Coordination chemistry of mercury-containing anticrowns. Self-assembly of unusual supramolecular aggregates in the interaction of the three-mercury anticrown (*o*-$C_6F_4Hg)_3$ with crown ethers in the presence of neutral monodentate oxygenous Lewis bases

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Dedicated to Prof. Usein M. Dzhemilev on the occasion of his 65th anniversary

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Abstract

The interaction of the three-mercury anticrown (*o*-$C_6F_4Hg)_3$ **1** with a large excess of aqueous [15]crown-5 results in the formation of a complex, {[(*o*-$C_6F_4Hg)_3$]([15]crown-5)($H_2O)_2$} **3**, having a polydecker sandwich structure in the crystal. Every double-decker sandwich fragment of this supramolecular aggregate contains one crown ether and two water molecules in the space between the mutually parallel planes of two anticrown units. The water species in **3** are η^3-coordinated via the oxygen atom to the Hg centres of the neighbouring anticrown whereas both water protons are involved in the formation of H-bonds with the [15]crown-5. Each crown ether ligand in **3** forms also a weak Hg–O contact with one of the nearest molecules of **1**. The reaction of **1** with aqueous [18]crown-6 in methanol leads to a self-assembly of an unusual supramolecular aggregate {[(*o*-$C_6F_4Hg)_3]_2$([18]crown-6)($H_2O)_2$(MeOH$)_2$} **5**, containing one crown ether molecule, two molecules of H_2O and two molecules of methanol per two anticrown species. The crown ether and water guests in this adduct are sandwiched by two mutually parallel anticrown moieties while the methanol species are located on the free sides of the planes of the mercuramacrocycles and are coordinated with their Hg centres via the oxygen atom in an η^3-type. The bonding of the water species in **5** is analogous to that in **3** but the crown ether oxygen atoms form here four shortened Hg–O contacts with the anticrown units. The complex of similar composition and structure, {[(*o*-$C_6F_4Hg)_3]_2$([18]crown-6)($H_2O)_2$($Me_2CO)_2$} **6**, is produced when the interaction of **1** with aqueous [18]crown-6 is carried out in acetone as a solvent.

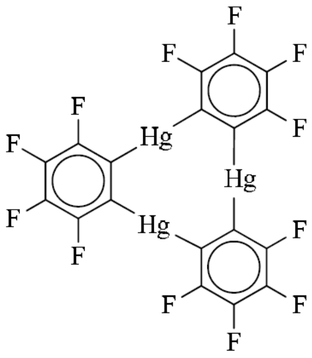
Keywords: Anticrowns, complexes, crown ethers, mercury, monodentate oxygenous Lewis bases, self-assembly, X-ray diffraction

Introduction

Macrocyclic multidentate Lewis acids or anticrowns[1] represent a novel class of anion receptors and catalysts (see reviews references 2–8 and references cited in recent papers references 9–17). Owing to the presence of several Lewis acidic centres in the macrocyclic chain of anticrowns, these charge-reversed analogues of crown ethers and related species are able to bind cooperatively various anions and neutral Lewis bases with the formation of complexes of unique structures.

Previously, we have reported the ability of one of the most studied anticrowns, viz., cyclic trimeric perfluoro-*o*-phenylenemercury (o-$C_6F_4Hg)_3$ **1**, having a plane structure,[18] to coordinate [12]crown-4, [18]crown-6 and the simplest representative of crown ethers – 1,3,5-trioxane.[15] In the case of [12]crown-4 and [18]crown-6, the complexation reactions proved to be extremely sensitive to the presence of moisture in the system. It turned out that when aqueous crown ethers are used in these experiments or when the reactions of the corresponding anhydrous crown ethers with **1** are carried out in contact with air moisture, the resulting complexes $\{[(o\text{-}C_6F_4Hg)_3]_2([12]\text{crown-4})(H_2O)_2\}$ and $\{[(o\text{-}C_6F_4Hg)_3]_2([18]\text{crown-6})(H_2O)_2\}$ **2** contain the coordinated water molecules along with the starting crown compound. An X-ray diffraction study of these supramolecular adducts has shown that they have a double-decker sandwich structure. Particularly interesting is complex **2** which was isolated from the reaction of **1** with aqueous [18]crown-6 in dry CH_2Cl_2 in 79% yield. In this complex, each water species is cooperatively bound through the oxygen atom by three Hg sites of the adjacent anticrown whereas both its protons form H-bonds with the oxygen atoms of [18]crown-6. An additional contribution in the formation of **2** is made by the interaction of four oxygen atoms of the crown ether with the Hg centres of the anticrown molecules. The synthesis of an anhydrous adduct of **1** with [12]crown-4 has been accomplished by the reaction of **1**·EtOH[14] with the corresponding anhydrous crown ether in dry diethyl ether under Ar.[15] However, attempts to obtain anhydrous complexes of **1** with [18]crown-6 in an analytically pure state failed.

In the present article, we report the results of our study on the complexation of macrocycle **1** with [15]crown-5 as well as the data on the self-assembly of unique supramolecular aggregates in the interaction of **1** with aqueous [18]crown-6 in methanol and acetone as solvents.



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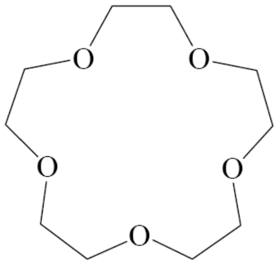
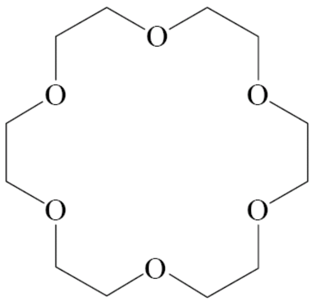


[15]crown-5



[18]crown-6

Results and Discussion

The reaction of **1** with [15]crown-5 proved also to be very sensitive to the presence of traces of moisture in the system. The use of an aqueous commercial sample of [15]crown-5 (Reanal, 98%; $\nu(OH) = 3483\ cm^{-1}$) in these experiments led again to the involvement of water together with the starting crown compound in the complexation with the mercury macrocycle. In attempts to prepare anhydrous adducts of **1** with [15]crown-5, a commercial sample of this crown ether (Aldrich, 98%), not containing water according to IR spectrum, was employed. The experiments were conducted in dry solvents in an argon atmosphere. However, even under such conditions, we could not obtain anhydrous complexes of **1** with [15]crown-5 in an analytically pure state.

Dissolution of macrocycle **1** at 100 °C in aqueous [15]crown-5 as a solvent followed by slow cooling of the resulting solution to 20 °C leads to precipitation of colourless crystals of a complex, $\{[(\textit{o}\text{-}C_6F_4Hg)_3]([15]\text{crown-5})(H_2O)_2\}$ **3**, containing one molecule of the crown ether and two molecules of H_2O per one anticrown molecule on the basis of elemental analysis. The IR spectrum of **3** in Nujol mull exhibits the broad $\nu(OH)$ bands at 3397 and 3290 cm^{-1}. The room-temperature ^{199}Hg NMR spectrum of **3** in THF ($[\mathbf{3}]_0 = 8 \times 10^{-2}$ M) shows a small downfield ^{199}Hg shift (by 3 ppm) relative to that of free **1**. On the addition of a 40-fold excess of aqueous [15]crown-5 to **3** in THF, the value of this downfield shift is enhanced only to 4 ppm.

Figure 1 shows the structure of a fragment of complex **3**. Selected bond lengths and angles for **3** are presented in Table 1.

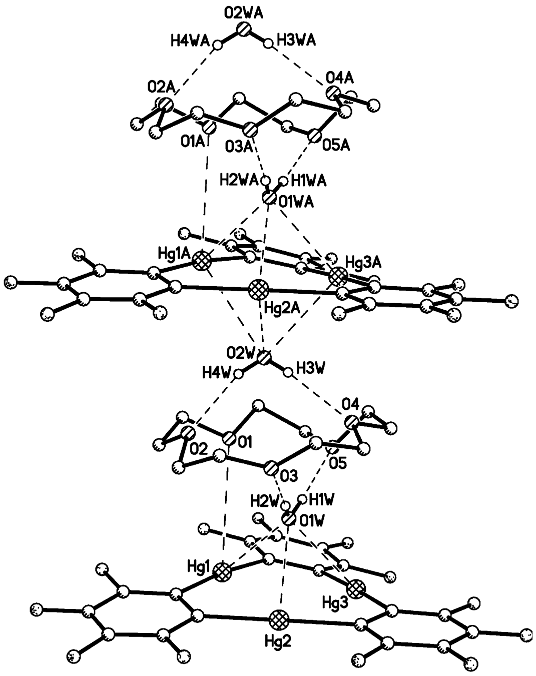


Figure 1. View of a fragment of complex **3** in the crystal. The hydrogen atoms of the crown ether are omitted. Symmetry transformation *x*–1, *y*, *z* was used to generate equivalent atoms.

The complex forms in the crystal extended stacks representing polydecker sandwiches. Every double-decker sandwich fragment of **3** in these stacks contains, like **2**, one molecule of the crown compound and two water guests in the space between the mutually parallel planes of two anticrown units. As in complex **2**, each water species in **3** is η^3-coordinated through the oxygen atom to the Hg centres of the neighbouring anticrown, whereas both its protons are involved in the formation of H-bonds with the oxygen atoms of [15]crown-5. The Hg–O distances range here from 2.757(5) to 3.135(5) Å (av. 2.92 Å) and all these distances are significantly shorter than the sum of van der Waals radii of Hg (1.73–2.00 Å,[19a,b] 2.1 Å[19c]) and O (1.54 Å)[19d] atoms. The lengths of the hydrogen O···H bonds are in the range 2.00(10)–2.16(7) Å. One of the oxygen atoms of each crown ether ligand in **3** interacts also very weakly, if any, with a single Hg centre of one of neighbouring molecules of **1** (Hg–O 3.593(4) Å). By contrast, in complex **2**, four considerably shorter Hg–O contacts between the crown ether and the anticrown moieties are observed.[15] The mutual orientation of the neighbouring mercury macrocycles in each of the stacks, formed by **3**, is close to an eclipsed conformation and the projections of their centroids onto the plane parallel to these cycles are shifted with respect to one another by 1.49 Å.

Table 1. Selected bond lengths [Å] and angles [°] in complex **3**

Hg1–O1W	2.757(5)	O3···O1W	2.825(6)
Hg2–O1W	2.950(5)	O4···H3W	2.09(7)
Hg3–O1W	2.925(5)	O4···O2W	2.807(7)
Hg1A–O2W	3.135(5)	O2···H4W	2.00(10)
Hg2A–O2W	2.822(5)	O2···O2W	2.758(7)
Hg3A–O2W	2.927(5)	O1W–H1W	0.82(8)
Hg1–O1	3.593(4)	O1W–H2W	0.67(6)
O5···H1W	2.03(8)	O2W–H3W	0.72(7)
O5···O1W	2.842(7)	O2W–H4W	0.79(9)
O3···H2W	2.16(7)		
H1W–O1W–H2W	110(8)	O1W–H2W–O3	175(6)
H3W–O2W–H4W	116(8)	O2W–H3W–O4	173(8)
O1W–H1W–O5	174(9)	O2W–H4W–O2	162(10)

The complex of different composition is produced in the interaction of **1**·EtOH[14] with a 5-fold excess of aqueous [15]crown-5 in diethyl ether at 20 °C. Under these conditions, the reaction yields a colourless, fine crystalline adduct which can be formulated as $\{[(o\text{-}C_6F_4Hg)_3]_2([15]\text{crown-5})(H_2O)_2\}$ **4** according to elemental analysis. Like **2**, complex **4** contains one crown ether and two water molecules per two molecules of the anticrown. The IR spectrum of **4** (Nujol mull) displays the broad ν(OH) bands at 3387 and 3284 cm^{-1}. The room-temperature ^{199}Hg NMR spectrum of **4** in THF ($[\mathbf{4}]_0 = 4 \times 10^{-2}$ M) exhibits a downfield ^{199}Hg shift of 5 ppm with respect to that of neat **1**. In the presence of a 40-fold excess of aqueous [15]crown-5, the value of this downfield shift increases to 7 ppm. An X-ray diffraction study of **4** has shown that the complex has a discrete, double-decker sandwich structure, wherein the crown ether and water species are disposed, as in **2**, between the mutually parallel planes of two mercury macrocycles. The water molecules in **4** are again bound to the Hg centres of the adjacent anticrown unit in an η^3-manner (Hg–O 2.861(3), 2.885(3) and 2.937(4) Å; av. 2.89 Å). However, the crown ether ligand in the crystal of **4** is strongly disordered and, therefore, a more detailed discussion of the structure of this complex becomes impossible.

As mentioned above, complex **2** was earlier synthesized by the interaction of **1** with aqueous [18]crown-6 in dichloromethane.[15] We have found, however, that if this reaction is carried out in methanol as a solvent instead of CH_2Cl_2, a self-assembly of a unique supramolecular aggregate, $\{[(o\text{-}C_6F_4Hg)_3]_2([18]\text{crown-6})(H_2O)_2(MeOH)_2\}$ **5**, containing one crown ether molecule, two molecules of H_2O and two molecules of methanol per two anticrown species, occurs according to an X-ray analysis of the isolated crystalline product. The obtained complex is unstable and loses both methanol molecules on drying in vacuum at 20ºC for 2 h to give **2**.

An analogous supramolecular aggregate, $\{[(o\text{-}C_6F_4Hg)_3]_2([18]\text{crown-6})(H_2O)_2(Me_2CO)_2\}$ **6**, is formed in 84% isolated yield when the reaction of **1** with aqueous [18]crown-6 is conducted in acetone as a solvent. However, this adduct is considerably more stable than **5** and does not lose the coordinated acetone species on drying in vacuum at 20 ºC. The same complex **6** is produced in the interaction of acetone with **2**. The IR spectrum of **6** (Nujol mull) is characterized by the presence of the broad ν(OH) bands at 3450 and 3250 cm^{-1} as well as the carbonyl ν(CO) band at 1695 cm^{-1}, which is shifted by 24 cm^{-1} in the low-frequency region relative to the corresponding ν(CO) band of free acetone. In the case of the previously described 1 : 1 acetone adduct $\{[(o\text{-}C_6F_4Hg)_3](Me_2CO)\}$ **7**, the ν(CO) band in the IR spectrum is observed at 1683 cm^{-1}.[20] The room-temperature ^{199}Hg NMR spectrum of **6** in THF ($[\mathbf{6}]_0 = 4 \times 10^{-2}$ M) shows a downfield ^{199}Hg shift of 3 ppm relative to that of **1**. On the addition of a 10-fold excess of aqueous [18]crown-6 and 20-fold excess of acetone to **3** in THF, the value of this downfield shift is enhanced to 7 ppm.

The structure of **5** is shown in Figure 2. The complex contains a double-decker sandwich unit, analogous to **2**, and two coordinated methanol species which are located on the free sides of the planes of the mercuramacrocycles. Every methanol molecule in **5** is bound via the oxygen atom to the Hg sites of **1** in an η^3-type, forming a pyramidal fragment with the Hg–O distances of 2.906(6), 2.906(6) and 3.327(7) Å (av. 3.05 Å; Table 2). A similar pyramidal structure with the Hg–O distances of 2.907(3), 3.134(3) and 3.145(3) Å (av. 3.06 Å) is realized in the recently reported 1 : 1 complex of **1** with ethanol.[14] The C13–O3 and C13A–O3A bond vectors in **5** deviate from the perpendicular to the mean planes of the central nine-membered rings of the molecules of **1** by 40.9°.

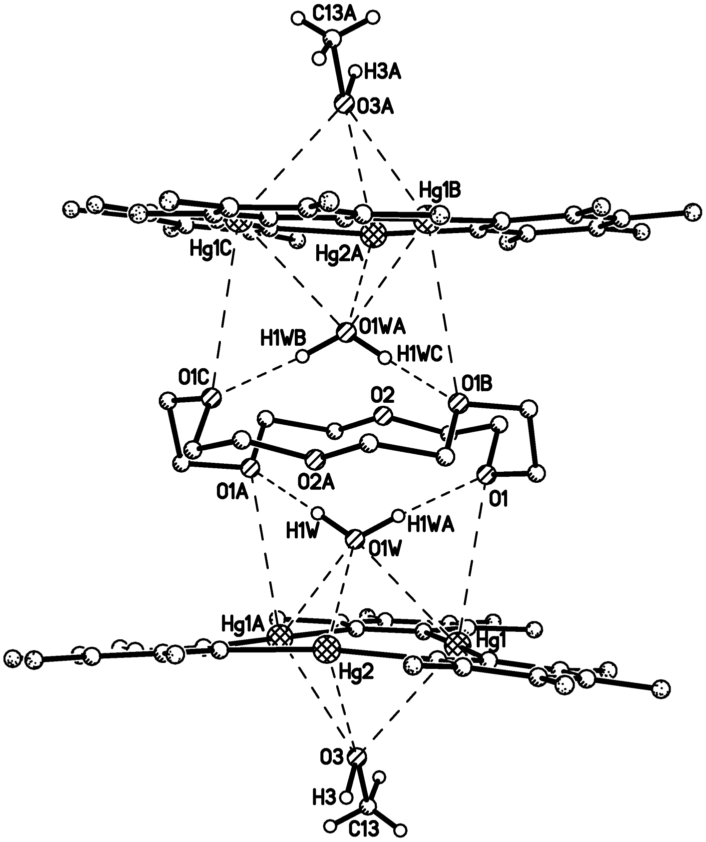


Figure 2. Molecular structure of complex **5** in the crystal. The hydrogen atoms of the crown ether are omitted for clarity. Symmetry transformations *x*, –*y*, *z* and –*x*, *y*, 1–*z* were used to generate equivalent atoms.

The crown ether and water molecules in **5** are sandwiched by two mutually parallel anticrown moieties and are linked with them in the same manner as in **2**. Each water species in **5** is cooperatively coordinated through the oxygen atom by three Hg centres of the adjacent mercury macrocycle, while both water protons form H-bonds with the oxygen atoms of [18]crown-6. The Hg–O distances in this coordination fragment of **5** are 2.728(6), 2.971(5) and 2.971(5) Å (av. 2.89 Å) and the lengths of the hydrogen O···H bonds are 1.88 Å (O1A···O1W 2.814(6) Å). In the structure of **2**, the corresponding Hg–O separations are 2.773(2), 2.816(2) and 3.123(2) Å (av. 2.90 Å) and the lengths of the hydrogen O···H bonds are equal to 2.03(7) and 2.09(7) Å (O···O 2.752(4) and 2.834(5)Å).[15] The anticrown species in **5** also interact with the crown ether. In this interaction, two Hg centres of each molecule of **1** and four oxygen atoms of [18]crown-6 take part, which results in the formation of four Hg–O bonds of an η^1-type with the Hg–O distances of 3.398(5) Å. The corresponding Hg–O distances in complex **2** are significantly shorter (3.186(4) and 3.277(4) Å),[15] thus indicating that the coordination of the methanol molecules with **2** leads to a considerable weakening of the bonding of [18]crown-6 to the Hg sites of the anticrown units.

Despite the general structural similarity of the double-decker sandwich fragment of **5** to complex **2**, they differ from each other in some essential details. In the case of **5**, one and the same crown ether oxygen atoms take part in the formation of the H-bonds with the water protons and in the coordination with the Hg atoms of **1**. As a result, only four oxygen atoms of [18]crown-6 in **5** participate in the binding of the anticrown and water species. By contrast, all six oxygen atoms of the crown compound in **2** are involved in the complexation reaction.[15]

Table 2. Selected bond lengths [Å] and angles [°] in complexes **5** and **6**

	5	**6**
Hg1–O3	2.906(6)	2.990(3)
Hg2–O3	3.327(7)	3.138(4)
Hg1–O1W	2.971(5)	2.970(3)
Hg2–O1W	2.728(6)	2.787(4)
Hg1–O1	3.398(5)	3.402(3)
O1A···H1W	1.88	1.91
O1A···O1W	2.814(6)	2.820(3)
O1W–H1W	0.94	0.93
C13–O3	1.441(13)	1.225(7)
O3–H3	1.01	–
H1W–O1W–H1WA	97	116
O1W–H1W···O1A	170	165

The structure of complex **6** is similar to that of **5** and is depicted in Figure 3. The triply coordinated acetone ligands in **6** form with the molecules of **1** pyramidal fragments with the Hg–O distances of 2.990(3), 2.990(3) and 3.138(4) Å (av. 3.04 Å; Table 2). These distances are essentially longer than the corresponding Hg–O separations (2.810(12), 2.822(12) and 2.983(12) Å; av. 2.87 Å) in the above-mentioned acetone adduct **7**, also having a pyramidal structure.[20] The C13–O3 and C13A–O3A bond vectors in **6** deviate from the normal to the mean planes of the central Hg_3C_6 cycles of the anticrown molecules by 28.8°.

The Hg–O contacts between the η^3-coordinated water ligands and the Hg centres of **1** in **6** (2.787(4), 2.970(3), 2.970(3) Å; av. 2.91 Å) are comparable with those in **5** (see above). As in **2**, **3** and **5**, both protons of each water species in **6** are involved in the formation of H-bonds with the oxygen atoms of the crown ether (O1A···H1W 1.91 Å, O1A···O1W 2.820(3) Å). The crown ether guest in **6** is bonded to the anticrown hosts by four Hg–O contacts of an η^1-type. The Hg–O separations (3.402(3) Å), observed here, are close to those in **5** (3.398(5) Å) and are again significantly longer than the corresponding Hg–O distances in **2**. Thus, the coordination of the acetone molecules with complex **2** also considerably weakens the bonding of [18]crown-6 to the Hg centres of the anticrown species. As in **5**, only four oxygen atoms of the crown ether in **6** take part in the formation of the adduct.

The mutual orientation of the mercury macrocycles in **5** and **6** is close to a staggered conformation and the projections of their centroids onto the plane parallel to these cycles are shifted relative to each other by 1.56 and 1.32 Å, respectively. The C–Hg–C bond angles in **3**–**6**, as in free **1**, are close to 180°.

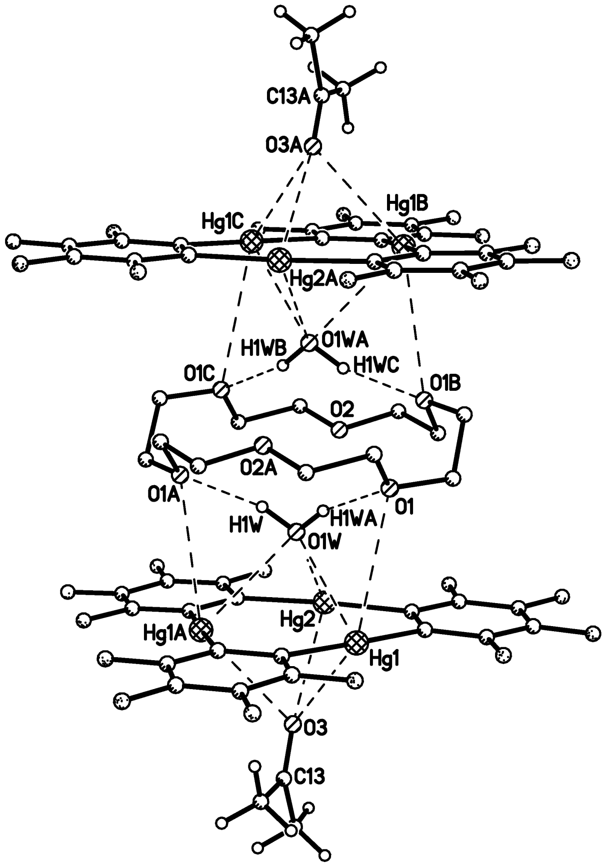


Figure 3. Molecular structure of complex **6** in the crystal. The hydrogen atoms of the crown ether are omitted for clarity. Symmetry transformations *x*, 1–*y*, *z* and 1–*x*, *y*, 1–*z* were used to generate equivalent atoms.

In contrast to [18]crown-6, other tested crown ethers such as aqueous [12]crown-4 and [15]crown-5 do not form supramolecular aggregates analogous to **6** in the interaction with macrocycle **1** in acetone according to IR spectra. Thus, in the case of [12]crown-4, only the 1 : 1 acetone adduct **7** (ν(CO) = 1684 cm^{-1}) together with the double-decker sandwich complex {[(*o*-$C_6F_4Hg)_3]_2$([12]crown-4)$(H_2O)_2$} (ν(OH) = 3231 (br), 3362 (br), 3633 cm^{-1})[15] were found in the isolated products after their drying in vacuum at 20 °C for 2 h ([12]crown-4 : **1** = ca. 5 : 1). Correspondingly, in the case of aqueous [15]crown-5, products of its reaction with **1** in acetone at a [15]crown-5 : **1** molar ratio of 1 : 2 represent a mixture of **7** and **4**, and when this ratio is 5 : 1, only complex **4** is produced.

Table 3. Crystal data, data collection and structure refinement parameters for **3**–**6**

	3	**4**	**5**	**6**
Molecular formula	$C_{28}H_{24}F_{12}Hg_3O_7$	$C_{46}H_{24}F_{24}Hg_6O_7$	$C_{50}H_{36}F_{24}Hg_6O_{10}$	$C_{54}H_{40}F_{24}Hg_6O_{10}$
Formula weight	1302.24	2348.19	2456.33	2508.40
Crystal size [mm]	0.30 × 0.12 × 0.10	0.35 × 0.33 × 0.08	0.31 × 0.27 × 0.07	0.19 × 0.17 × 0.16
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/m$	$C2/m$
a [Å]	8.3731(7)	10.9164(10)	14.196(2)	14.4357(9)
b [Å]	11.5966(10)	11.4334(10)	16.497(2)	16.7555(11)
c [Å]	17.8694(15)	12.3361(11)	12.300(2)	12.4153(8)
α [°]	78.331(2)	116.293(1)	90	90
β [°]	80.718(2)	108.119(2)	90.137(2)	90.775(1)
γ [°]	78.713(2)	90.971(2)	90	90
V [Å^3]	1652.9(2)	1290.1(2)	2880.4(6)	3002.7(3)
Z	2	1	2	2
ρ_{calc} [g·cm^{-3}]	2.616	3.022	2.832	2.774
Linear absorption (μ) [mm^{-1}]	14.009	17.921	16.064	15.413
T_{min}/T_{max}	0.039/0.343	0.012/0.248	0.083/0.399	0.091/0.226
$2\theta_{max}$ [°]	58	60	60	58
No. of unique refl. (R_{int})	8756 (0.0457)	7494 (0.0466)	3935 (0.0607)	4092 (0.0566)
No. of observed refl. ($I>2\sigma(I)$)	7534	6461	3099	3702
No. of parameters	467	424	211	223
R_1 (on F for observed refl.)[a]	0.0310	0.0222	0.0297	0.0240
wR_2 (on F^2 for all refl.)[b]	0.0616	0.0497	0.0750	0.0626
GOOF	1.093	1.000	1.045	1.031

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

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

In summary, new unusual supramolecular adducts (**3**, **5** and **6**) of macrocycle **1** have been synthesized by the interaction of this three-mercury anticrown with [15]crown-5 and [18]crown-6 in the presence of neutral monodentate oxygenous Lewis bases (water, methanol, acetone). Complex **3** is the first example of a polydecker sandwich containing three Lewis basic guests between the planes of anticrown hosts in each double-decker sandwich fragment. Complexes **5** and **6** have a discrete structure and contain three Lewis basic species between the planes of the anticrown units, whereas two other molecules of a Lewis base are located above these planes. In the series of the tested aqueous crown ethers, only [18]crown-6 is able to form a stable supramolecular assembly including the coordinated molecules of acetone, crown ether, water and the three-mercury anticrown.

Experimental Section

General. The starting macrocycle **1** and its ethanol adduct **1**·EtOH were prepared according to the published procedures.[18a,14] Commercial aqueous [15]crown-5 (Reanal; 98%) and [18]crown-6 (Reanal; 98%) were used without an additional purification. Solvents were purified by conventional methods and freshly distilled prior to use over calcium hydride (acetone, methanol), P_2O_5 (CH_2Cl_2), metallic sodium (*n*-hexane) or from sodium/benzophenone (ether) under Ar. The ^{199}Hg NMR spectra were recorded on a Bruker Av-600 instrument using a 0.2 M solution of Ph_2Hg in pyridine (δ = –791.1 ppm)[21] as an external standard. The IR spectra of complexes were recorded as Nujol mulls on a Nicolet Magna-IR 750 Series II Fourier spectrometer.

{[(*o*-C_6F_4Hg)$_3$]([15]crown-5)(H_2O)$_2$} (3). Macrocycle **1** (0.1049 g, 0.1 mmol) was dissolved under heating to 100ºC for 30 min in 1.5 ml of aqueous [15]crown-5, after which the resulting mixture was slowly cooled for 3 h to 20ºC in a water bath. The precipitated colourless crystals of complex **3** were filtered off, washed with CH_2Cl_2 (3 × 1 ml) and *n*-hexane (3 × 1 ml) and dried at 20 ºC in vacuum for 3 h. Yield of **3**: 0.0568 g (44%). Anal. calcd for $C_{28}H_{24}F_{12}Hg_3O_7$: C, 25.82; H, 1.86; F, 17.51. Found: C, 26.12; H, 1.57; F, 17.51. IR (cm^{-1}): ν(OH) = 3397 (br), 3290 (br); δ(HOH) = 1651 (w). Single crystals of **3** for the X-ray diffraction study, obtained as described above, were not washed and were not dried in vacuum.

{[(*o*-C_6F_4Hg)$_3$]$_2$([15]crown-5)(H_2O)$_2$} (4). To a solution of aqueous [15]crown-5 (0.10 ml, ca. 0.5 mmol) in diethyl ether (5.5 ml) was added a solution of **1**·EtOH (0.1150 g, 0.105 mmol) in a mixture of ether (3 ml) and ethanol (0.1 ml). Immediately, the solution became turbid, and after 30 min the white precipitate of complex **4** began to form. Then, the reaction mixture was allowed to slowly evaporate for 4 days at room temperature to 3 ml, and the resulting fine crystalline complex **4** was filtered off, washed with ether (2 × 1 ml) and *n*-hexane (3 × 1 ml) and dried at 20 ºC in vacuum for 3 h. Yield of **4**: 0.0572 g (46%). Anal. calcd for $C_{46}H_{24}F_{24}Hg_6O_7$: C, 23.54; H, 1.03; F, 19.42. Found: C, 23.77; H, 1.04; F, 19.62. IR (cm^{-1}): ν(OH) = 3387 (br), 3294 (br). Single crystals of complex **4** for the X-ray diffraction study were grown by a slow evaporation of its solution in diethyl ether.

{[(*o*-C_6F_4Hg)$_3$]$_2$([18]crown-6)(H_2O)$_2$(MeOH)$_2$} (5). To a solution of **1** (0.1045 g, 0.1 mmol) in methanol (2 ml) was added at room temperature a solution of aqueous [18]crown-6 (0.1317 g, ca. 0.5 mmol) in methanol (4 ml). Then, the reaction mixture was allowed to slowly evaporate for 3 days at room temperature to 1 ml, and the resulting colourless crystals of **5** were filtered off, washed with MeOH (3 × 0.5 ml) and CH_2Cl_2 (2 × 1 ml) and dried at 20 ºC in vacuum for 2 h. Drying of **5** led to loss of two coordinated methanol molecules to afford the previously described complex **2**.[15] Yield of **2**: 0.0737 g (62%). Anal. calcd for $C_{48}H_{28}F_{24}O_8Hg_6$: C, 24.10; H, 1.18; F, 19.06. Found: C, 24.25; H, 1.52; F, 18.60. IR (cm^{-1}): ν(OH) = 3416 (br), 3260 (br); δ(HOH) = 1636 (w). For carrying out the X-ray diffraction study of **5**, the crystals of the complex were not washed and were not dried in vacuum.

{[(*o*-$C_6F_4Hg)_3]_2$([18]crown-6)($H_2O)_2(Me_2CO)_2$} (6). To a solution of **1** (0.1048 g, 0.1 mmol) in acetone (3 ml) was added at room temperature a solution of aqueous [18]crown-6 (0.1322 g, ca. 0.5 mmol) in acetone (2 ml). Immediately, a white precipitate began to form. After a day, the reaction mixture was allowed to slowly evaporate for 2 h to 0.5 ml at 20ºC. The resulting colourless crystals of complex **6** were filtered off, washed with acetone (3 × 0.5 ml) and *n*-hexane (2 × 1 ml) and dried at 20ºC in vacuum for 2 h. Yield of **6**: 0.1056 g (84%). Anal. calcd for $C_{54}H_{40}F_{24}Hg_6O_{10}$: C, 25.86; H, 1.61; F, 18.18. Found: C, 25.73; H, 1.80; F, 18.01. IR (cm^{-1}): ν(OH) = 3450 (br), 3250 (br); ν(CO) = 1695 (m). The IR spectrum of the evaporated to dryness mother liquor (after the separation of **6**) showed the presence of complex **2** in the solid residue (ν(OH) = 3418 (br), 3269 (br) cm^{-1}).

X-ray diffraction study

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo K_α radiation, λ = 0.71073 Å, ω-scan technique, T = 100 K). The APEX II software[22] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL[23] was applied for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of water and the OH groups of the methanol molecules were located in difference Fourier synthesis. The other hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation. The main experimental and crystallographic parameters for **3**–**6** are presented in Table 3.

Supplementary Material

CCDC 783770–783773 contain the supplementary crystallographic data for the structural analysis of **3**–**6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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