Coordination chemistry of mercury-containing anticrowns. Synthesis and structures of the complexes of cyclic trimeric perfluoro-*o*-phenylenemercury with ethanol, THF and bis-2,2′-tetrahydrofuryl peroxide

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ABSTRACT

Cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-$C_6F_4Hg)_3$ (**1**) is capable of reacting with ethanol to form a 1:1 complex, {[(*o*-$C_6F_4Hg)_3$](EtOH)} (**2**), having a pyramidal structure. The ethanol molecule in **2** is coordinated through the oxygen atom to all Hg atoms of the macrocycle. The interaction of **1** with THF followed by drying of the product obtained in vacuum also gives the corresponding pyramidal 1:1 complex {[(*o*-$C_6F_4Hg)_3$](THF)} (**3**). However, when a THF solution of **1** is slowly concentrated to a small volume and the resulting crystals are not dried, three cocrystallized adducts, viz., {[(*o*-$C_6F_4Hg)_3$](THF)_2} (**4**), {[(*o*-$C_6F_4Hg)_3$](THF)_3} (**5**) and {[(*o*-$C_6F_4Hg)_3$](THF)_4} (**6**), containing two, three and even four THF molecules, respectively, are produced. Complex **4** has a bipyramidal structure. Complexes **5** and **6** are also characterized by the presence of a bipyramidal fragment formed by two coordinated THF species. The topological analysis of the DFT-calculated function of the electron density distribution in the crystals of **2** and **3** revealed the critical points $(3, -1)$ on each of the three Hg⋯O lines, which is in accord with the X-ray diffraction data indicating on the presence of the triply coordinated Lewis base molecule in both adducts. If a THF solution of **1** is held for a month at 20 °C on air under stirring, a sandwich complex of **1** with previously unknown bis-2,2′-tetrahydrofuryl peroxide (THFPO) is formed. The THFPO ligand in this sandwich, {[(*o*-$C_6F_4Hg)_3]_2$(THFPO)} (**7**), provides all its four oxygen atoms for the bonding to the molecules of **1**. Two of these oxygen atoms, belonging to the tetrahydrofuryl moieties, are cooperatively bound each by three Hg atoms of the neighbouring macrocyclic unit whereas two others, belonging to the peroxide group, coordinate to a single Hg atom of the adjacent macrocycle.

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1. Introduction

Anticrowns [1] constitute a remarkable class of promising reagents whose coordination and catalytic chemistry has received considerable development over the last two decades (see e.g. reviews [2a–g] and papers cited in [3a–c]). Being charge-reverse analogues of conventional crown compounds, these macrocyclic multidentate Lewis acidic hosts exhibit a high activity in the binding of various anions and neutral Lewis bases to form complexes of the unique structures. The successful applications of anticrowns in catalysis [2a–c,4,5] and as ionophores for ion-selective electrodes [2b,6] have also been reported.

Among the presently known anticrowns, one of the most studied ones is cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-$C_6F_4Hg)_3$ (**1**) [7] containing three Hg atoms in a planar nine-membered ring. For this macrocycle, a large number of complexes with different anionic and neutral Lewis basic species has been prepared

[2a,c,d,3a–c]. In the majority of structurally characterized complexes, there is at least one motif wherein a molecule of a Lewis base is cooperatively coordinated by all Lewis acidic Hg sites of **1**, thereby leading to the unusual pyramidal, bipyramidal and sandwich structures or fragments.
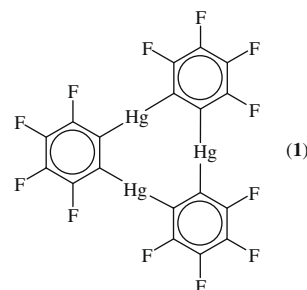
The synthesis of complexes of **1** is often carried out using THF and alcohols (MeOH, EtOH) as solvents. Because molecules of these

solvents possess donor properties they could coordinate with the mercury anticrown and, as a consequence, compete with a Lewis basic guest for the coordination sites of **1**. The existence of such a competition is supported by [199]Hg NMR data which indicate that adducts of **1** with so weak Lewis bases as nitriles [8], ethyl acetate [9], nitrobenzene [3b] and some others can persist in a THF solution only in the presence of a large excess of the corresponding free Lewis basic guest.

Taking these data into account, we decided to examine the state of macrocycle **1** in THF and ethanol media, and the results of this study are described in detail below. An unusual complex **1** with bis-2,2′-tetrahydrofuryl peroxide, formed on a prolonged contact of a THF solution **1** with air, is also reported.

2. Results and discussion

Slow concentration of an ethanol solution of **1** results in the formation of a colourless crystalline solid which has been identified as a 1:1 complex of **1** with ethanol, {[(o-C_6F_4Hg)$_3$](EtOH)} (**2**), on the basis of elemental analysis. The isolated compound is moderately stable at room temperature and is much better soluble in CH_2Cl_2 and ether than the starting macrocycle. The IR spectrum of **2** in Nujol mull exhibits the weak v(O–H) band at 3593 cm^{-1} shifted by 40 cm^{-1} to lower frequencies relative to the corresponding v(O–H) band (3633 cm^{-1}) for free, non-associated EtOH [10]. The ^{1}H NMR spectrum of **2** in CD_2Cl_2 is similar in its parameters to that of free EtOH in the same solvent with the exception of the coupling constant of the CH_2 and OH protons (3.0 Hz in **2** and 5.2 Hz in EtOH).

An X-ray diffraction study of the complex has shown that it has a pyramidal structure (Fig. 1). The ethanol molecule in **2** is coordinated through the oxygen atom to all Hg atoms of the macrocycle and forms with **1** one comparatively short Hg–O distance (2.907(3) Å; see Table 1) and two somewhat longer ones (3.145(3) and 3.134(3) Å). All these distances are significantly shorter, however, than the sum of the van der Waals radii of mercury (1.73–2.00 Å [11a,b], 2.1 Å [11c]) and oxygen (1.54 Å [11d]) atoms. The C(19)–O(1) bond vector in **2** deviates from the perpen-

dicular to the mean plane of the central nine-membered ring of **1** by 40.9°. In the crystal, molecules of **2** are associated into a complex three-dimensional structure due to shortened (as compared to the sum of the van der Waals radii) intermolecular Hg···F (3.107(3)–3.351(3) Å), Hg···C (3.444(4) and 3.446(4) Å) and C···C (3.188(6)–3.300(6) Å) contacts between the adjacent macrocyclic units (r_{vdw}(F) = 1.4 Å [11c], r_{vdw}(C_{arom}) = 1.7 Å [11c]). The H(1) atom is not involved in the formation of intermolecular hydrogen bonds O–H···O–H in the crystal structure of **2** but it forms a weak hydrogen bond with the fluorine atom of the neighbouring molecule of **2** (H(1)···F(4)$_{x,1+y,z}$ 2.42 Å, O(1)···F(4)$_{x,1+y,z}$ 3.041(4) Å, O(1)–H(1)···F(4)$_{x,1+y,z}$ 131°). The IR data also indicate on the absence of intermolecular hydrogen O–H···O–H bonds in the crystal of **2**.

When a solution of **1** in THF is evaporated at 20 °C in vacuum, a white powder of a 1:1 THF complex of **1**, {[(o-C_6F_4Hg)$_3$](THF)} (**3**), is produced after drying at 20 °C for 15 min. The isolated adduct is somewhat worse soluble than **2** in CH_2Cl_2 and ether but is again considerably better soluble in these solvents than **1**. The ^{1}H NMR spectrum of **3** in [D_6]acetone is practically identical to that of free THF in the same solvent. A slow evaporation of a solution of **1** in a THF–CHCl$_3$ (1:2) mixture gives crystals of **3** suitable for the X-ray diffraction study.

The structure of **3** is shown in Fig. 2. The complex has also a pyramidal structure with the THF molecule simultaneously coordinated via the oxygen atom to the three Hg atoms of **1**. Like the ethanol ligand in **2**, the THF ligand in **3** forms with **1** one comparatively short Hg–O bond (2.853(3) Å; see Table 2) and two noticeably longer ones (3.229(3) and 3.251(3) Å). The molecule of THF in **3** is in a twist conformation: the C(20) and C(21) atoms deviate from the C(19)–O(1)–C(22) plane in the opposite directions by 0.30 and 0.32 Å. In the crystal, molecules of **3** as those of **2** are associated due to shortened intermolecular Hg···F (3.136(3) and 3.285(3) Å), Hg···C (3.387(4)–3.488(4) Å) and C···C (3.133(8)–3.326(6) Å) contacts between the juxtaposed macrocycle moieties.

A quite different situation is observed when a THF solution of **1** is slowly concentrated to a small volume and the resulting crystals
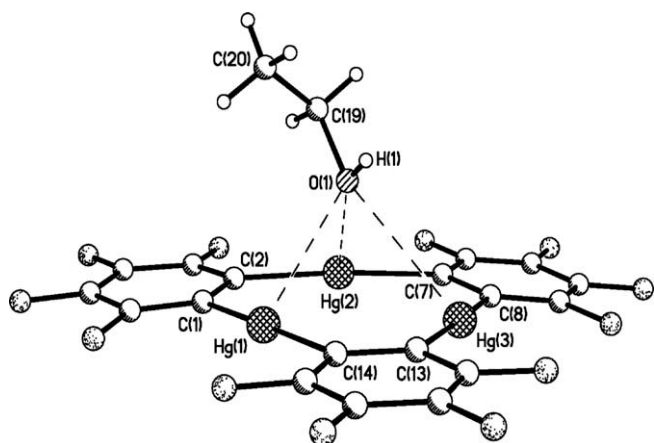

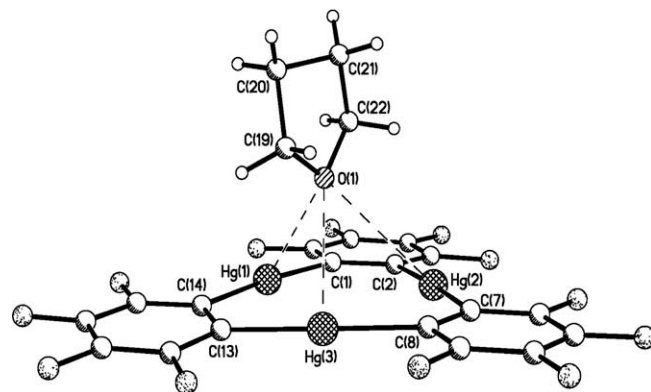**Fig. 1.** Molecular structure of complex **2** in the crystal.

Fig. 2. Molecular structure of complex **3** in the crystal.

Table 1
Selected bond lengths (Å) and angles (°) in complex **2**.

Hg(1)–O(1)	2.907(3)	C(19)–O(1)	1.447(5)
Hg(2)–O(1)	3.145(3)	O(1)–H(1)	0.84
Hg(3)–O(1)	3.134(3)	C(19)–C(20)	1.509(6)
C(19)–O(1)–H(1)	109.5	O(1)–C(19)–C(20)	112.7(4)

Table 2
Selected bond lengths (Å) and angles (°) in complex **3**.

Hg(1)–O(1)	2.853(3)	C(22)–O(1)	1.461(5)
Hg(2)–O(1)	3.251(3)	C(19)–C(20)	1.522(6)
Hg(3)–O(1)	3.229(3)	C(20)–C(21)	1.520(6)
C(19)–O(1)	1.442(5)	C(21)–C(22)	1.494(7)
C(19)–O(1)–C(22)	108.7(3)	C(20)–C(21)–C(22)	102.1(4)
O(1)–C(19)–C(20)	105.7(3)	O(1)–C(22)–C(21)	106.3(4)
C(19)–C(20)–C(21)	102.1(4)		