Russian Chemical Bulletin, International Edition, Vol. 53, No. 12, pp. 2871—2873, December, 2004 2871

Brief Communications

Binding of ferrocene by cyclic trimeric perfluoro-*o*-phenylenemercury. Synthesis and structure of the first double-decker sandwich complex of a sandwich

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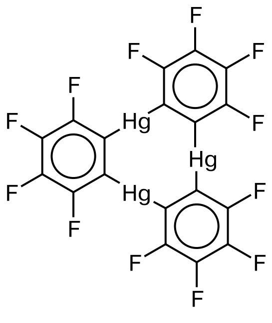
The first double-decker sandwich complex of a sandwich was synthesized and fully characterized. The complex was prepared by the reaction of cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) with ferrocene in an ethereal solution at 20 °C and has the composition $\{[(o\text{-}C_6F_4Hg)_3]_2(Cp_2Fe)\}$ (**2**). The ferrocene sandwich in **2** is located between the planes of two mercury-containing macrocycles and is coordinated to each of them through donation of the π-electrons of the η^5-Cp ligands to vacant orbitals of the mercury atoms of the adjacent molecule **1**. It was concluded that all carbon atoms of the η^5-Cp rings in complex **2** are involved in the bonding to the macrocycles. Complexation with **1** leads to considerable shifts of the ν(C—H) and ρ(C—H) bands of ferrocene in the IR spectrum to high frequencies. The structure of complex **2** was determined by X-ray diffraction.

Key words: anticrowns, complexation, ferrocene, perfluorinated polymercuramacrocycles, sandwich complexes.

Cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) containing three Hg atoms in the planar nine-membered ring has been described many years ago.[1,2] However, its high efficiency in the binding of various anions and neutral Lewis bases has been revealed only relatively recently (see the reviews[3—5]). Nowadays, data on the complexation of macrocycle **1** with the halide, thiocyanate, borohydride, *closo*-$[B_{10}H_{10}]^{2-}$, *closo*-$[B_{12}H_{12}]^{2-}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_5NO]^{2-}$, and some other anions are available. Complexes of macrocycle **1** with nitriles, carbonyl compounds, dimethyl sulfide, and even aromatic hydrocarbons were also synthesized. In all structurally characterized complexes, the Lewis base molecule is simultaneously coordinated to all Hg atoms of the macrocycle.



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In the present paper, we report on the ability of macrocycle **1** to bind ferrocene with the formation of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2754—2756, December, 2004.

the {[(o-C_6F_4Hg)$_3$]$_2$(Cp_2Fe)} complex (**2**) having a unique structure of a sandwich complex of a sandwich. In this unusual sandwich, the ferrocene molecule is coordinated to the Hg atoms of the macrocycles by its η^5-Cp rings, whose C atoms bear[6] a partial negative charge.

Complex **2** is readily formed in the reaction of ferrocene with macrocycle **1** in diethyl ether at 20 °C as air-stable red-orange crystals. The IR spectrum of compound **2** (in Nujol mull) shows the C—H out-of-plane bending vibrations of the Cp rings at 842 and 859 cm^{-1}, which are shifted to high frequencies by 26 and 43 cm^{-1}, respectively, relative to the corresponding band of uncoordinated ferrocene. The C—H stretching band of the Cp rings at 3124 cm^{-1} in the IR spectrum of the complex (suspension in hexachlorobutadiene) is also shifted to high frequencies (by 19, 30, and 40 cm^{-1}) compared to the analogous bands (3105, 3094, and 3084 cm^{-1}) for free ferrocene. The ^{199}Hg NMR spectrum of complex **2** in THF ($[\mathbf{2}]_0 = 8 \cdot 10^{-2}$ mol L^{-1}) differs only insignificantly from the spectrum of the starting macrocycle, which is, apparently, due to the displacement of the ferrocene ligand from the complex with a large excess (~150 : 1) of the solvent. However, the addition of excess ferrocene to a solution of compound **2** in THF leads to a noticeable downfield shift of the Hg resonance in the NMR spectrum (by 5 ppm for Cp_2Fe : **2** = 40 : 1). Therefore, complex **2** can exist in THF only in the presence of an excess of ferrocene.

The structure of complex **2** is shown in Fig. 1. The complex is a double-decker sandwich, in which the ferrocene guest is located between the mutually parallel planes of two macrocyclic hosts and is bound to each of these macrocycles through donation of the π-electrons of the η^5-Cp ligands to vacant orbitals of the mercury atoms of the adjacent molecule **1**. The shortest Hg—C distances between the η^5-Cp rings of ferrocene and the macrocycles in compound **2** are observed for the C atoms involved in the C(10)—C(10C) and C(10A)—C(10B) bonds of the η^5-Cp groups. Each of these C atoms interacts only with one mercury center (Hg(2), Hg(2C) and Hg(2A), Hg(2B), respectively). The Hg(2)—C(10), Hg(2C)—C(10C), Hg(2A)—C(10A), and Hg(2B)—C(10B) distances in complex **2** equal to 3.189(10) Å, which is substantially smaller than the sum of the van der Waals radii of the Hg (1.73—2.0 Å,[7,8] 2.1 Å [9]) and C (1.7 Å [9]) atoms. Three other C atoms of each of the η^5-Cp ligands of ferrocene are coordinated to a single mercury center of the adjacent molecule **1** (Hg(1) and Hg(1A), respectively). Here, the central C(12) and C(12A) atoms of these allyl fragments are involved in the shortest Hg—C contacts (3.257(13) Å). Two other C atoms of each of these fragments (C(11), C(11C) and C(11B), C(11A), respectively) form substantially longer Hg—C contacts (3.561(14) Å), which do, however, remain slightly shorter than the distance corresponding to the sum of the van der Waals radii. Therefore, all carbon atoms of the η^5-Cp ligands of ferrocene in complex **2** are, apparently, involved in the bonding to the mercury atoms of molecules **1**.

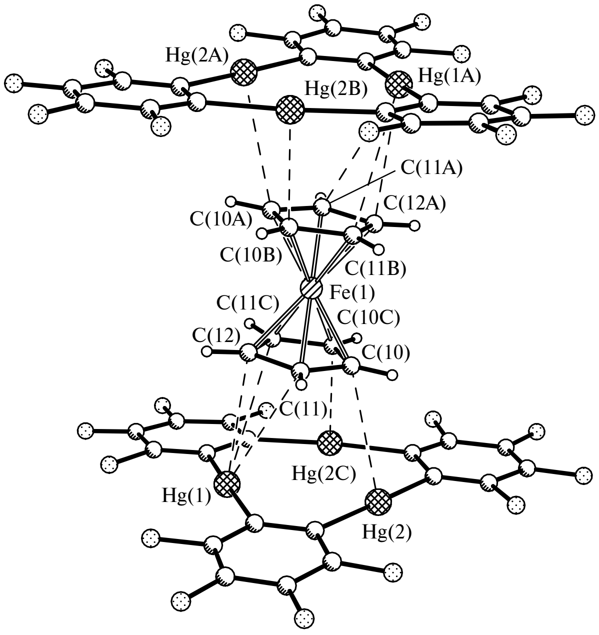

Fig. 1. Molecular structure of complex **2**.

The geometry of the macrocycle and ferrocene changes only slightly upon the complexation. The mutual orientation of molecules **1** in the complex corresponds to a staggered conformation. The planes of the mercuracarbon and Cp rings in compound **2** are not parallel to each other (dihedral angle is 7.3°). In the crystal, the molecules of complex **2** form extended stacks, wherein the external sides of the mercuracarbon rings of each two adjacent molecules **2** face each other (distance between the mean planes is 3.35 Å). The stacks have the shortened intermolecular Hg...Hg (3.3905(9) Å) and Hg...C (3.51, 3.62, 3.78(1) Å) contacts between the adjacent molecules **2**.*

Experimental

Synthesis of complex 2. A solution of ferrocene (0.0093 g, 0.05 mmol) in diethyl ether (2 mL) was added to a solution of macrocycle **1** (0.1044 g, 0.1 mmol) in diethyl ether (38 mL). The reaction mixture was allowed to slowly evaporate at 20 °C until it was concentrated to ~2 mL. After 2 days, red-orange crystals of complex **2** that precipitated were filtered off, washed with diethyl ether (2×1 mL), and dried *in vacuo* at 20 °C. The yield was 0.0845 g (75%). Found (%): C, 24.14; H, 0.34; F, 20.20. $C_{46}H_{10}F_{24}FeHg_6$. Calculated (%): C, 24.25; H, 0.44; F, 20.02.

X-ray diffraction study of complex 2. Crystals are monoclinic, space group $C2/m$, at 220 K a = 10.4099(7), b = 19.451(1), c = 12.2162(9) Å, β = 110.560(2)°, V = 2316.0(3) Å^3, Z = 2,

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* When this paper has been prepared for publication, the synthesis and structure of complex **2** were described in the study.[10]

d_{calc} = 3.266 g cm^{-3}, μ(Mo-Kα) = 202.47 cm^{-1}. The X-ray diffraction data were collected on a Bruker SMART 1000 CCD diffractometer; 3015 independent reflections with 2θ < 58° were measured. The final R_1 factor was 0.0488 for 1894 reflections with $I > 2\sigma(I)$. The atomic coordinates were deposited with the Cambridge Structural Database.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33304).

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Received November 12, 2004