\sigma(I)$]	6865	6271	8771	9939
Unique reflections (R_{int})	7917 (0.0544)	12 025 (0.0564)	10 762 (0.0702)	18 734 (0.0436)
Transmission factors, min/max	0.345/0.948	0.260/0.493	0.232/0.695	0.378/0.845
Parameters	444	531	460	811
R_1 (on F for observed reflections) [a]	0.0416	0.0329	0.0534	0.0372
wR_2 (on F^2 for all reflections) [b]	0.1075	0.0658	0.1312	0.0778

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

sponding O(2)–Hg(1)–O(3) bond angle is equal to 167.3° in **VIA** and 169.2° in **VIB**). The Hg(l)–O(3)–S(3) bond angle in **VIA** and **VIB** is 135.4 and 144.0°, respectively. Coordination at the sulfur atoms is close to tetrahedral one.

The complexation of **I** with the above Lewis bases does not lead to any essential changes in the geometry of the macrocycle. The Hg–C bond lengths in **II**–**IV** and **VI** (2.06–2.10 Å) are unexceptional. The C–Hg–C bond angles span the range from 175.5(3) to 178.0(2)°, thus showing the insignificant perturbation of the sp hybridization of the Hg atoms, if any.

3. Conclusion

The results obtained show that macrocycle **I** readily reacts with neutral oxygeneous Lewis bases such as DMF, HMPA, ethyl acetate and DMSO to form complexes of two types. One type is the complexes of **I** with DMF and HMPA (**II** and **III**), which contain two Lewis basic ligands per molecule of the macrocycle. The other type involves the complexes of **I** with ethyl acetate and DMSO (**IV** and **VI**), in which three Lewis basic species are bonded to the macrocycle. Both types of adducts are characterized by the presence of a bipyramidal fragment formed by two molecules of a Lewis base, each of which is simultaneously coordinated through the oxygen atom with all Hg centres of the macrocycle. The third Lewis basic species in the complexes of the second type is bonded only to one mercury atom of **I** and the coordination number of this Hg atom is equal to five. The ^{199}Hg-NMR data described above demonstrate that there is a good correlation between the Lewis basicity of the nucleophilic guest and the stability of the resulting complex. According to the IR data, the complexation with the macrocycle leads to a noticeable weakening of the carbonyl C–O, P–O or S–O bond of a Lewis base which is of interest for organic synthesis and catalysis.

4. Experimental

The starting macrocycle **I** was synthesized according to the published procedure [10a]. Commercial DMF, HMPA, DMSO and EtOAc were distilled prior to use. The IR spectra were taken as Nujol mulls on a Specord M-82 instrument. The ^{199}Hg- and ^{31}P-NMR spectra were recorded on a Bruker WP-200 SY spectrometer using Ph_2Hg and 85% aq. solution of H_3PO_4, respectively, as external standards.

4.1. Synthesis of complex **II**

Compound **I** (105 mg, 0.1 mmol) was dissolved in 3 ml of DMF under heating and the resulting solution was allowed to stand at room temperature (r.t.). Within 24 h, colourless crystals of complex **II** were precipitated from the solution. The crystals were filtered off and dried at r.t. in vacuum. The yield of **II** was 86 mg (72%). Anal. Calc. for $C_{24}H_{14}F_{12}Hg_3N_2O_2$: C, 24.14; H, 1.17; F, 19.13; N, 2.35. Found: C, 23.87; H, 1.10; F, 19.80; N, 2.29%. IR (ν_{CO}, cm^{-1}): 1646 (s).

4.2. Synthesis of complex *III*

Compound **I** (105 mg, 0.1 mmol) was dissolved under heating in 2 ml of HMPA and the resulting solution was allowed to stand in refrigerator at 5 °C. Within 1 day, colourless crystals of complex **III** appeared in the solution. After 2 days the crystals were filtered off, washed with cooled ether and dried at r.t. in vacuum. The yield of **III** was 74 mg (53%). Anal. Calc. for $C_{30}H_{36}F_{12}Hg_3N_6O_2P_2$: C, 25.64; H, 2.56; F, 16.24; P, 4.42. Found: C, 25.38; H, 2.57; F, 16.53; P, 4.39%. IR (ν_{PO}, cm^{-1}): 1138 (s).

4.3. Synthesis of complexes *IV* and *V*

Compound **I** (209 mg, 0.2 mmol) was dissolved in 5 ml of EtOAc under heating and the resulting solution was allowed to stand at r.t. Within 2 h, colourless crystals of complex **IV** were formed in the solution. The crystals were filtered off and dried at r.t. in vacuum. Drying of **IV** led to loss of two coordinated EtOAc molecules to afford **V**. The yield of **V** was 225 mg (94%). Anal. Calc. for $C_{22}H_8F_{12}Hg_3O_2$: C, 23.25; H, 0.71; F, 20.08. Found: C, 23.12; H, 0.76; F, 20.10%. IR (ν_{CO}, cm^{-1}): 1678 (s).

4.4. Synthesis of complex *VI*

Complex **VI** was obtained using the same procedure as described above for **II**. The amounts of the reagents were 105 mg (0.1 mmol) of **I** and 5 ml of DMSO. The yield of **VI** was 111 mg (87%). Anal. Calc. for $C_{24}H_{18}F_{12}Hg_3O_3S_3$: C, 22.50; H, 1.41; F, 17.81; S, 7.50. Found: C, 22.55; H, 1.57; F, 18.26; S, 7.69%. IR (ν_{SO}, cm^{-1}): 1001 (s).

4.5. X-ray diffraction study

Crystals of **II**–**IV** and **VI** for an X-ray diffraction study were obtained as described above but were not dried in vacuum. Details of crystal data, data collection and structure refinement parameters for the complexes are presented in Table 6. X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD diffractometer (graphite-monochromated Mo–K_α radiation, $\lambda = 0.71073$ Å, ω and φ scan technique). The semi-empirical absorption correction from equivalents (SADABS program [15]) was applied. The structures were solved by direct methods. All non-hydrogen atoms in **II**–**IV** and **VI** were refined with the anisotropic temperature factors. One of two HMPA molecules in **III** is disordered with 0.7/0.3 occupancies and atoms from minor component were refined isotropically. The hydrogen atoms in **II** were located in the difference map and refined in the isotropic approximation. All H atoms in complexes **III**, **IV** and **VI** were included in the least-squares refinement in the riding model approximation. Data reduction and further calculations were performed using SAINT [16] and SHELXTL-97 [17] program on IBM PC AT.

5. Supplementary material

Final positional and thermal parameters for non-hydrogen atoms and full list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 174903–174906 for compounds **II**, **III**, **IV** and **VI**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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