



Coordination chemistry of mercury-containing anticrowns. Synthesis and structure of an unusual discrete, double-decker sandwich complex of cyclic trimeric perfluoro-*o*-phenylenemercury with an aromatic hydrocarbon

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ARTICLE INFO

Article history:

Received 8 March 2010

Accepted 18 April 2010

Available online 24 April 2010

Dedicated to Professor Uwe Rosenthal on the occasion of his 60th birthday

Keywords:

Anticrowns

Arenes

Complexes

[2.2]Paracyclophane

Polymercuramacrocycles

ABSTRACT

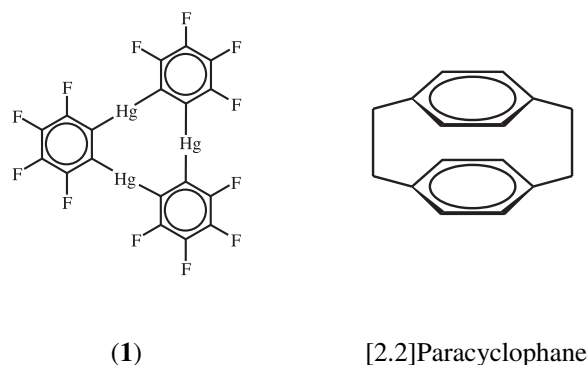
The reaction of the three-mercury anticrown (*o*-C₆F₄Hg)₃ (**1**) with [2.2]paracyclophane (PCP) yields a complex {[*o*-C₆F₄Hg)₃]₂(PCP)} (**2**), having a double-decker sandwich structure in the crystal. The PCP ligand in **2** is located between the mutually parallel planes of the two anticrown units and it coordinates to them by its benzene rings in an η²:η²:η² fashion. As a result of such a type of the bonding, all carbon atoms of the benzene rings of PCP are involved in the coordination to the Lewis acidic Hg sites of the anticrown species. The synthesized **2** is the first example of a discrete, double-decker sandwich complex of macrocycle **1** with an aromatic hydrocarbon as well as the first complex of PCP in which both benzene rings of the PCP molecule are η²:η²:η² bonded to trimetal units.

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1. Introduction

Over the last two decades, there has been a considerable progress in coordination and catalytic chemistry of anticrowns [1], representing charge-reversed analogues of crown ethers and related macrocycles (see e.g. reviews [2–8] and recent papers cited in [9–15]). The presence of several Lewis acidic centres in the macrocyclic chain of anticrowns and, as a consequence, the ability of anticrowns to cooperatively coordinate anions and neutral Lewis bases open new promising prospects for the areas of molecular recognition, organic synthesis and catalysis. One of the most studied anticrowns is cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄Hg)₃ (**1**) [16] containing three Hg atoms in a planar nine-membered ring.

Owing to a strong electron-withdrawing effect of the fluorine substituents and ready steric accessibility of the Hg centres, macrocycle **1** exhibits an extremely high affinity towards various anionic and neutral Lewis basic species [2,4–6,9–15]. As has been established by Gabbaï et al., even such weak Lewis bases as arenes can be bound by this remarkable macrocycle [5,6]. In the case of benzene, the isolated 1:1 adduct forms in the crystal extended binary stacks representing polydecker sandwiches wherein the benzene molecules alternate with the molecules of **1**. A characteristic structural



feature of this adduct is an unprecedented μ₆-η²:η²:η²:η²:η²:η² coordination of each benzene moiety with the Hg atoms of the neighbouring anticrown units [17]. Other tested arenes such as toluene, xylenes, mesitylene, biphenyl, naphthalene, phenanthrene, fluorene, triphenylene and pyrene [5,6] as well as nonplanar, bowl-shaped corannulene and indenocorannulene [18] react with macrocycle **1** in a similar manner giving rise to 1:1 complexes of the analogous, although less symmetrical structure. Organic non-

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benzenoid aromatic compounds such as azulene and 6-(*N,N*-dimethylamino)pentafulvene also yield polydecker sandwiches in the interaction with **1** [19].

In the present article, we report that when macrocycle **1** is introduced into the reaction with such an arene as [2.2]paracyclophane (PCP), a unique 2:1 complex $\{[(o-C_6F_4Hg)_3]_2(PCP)\}$ (**2**), having a discrete, double-decker sandwich structure, is produced.

2. Results and discussion

Slow concentration of a CH_2Cl_2 solution of PCP and **1** to a small volume (**1**:PCP = 2:1) leads to precipitation of a colourless, fine crystalline solid which has been identified as complex **2** on the basis of elemental analysis. The same complex **2** is formed on the use of an excess of PCP in respect to **1** (PCP:**1** = 2:1). Crystals of **2** suitable for the X-ray diffraction study were grown from diethyl ether.

The IR spectrum of **2** (in Nujol mull) shows the band of the C–H out-of-plane bending vibrations of the PCP ligand at $816 (m) cm^{-1}$, which is shifted by $9 cm^{-1}$ to a high-frequency region relative to the corresponding band ($807 (s) cm^{-1}$) of free PCP. The spectrum contains also the weak $\nu(C-H)$ vibration bands of the benzene rings (at 2985, 3014, 3034, 3052 cm^{-1}) and CH_2 groups (at 2866, 2901, 2935 cm^{-1}) of the coordinated PCP (hexachlorobutadiene mull). In the IR spectrum of free PCP, these $\nu(C-H)$ bands are observed at 2987, 3012, 3033, 3056, 3067 and 2851, 2887, 2925, 2953 cm^{-1} , respectively. The room-temperature ^{199}Hg NMR spectrum of **2** in THF ($[2]_0 = 4 \times 10^{-2} M$) practically does not differ from that of free **1** in the same solvent even in the presence of a large excess of PCP (ca. 15:1), thus suggesting the full displacement of the coordinated PCP species from the complex by considerably more basic THF molecules. Attempts to obtain a satisfactory ^{199}Hg NMR spectrum of complex **2** in a less-coordinating solvent such as CD_2Cl_2 failed because of very low solubility of **2** in dichloromethane.

The structure of **2** is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The complex occupies in the crystal a special position on an inversion centre and represents a double-decker sandwich. The PCP ligand in **2** is disposed between the mutually parallel planes of the two mercuramacrocycles and it coordinates to them by its benzene rings through secondary π -

Table 1
Selected bond lengths (Å) and angles ($^\circ$) in complex **2**.

Hg(1)–C(2)	3.110(4)	C(2)–C(3)	1.373(6)
Hg(1)–C(3)	3.557(4)	C(3)–C(4)	1.398(5)
Hg(2)–C(4)	3.455(4)	C(4)–C(5)	1.392(5)
Hg(2)–C(5)	3.377(4)	C(5)–C(6)	1.399(5)
Hg(3)–C(1)	3.447(4)	C(1)–C(7)	1.506(6)
Hg(3)–C(6)	3.390(4)	C(4)–C(8)	1.508(5)
C(1)–C(2)	1.401(7)	C(7)–C(8A) ^a	1.583(6)
C(1)–C(6)	1.399(7)		
C(2)–C(1)–C(6)	116.7(4)	C(3)–C(4)–C(8)	118.6(4)
C(1)–C(2)–C(3)	121.0(4)	C(5)–C(4)–C(8)	123.2(3)
C(2)–C(3)–C(4)	121.3(4)	C(2)–C(1)–C(7)	119.6(4)
C(3)–C(4)–C(5)	116.8(4)	C(6)–C(1)–C(7)	122.5(5)
C(4)–C(5)–C(6)	120.7(4)	C(1)–C(7)–C(8A) ^a	112.9(3)
C(1)–C(6)–C(5)	120.5(4)	C(4)–C(8)–C(7A) ^a	112.6(3)

^a Symmetry transformation $-x+1, -y+2, -z+2$ was used to generate equivalent atoms.

Hg–C interactions. Every Hg centre of the anticrown molecules in **2** forms two relatively short Hg–C contacts with one of the C–C bonds of the nearest benzene unit of PCP and, thus, each of these units is bound to three Hg atoms of **1** in an $\eta^2:\eta^2:\eta^2$ fashion. The resulting Hg–C distances range here from 3.110(4) to 3.557(4) Å (av. 3.39 Å) and they are all within the sum of the van der Waals radii of mercury (1.73–2.00 Å [20a,b], 2.1 Å [20c]) and carbon (1.7 Å [20c]) atoms. As a result of the $\eta^2:\eta^2:\eta^2$ -coordination of the benzene rings of PCP, all their carbon atoms are involved in the bonding to the Lewis acidic Hg sites of the anticrown species. In the previously described 1:1 *p*-xylene complex of **1**, having a polydecker sandwich structure (see above), only four benzene carbon atoms of each *p*-xylene molecule interact with the Hg centres of the neighbouring mercuramacrocycles (Hg–C 3.19(2)–3.48(3) Å; av. 3.35 Å [21]). The shortest Hg–C_{arene} contact (3.052 Å) in the series of arene complexes of macrocycle **1** was observed in the structure of the 1:1 adduct of **1** with nonplanar indenocorannulene [18]. The carbon atoms of the C=C bond connecting the two C₅ rings of indenocorannulene take part in this interaction. In the case of the 1:1 complex of **1** with 6-(*N,N*-dimethylamino)pentafulvene, the corresponding shortest Hg–C contacts (formed by the Hg centres of **1** and the C₅ ring carbon atoms bearing a partial negative charge) are 3.07(2) Å [19].

As in free PCP, the benzene rings of the PCP ligand in **2** adopt a symmetrical boat conformation with equal deviations (0.152 Å) of the C(1) and C(4) atoms from the C(2)C(3)C(5)C(6) plane (the corresponding deviation in free PCP is 0.156 Å [22]). The C–C bond lengths in the benzene rings of the coordinated PCP are in the range 1.373(6)–1.401(7) Å (av. 1.39 Å). In uncoordinated PCP, the analogous C–C distances are equal to 1.392(1) and 1.400(1) Å [22]). The C(1)–C(7), C(4)–C(8) and C(7)–C(8A) bond lengths in **2** (1.506(6), 1.508(5) and 1.583(6) Å) are close to the corresponding distances in neat PCP [22]. The C–Hg–C bond angles in the coordinated mercuramacrocycles (177.1(1), 175.2(1) and 173.8(1) $^\circ$), as in free **1**, are close to 180 $^\circ$.

Noteworthy, the C(2)C(3)C(5)C(6) and C(2A)C(3A)C(5A)C(6A) planes of the PCP benzene units in **2** are not parallel to the planes of the central nine-membered mercuracarbon rings of the anticrown molecules (the dihedral angle is 8.5 $^\circ$). A similar arrangement of an aromatic guest in the space between the planes of the molecules of **1** is realized in the previously reported complexes of **1** with ferrocene [23,24] and nickelocene [23]. In these double-decker sandwich complexes of a sandwich, $\{[(o-C_6F_4Hg)_3]_2(Cp_2M)\}$ (where M = Fe, Ni), the Cp rings of a metallocene are bound to the Hg centres of the adjacent anticrown species and are also not parallel to the planes of the central Hg₃C₆ cycles (the dihedral angles are 7.3 $^\circ$ for M = Fe [24] and 5.2 $^\circ$ for M = Ni [23]).

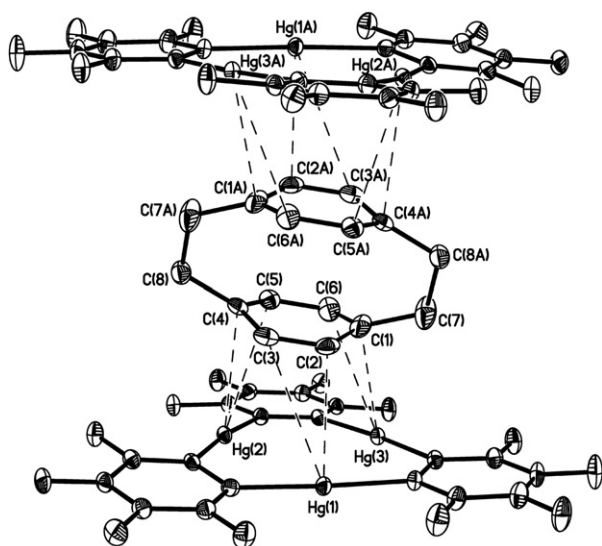


Fig. 1. ORTEP representation of the molecular structure of complex **2** with thermal ellipsoids drawn at the 50% probability level.

The mutual orientation of the mercuramacrocycles in **2** corresponds to a staggered conformation and that of the benzene rings is close (as in free PCP) to an eclipsed conformation. The projections of the centroids of the mercuramacrocycles onto the plane parallel to these cycles are shifted relative to each other by 0.889 Å. The corresponding relative shift of the projections of the centroids of the benzene rings onto the plane parallel to these rings is 0.573 Å, and the torsion C(1)–C(7)–C(8A)–C(4A) angle amounts to 9.8°. In the case of free PCP, no shift of the projections of the centroids of the benzene rings occurs due to *mmm* symmetry of PCP in the crystal [22], and, as a consequence, the above torsion C(1)–C(7)–C(8A)–C(4A) angle is equal to zero.

In the crystal, molecules of **2** are associated into complex structures formed mainly due to intermolecular H...F interactions involving the CH₂ groups of PCP and the fluorine atoms of **1** as well as aromatic stacking interactions between the C₆F₄ rings of the neighbouring molecules of the adduct. The distances between the planes of these C₆F₄ rings in **2** are 3.33 and 3.41 Å and the corresponding intermolecular C...C distances range from 3.222(5) to 3.506(5) Å. The shortest intermolecular H...F distances in the crystal structure of **2** span the range 2.37–2.54 Å.

In summary, the first discrete, double-decker sandwich complex of an aromatic hydrocarbon with macrocycle **1** has been synthesized by the interaction of **1** with PCP. In this adduct, all Hg centres of the anticrown moieties and all carbon atoms of the benzene rings of PCP take part in the bonding. In its reactivity towards **1**, PCP is similar to ferrocene and nickelocene which yield analogous sandwiches in the interaction with this three-mercury macrocycle [23,24]. Previously, Hawthorne and co-workers have described a double-decker sandwich complex of *o*-carboranylmercury anticrown (9,12-Me₂-*o*-C₂B₁₀H₈Hg)₃ with one benzene and two water molecules [25]. The benzene guest in this unusual supramolecular aggregate {[(9,12-Me₂-*o*-C₂B₁₀H₈Hg)₃]₂(C₆H₆)(H₂O)₂} forms the π -hydrogen bonds with the water protons but, in contrast to the benzene rings in **2**, does not interact with the Hg sites of the anticrown species. The ability of PCP to coordinate with trimetal units in an $\eta^2:\eta^2:\eta^2$ fashion has now been established for its complexes with some ruthenium and palladium clusters (see e.g. [26–31]). However in all these complexes, only one benzene ring of PCP takes part in the coordination of such a type, whereas the other ring remains uncoordinated. Thus, the synthesized **2** can be considered as the first example of a structurally characterized PCP complex wherein both benzene moieties of the PCP ligand are involved in an $\eta^2:\eta^2:\eta^2$ bonding to three metal centres.

3. Experimental

The starting macrocycle **1** was prepared according to the published procedure [16a]. Commercial PCP was additionally purified by recrystallization from toluene. Solvents were purified by conventional methods and were distilled prior to use. The IR spectra were measured on a Nicolet Magna-IR 750 Series II Fourier spectrometer. The ¹⁹⁹Hg NMR spectra were recorded on a Bruker Avance-600 instrument using a 0.2 M solution of Ph₂Hg in pyridine ($\delta = -791.1$ ppm [32]) as an external standard.

3.1. Synthesis of complex **2**

To a solution of **1** (0.1044 g, 0.1 mmol) in CH₂Cl₂ (15 mL) was added at room temperature a solution of PCP (0.0100 g, 0.048 mmol) in CH₂Cl₂ (5 mL) and the resulting mixture was allowed to slowly evaporate at 20 °C. After 0.5 h, fine colourless crystals of complex **2** began to precipitate. Then, the mixture was held in a closed system at room temperature for 3 days, after which it was allowed to slowly evaporate for 6 h to 2 mL. The resulting fine

crystalline complex **2** was filtered off, washed with CH₂Cl₂ (3 × 1 mL), and dried in vacuo at 20 °C for 2 h. Yield: 0.0776 g (70%). Anal. Calcd. for C₅₂H₁₆F₂₄Hg₆: C, 27.15; H, 0.70; F, 19.82. Found: C, 26.88; H, 0.71; F, 19.75%.

3.2. X-ray diffraction study of complex **2**

C₅₂H₁₆F₂₄Hg₆, *M* = 2300.19, triclinic, space group *P* $\bar{1}$, *a* = 9.7592(1), *b* = 11.0324(2), *c* = 12.8271(2) Å, α = 110.330(1), β = 108.865(1), γ = 92.826(1)°, *V* = 1204.96(3) Å³, *T* = 100(2) K, *Z* = 1, μ (Mo-K α) = 19.174 mm⁻¹, crystal size 0.24 × 0.16 × 0.12 mm. The single-crystal X-ray diffraction experiment was carried out with a Bruker SMART APEX II diffractometer, using graphite monochromated Mo-K α radiation (λ = 0.71073 Å, ω -scan technique, $2\theta < 62^\circ$) at 100 K. The APEX II software [33] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction (*T*_{min}/*T*_{max} = 0.129/0.217), and SHELXTL [34] was applied for space group and structure determination, refinements, graphics, and structure reporting. A total of 44793 reflections were measured, and 7639 (*R*_{int} = 0.0408) independent reflections were used in further calculations and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares against *F*² in anisotropic (for non-hydrogen atoms) approximation. Hydrogen atoms were placed geometrically and included in the structure factor calculation in the riding motion approximation. The final refinement was converged to *R*₁(*F*) = 0.0208 (for 7041 observed reflections with *I* > 2 σ (*I*)) and *wR*₂(*F*²) = 0.0489 (for all unique reflections), *GOOF* = 1.081; the number of refined parameters is 370.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Project code 08-03-00332) and the Russian Science Support Foundation (K.I.T.).

Appendix A. Supplementary material

CCDC 767760 contains the supplementary crystallographic data for the structural analysis of **2**. 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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