

Crown compounds for anions. Sandwich complexes of cyclic trimeric perfluoro-*o*-phenylenemercury with hexacyanoferrate(III) and nitroprusside anions

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Abstract

Cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄Hg)₃ (**1**) is able to bind hexacyanoferrate(III) and nitroprusside anions to form complexes {[*o*-C₆F₄Hg)₃]₂[Fe(CN)₆]}³⁻ and {[*o*-C₆F₄Hg)₃]₂[Fe(CN)₅NO]}²⁻, respectively, which contain one anionic species per two macrocycles. According to X-ray diffraction data, the complexes have unusual sandwich structures wherein the anionic guest is located between the planes of two molecules of **1** and is coordinated to each of these through two types of Fe–C–N–Hg bridges. One type is the simultaneous coordination of a cyanide ligand to all three Hg centres of the cycle. The other type is the coordination of a cyanide group to a single Hg atom of the macrocycle. In both types, the bonding of the anionic guest with the macrocyclic host is accomplished with the participation of π -electrons of the cyanide ligands. The synthesized compounds are the first examples of host–guest complexes of a macrocyclic multidentate Lewis acid with anionic metal complexes.

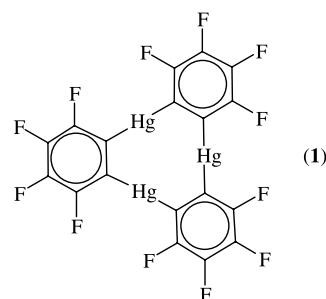
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1. Introduction

Cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄Hg)₃ (**1**) [1,2] which contains three Hg atoms in a planar nine-membered cycle, exhibits a high affinity towards various anions [3] and neutral Lewis bases [4], forming complexes wherein the Lewis basic species is simultaneously bonded to all Hg centres of the macrocycle. This remarkable property of **1**, being reminiscent of the behaviour of crown ethers and their thia and aza analogues in metal cation binding, may find useful applications in organic synthesis, ion transport and catalysis [5] (for complexing properties of other

polymetallamacrocycles, see e.g. [6] and papers cited therein).



One of the intriguing features of macrocycle **1** as a multidentate Lewis acidic host is its inclination to afford sandwich complexes with anions [3]. The first such complexes [(\cdots **1** \cdots X \cdots)_n]^{m-}, formed by bromide and iodide anions (X = Br, I), were found to have unprece-

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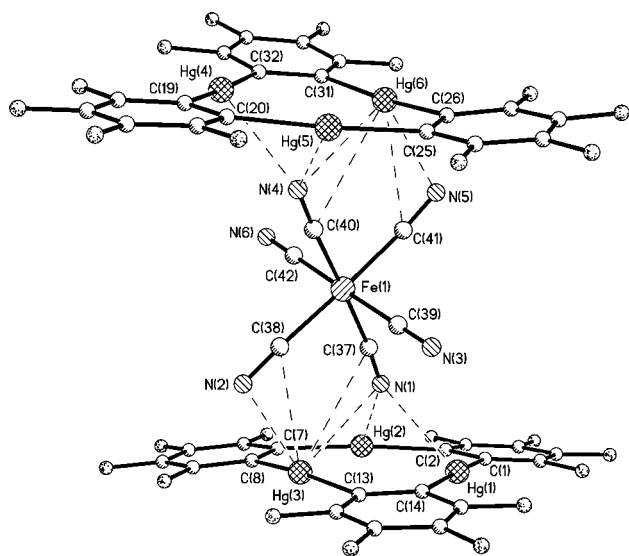


Fig. 1. Structure of the $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2[\text{Fe}(\text{CN})_6]\}^{3-}$ anion in the crystal of complex **2** · Et₂O · 3Me₂CO.

dedent structures of polydecker bent sandwiches [3a,3b]. The role of the coordinating centres in these unique sandwiches is played not by the metal atoms or cations as in the case of normal sandwich complexes but by the anions of the halogen. Recently, we have described the first double-decker sandwich complexes of **1** with anionic species [3e]. The complexes have been isolated from the reactions of **1** with *closo*-[B₁₀H₁₀]²⁻ and *closo*-[B₁₂H₁₂]²⁻ dianions. The anionic guest in these complexes $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2(\text{B}_n\text{H}_n)\}^{2-}$ ($n = 10, 12$) is bonded to the molecules of the macrocycle through B–H–Hg bridges. Similar sandwich $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2(\text{B}_{12}\text{H}_{11}\text{SCN})\}^{2-}$ has been obtained for *closo*-[B₁₂H₁₁SCN]²⁻ ion but here the sulfur atom of the SCN moiety is involved in the coordination to the Hg centres of **1** together with the B–H groups [3f].

In the present paper, we report on a remarkable ability of macrocycle **1** to bind hexacyanoferrate(III) and nitroprusside anions. As a result of the reactions, sandwich complexes $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2[\text{Fe}(\text{CN})_6]\}^{3-}$ (**2**) and $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2[\text{Fe}(\text{CN})_5\text{NO}]\}^{2-}$ (**3**), respectively, are produced. According to X-ray diffraction data, the bonding of the anionic species to the molecules of **1** in these unusual sandwiches is accomplished with the participation of π -electrons of the cyanide ligands. The synthesized compounds are the first examples of host–guest complexes of a macrocyclic multidentate Lewis acid with anionic metal complexes.

2. Results and discussion

Complex **2** has been prepared by the reaction of **1** with (PPN)₃[Fe(CN)₆] in ethanol at room temperature (PPN = (PPh₃)₂N⁺). The isolated compound is a bright

yellow crystalline solid moderately soluble in CH₂Cl₂, poorly soluble in acetone and EtOH and practically insoluble in water, ether, THF and methanol. According to elemental analysis, the complex can be formulated as [PPN]₃{[(*o*-C₆F₄Hg)₃]₂[Fe(CN)₆]}, i.e., contains one [Fe(CN)₆]³⁻ anion per two macrocycle molecules. The IR spectrum of **2** (in Nujol mull) shows the $\nu(\text{CN})$ band at 2079 cm⁻¹ which is shifted by 15–24 cm⁻¹ to a low-frequency region relatively to the $\nu(\text{CN})$ bands (2094, 2098 and 2103 cm⁻¹) in the spectrum of non-coordinated [PPN]₃[Fe(CN)₆]. The electronic spectrum of **2** in CH₂Cl₂ is characterized by an absorption band at 432 nm ($\epsilon = 6.3 \times 10^2$) shifted by 10 nm to a long-wave region as compared to the corresponding band (422 nm, $\epsilon = 5.1 \times 10^2$) for neat [PPN]₃[Fe(CN)₆].

Complex **3** has been obtained by the interaction of **1** with [PPN]₂[Fe(CN)₅NO] at 20 °C in ethanol. The isolated **3** is a grey-brown crystalline solid moderately soluble in acetone and CH₂Cl₂, poorly soluble in EtOH and practically insoluble in water, ether and MeOH. The complex has composition of [PPN]₂{[(*o*-C₆F₄Hg)₃]₂[Fe(CN)₅NO]}, i.e., also contains one anionic species per two molecules of the macrocycle. In the IR spectrum of **3** (Nujol mull), the $\nu(\text{CN})$ band (at 2124 cm⁻¹) is shifted by 11 cm⁻¹ to a low-frequency region while the $\nu(\text{NO})$ band (at 1883 cm⁻¹) is shifted by 14 cm⁻¹ to a high-frequency region in comparison to the $\nu(\text{CN})$ and $\nu(\text{NO})$ bands of free [PPN]₂[Fe(CN)₅NO]. The room-temperature ¹⁹⁹Hg NMR spectrum of **3** in [D₆] acetone ($[\mathbf{3}]_0 = 5.7 \times 10^{-3}$ M) exhibits a broad signal at $\delta = -264.0$ ppm (Ph₂Hg as an external standard) shifted by 50.8 ppm downfield relatively to the corresponding signal of non-coordinated **1**. The electronic spectrum of **3** in CH₂Cl₂ shows no essential differences from that of free [PPN]₂[Fe(CN)₅NO].

Crystals of complex **2** suitable for X-ray diffraction analysis were grown from Me₂CO/Et₂O and contained one ether and three acetone solvate molecules per molecule of **2**. Fig. 1 shows the structure of **2**. Selected bond lengths and angles are given in Table 1. The complex has a sandwich structure wherein the [Fe(CN)₆]³⁻ anion is located between the planes of two molecules of **1** and is coordinated to each of these through two types of Fe–C–N–Hg bridges. One type is the simultaneous bonding of the C(37)–N(1) and C(40)–N(4) cyanide ligands of the [Fe(CN)₆]³⁻ ion to all three Hg centres of the cycle. The Hg–N(1) and Hg–N(4) distances in **2** span the range of 2.719(4)–2.915(5) Å (av. 2.79 Å) and are considerably shorter than the sum of the van der Waals radii of mercury (1.73–2.00 Å [7,8], 2.1 Å [9]) and nitrogen (1.6 Å [9]) atoms. An important structural feature of **2** is a strong deviation (by 35.2° and 32.8°) of the C(37)–N(1) and C(40)–N(4) bond vectors from the perpendicular to the mean plane of the nearest nine-membered mercurocarbon ring towards the Hg(3) and Hg(6) atoms, respectively. As a result, the Hg(3)–C(37) and Hg(6)–

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

Hg(1)–N(1)	2.721(5)	Hg(4)–C(19)	2.074(6)
Hg(2)–N(1)	2.743(4)	Hg(4)–C(32)	2.064(6)
Hg(3)–N(1)	2.915(5)	Hg(5)–C(20)	2.079(6)
Hg(3)–N(2)	2.805(5)	Hg(5)–C(25)	2.070(6)
Hg(4)–N(4)	2.719(4)	Hg(6)–C(26)	2.080(6)
Hg(5)–N(4)	2.725(4)	Hg(6)–C(31)	2.078(6)
Hg(6)–N(4)	2.904(5)	Fe(1)–C(37)	1.924(5)
Hg(6)–N(5)	2.819(5)	Fe(1)–C(38)	1.938(6)
Hg(3)–C(37)	3.256(5)	Fe(1)–C(39)	1.953(6)
Hg(3)–C(38)	3.183(5)	Fe(1)–C(40)	1.908(5)
Hg(6)–C(40)	3.242(5)	Fe(1)–C(41)	1.946(6)
Hg(6)–C(41)	3.205(5)	Fe(1)–C(42)	1.934(6)
Hg(1)–C(1)	2.082(6)	C(37)–N(1)	1.142(6)
Hg(1)–C(14)	2.082(6)	C(38)–N(2)	1.156(7)
Hg(2)–C(2)	2.069(6)	C(39)–N(3)	1.144(7)
Hg(2)–C(7)	2.069(6)	C(40)–N(4)	1.158(6)
Hg(3)–C(8)	2.072(6)	C(41)–N(5)	1.152(7)
Hg(3)–C(13)	2.079(6)	C(42)–N(6)	1.156(7)
C(1)–Hg(1)–C(14)	175.1(2)	C(38)–Fe(1)–C(42)	89.7(2)
C(7)–Hg(2)–C(2)	175.4(2)	C(39)–Fe(1)–C(40)	91.5(2)
C(8)–Hg(3)–C(13)	171.6(2)	C(39)–Fe(1)–C(41)	89.5(2)
C(32)–Hg(4)–C(19)	174.9(2)	C(39)–Fe(1)–C(42)	178.0(2)
C(25)–Hg(5)–C(20)	175.7(2)	C(40)–Fe(1)–C(41)	84.9(2)
C(31)–Hg(6)–C(26)	171.8(2)	C(40)–Fe(1)–C(42)	89.9(2)
C(37)–Fe(1)–C(38)	84.8(2)	C(41)–Fe(1)–C(42)	89.2(2)
C(37)–Fe(1)–C(39)	88.8(2)	N(1)–C(37)–Fe(1)	174.6(5)
C(37)–Fe(1)–C(40)	178.3(2)	N(2)–C(38)–Fe(1)	174.7(5)
C(37)–Fe(1)–C(41)	96.8(2)	N(3)–C(39)–Fe(1)	179.8(5)
C(37)–Fe(1)–C(42)	89.9(2)	N(4)–C(40)–Fe(1)	176.3(5)
C(38)–Fe(1)–C(39)	91.6(2)	N(5)–C(41)–Fe(1)	174.0(5)
C(38)–Fe(1)–C(40)	93.5(2)	N(6)–C(42)–Fe(1)	178.8(5)
C(38)–Fe(1)–C(41)	178.1(2)		

C(40) distances in **2** (3.256(5) and 3.242(5) Å) become notably shorter than the sum of the van der Waals radii of mercury and carbon (1.7 Å [9]) atoms, thus suggesting the involvement of π -electrons of the C(37)–N(1) and C(40)–N(4) cyanide ligands in their bonding to the Hg(3) and Hg(6) centres (for π -interactions between the mercury centres of **1** and benzonitrile and arenes, see [4a,4b,4e]).

Different types of Fe–C–N–Hg bridges are observed for the coordinated C(38)–N(2) and C(41)–N(5) cyanide groups. Each of these is bonded (presumably also with the participation of their π -electrons) only to one Hg atom of the macrocycle (Hg(3) and Hg(6), respectively). The Hg(3)–N(2) and Hg(6)–N(5) distances in **2** are equal to 2.805(5) and 2.819(5) Å while the Hg(3)–C(38) and Hg(6)–C(41) distances are 3.183(5) and 3.205(5) Å. The C(38)–N(2) and C(41)–N(5) bond vectors deviate from the perpendicular to the mean plane of the nearest nine-membered mercuracarbon ring towards the Hg(3) and Hg(6) centres by 45.8° and 43.1°, respectively.

The complexation of the $[\text{Fe}(\text{CN})_6]^{3-}$ anion by **1** leads to a notable distortion of octahedral coordination at the Fe(1) atom and the geometry of the macrocycle. The C(37)–Fe(1)–C(38) and C(40)–Fe(1)–C(41) bond angles in the coordinated $[\text{Fe}(\text{CN})_6]^{3-}$ ion decrease from

90° to 84.8(2)° and 84.9(2)°, respectively, while the C(37)–Fe(1)–C(41) and C(40)–Fe(1)–C(38) bond angles increase from 90° to 96.8(2)° and 93.5(2)°. The C(8)–Hg(3)–C(13) and C(26)–Hg(6)–C(31) bond angles (171.6(2)° and 171.8(2)°, respectively) deviate from 180° somewhat greater than the other C–Hg–C angles in the macrocycles (174.9(2)–175.7(2)°). The coordinated Fe–C–N fragments in **2** also deviate slightly from linearity (the Fe–C–N bond angles are 174.0(5)–176.3(5)°). The equatorial C(37), C(38), C(40) and C(41) atoms as well as the Fe(1) atom are coplanar. The mutual orientation of the macrocyclic units in **2** is close to a staggered conformation. The dihedral angle between the mean planes of the central nine-membered rings of the macrocycles is equal to 11.1°. The centroids of the macrocycles are shifted relatively to each other by 3.88 Å.

Crystals of complex **3** were grown from ethanol. The structure of **3** is presented in Fig. 2. Selected bond lengths and angles are listed in Table 2. The complex occupies in the crystal a special position on an inversion centre which leads to the structure disorder (superposition of the NO and the opposite CN groups) because of asymmetry of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ ion. In Fig. 2, only one of two possible positions for the N(4)–O(1) and C(21)–N(3) ligands as well as for the Fe(1) atom is shown.

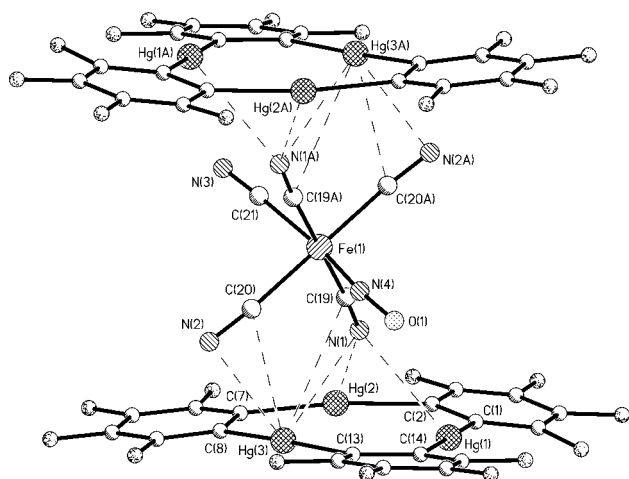


Fig. 2. Structure of the $\{[(o-C_6F_4Hg)_3]_2[Fe(CN)_5NO]\}^{2-}$ anion in the crystal of complex **3**.

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

Hg(1)–N(1)	2.966(7)	Hg(3)–C(13)	2.078(8)
Hg(2)–N(1)	2.834(7)	Fe(1)–C(19)	1.954(8)
Hg(3)–N(1)	3.029(6)	Fe(1)–C(20)	1.956(10)
Hg(3)–N(2)	3.031(7)	Fe(1)–C(19A) ^a	1.976(8)
Hg(3)–C(19)	3.316(8)	Fe(1)–C(20A) ^a	2.021(9)
Hg(3)–C(20)	3.262(8)	Fe(1)–C(21)	1.898(19)
Hg(1)–C(1)	2.064(7)	Fe(1)–N(4)	1.666(17)
Hg(1)–C(14)	2.084(7)	N(4)–O(1)	1.11(2)
Hg(2)–C(2)	2.087(7)	C(19)–N(1)	1.148(9)
Hg(2)–C(7)	2.085(8)	C(20)–N(2)	1.132(10)
Hg(3)–C(8)	2.059(7)	C(21)–N(3)	1.22(3)
C(1)–Hg(1)–C(14)	179.1(3)	C(8)–Hg(3)–C(13)	174.8(3)
C(2)–Hg(2)–C(7)	173.7(3)		

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

Like **2**, complex **3** has also a sandwich structure. The anionic guest in **3** is disposed between the mutually parallel planes of two molecules of **1** and is coordinated to each of them in the same manner as in **2**. The C(19)–N(1) and C(19A)–N(1A) cyanide groups in **3** are simultaneously bonded to all Hg atoms of the neighbouring molecule of **1**. The Hg(1)–N(1), Hg(2)–N(1) and Hg(3)–N(1) bond lengths in **3** are 2.966(7), 2.834(7) and 3.029(6) Å, respectively, while the Hg(3)–C(19) distance is 3.316(8) Å. An additional contribution to the bonding of the $[Fe(CN)_5NO]^{2-}$ ion to **1** is made by the C(20)–N(2) and C(20A)–N(2A) cyanide ligands, each of which is coordinated to a single Hg atom of **1** (Hg(3) and Hg(3A), respectively). The Hg–N distances for these cyanide groups are 3.031(7) Å and the corresponding Hg–C distances (Hg(3)–C(20) and Hg(3A)–C(20A)) are 3.262(8) Å. Notably, all these Hg–N and Hg–C distances are noticeably longer than the corresponding distances in complex **2**. This indicates a weaker coordination of the macrocycles with the anionic guest in **3** as

compared to that in **2** which can be explained by a decrease in the negative charge of the complex anion on going from $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_5NO]^{2-}$.

The C(19), C(20), C(19A) and C(20A) atoms in **3** are located in one plane but the Fe(1) atom deviates from this plane towards the NO group by 0.36 Å. The C(1)–Hg(1)–C(14), C(7)–Hg(2)–C(2) and C(8)–Hg(3)–C(13) bond angles are 179.1(3)°, 173.7(3)° and 174.8(3)°, respectively. The centroids of the macrocycles are shifted relatively to each other by 3.96 Å.

In the crystal, complexes **2** and **3** form extended stacks along the $[011]$ crystallographic direction. The fragment of the crystal packing of complex **2** is shown in Fig. 3. Each two neighbouring molecules of **2** in the stack are linked via inversion centres (different for the “Hg(1)Hg(2)Hg(3)” and “Hg(4)Hg(5)Hg(6)” macrocycles) and face each other by the exterior sides of their mercuracarbon rings. The distances between these juxtaposed rings are 3.39 and 3.36 Å. The mutual orientation of the neighbouring macrocycles in the stacks is close to a staggered conformation and their centroids are shifted relatively to one another by 1.08 and 0.45 Å. The stacks are also characterized by the presence of somewhat shortened intermolecular Hg···Hg and Hg···C contacts between the adjacent molecules of **2** ($Hg(1) \cdots Hg(2A)_{1-x,1-y,1-z}$ 3.780(1) Å, $Hg(4) \cdots Hg(6A)_{1-x,2-y,2-z}$ 3.899(1) Å, $Hg \cdots C$ 3.414(6)–3.531(6) Å). All other intermolecular distances in the structure of **2** including those between the complex anion and the ether and acetone solvate molecules correspond to usual van der Waals contacts.

In the stacks formed by **3**, the neighbouring macrocycles also adopt a staggered mutual orientation but their centroids are shifted with respect to each other considerably stronger (by 4.04 Å) than those in the case of **2** (see above). The shortest Hg···Hg intermolecular distances are equal here to 3.949(1) and 4.042(1) Å while the shortest Hg···C intermolecular distances are 3.300(7) and 3.364(7) Å.

Similar extended stacks with shortened Hg···Hg (3.52–3.91 Å) and Hg···C (3.38–3.47 Å) contacts are formed in crystals of the sandwich complexes of **1** with polyhedral $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$ and $[B_{12}H_{11}SCN]^{2-}$ dianions [3e,3f]. In the case of the cofacial dimers of the pyramidal 1:1 complexes of **1** with neutral molecules of *n*-butyronitrile [4c] and acetone [4f], the shortest Hg···Hg intermolecular contacts are 3.372 and 3.512 Å, respectively, and the shortest intermolecular Hg···C distances are 3.58, 3.59 and 3.40, 3.48 Å.

The measurement of the magnetic susceptibility of complex **2** has shown that its magnetic moment at 295 K is equal to $3.20\mu_B$ which is substantially higher than the corresponding value for non-coordinated $[Fe(CN)_6]^{3-}$ ($2.37\mu_B$). This result can be explained by the ferromagnetic exchange interaction between the Fe(III) centres due to formation of the stacks in the crystal packing of **2**.

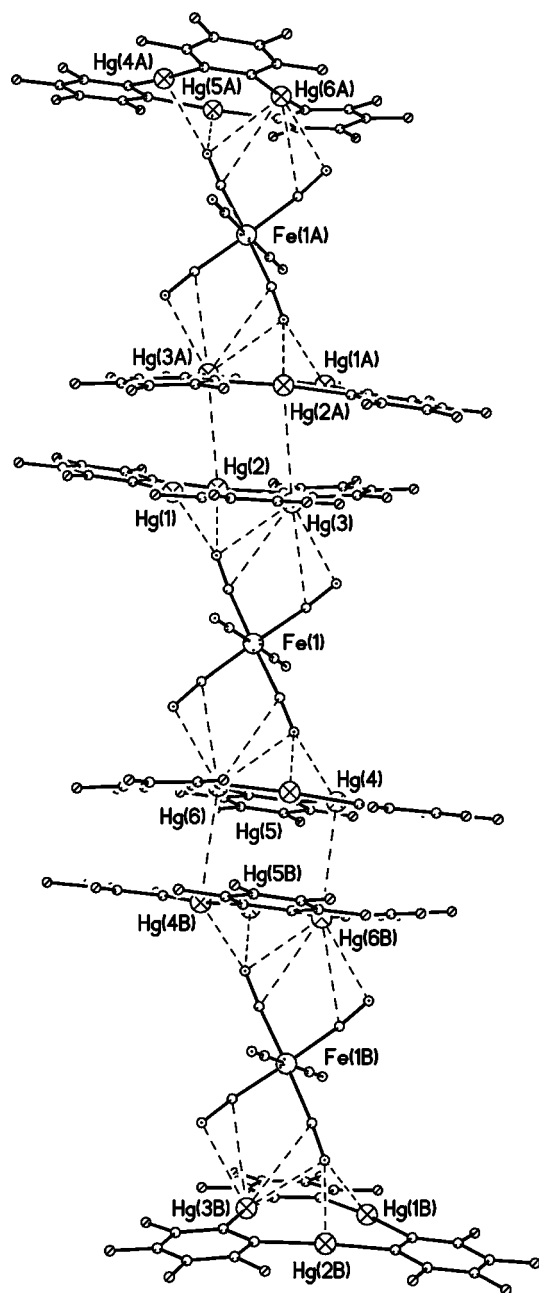


Fig. 3. Fragment of crystal packing of complex **2** · Et₂O · 3Me₂CO.

Macrocycle **1** forms also complex with [Fe(CN)₆]⁴⁻ anion. The structure of this compound is now under investigation.

In summary, the first host–guest complexes of a macrocyclic multidentate Lewis acid with anionic metal complexes have been prepared and structurally characterized. The complexes are formed in the interaction of macrocycle **1** with [Fe(CN)₆]³⁻ and [Fe(CN)₅NO]²⁻ anions and have unusual sandwich structures. A remarkable peculiarity of these sandwiches is the involvement of π -electrons of the cyanide ligands of the anionic guest in its bonding to the Lewis acidic Hg centres.

3. Experimental

The initial [PPN]₃[Fe(CN)₆] and [PPN]₂[Fe(CN)₅NO] were prepared by reactions of an aqueous ethanol solution of PPN⁺Cl⁻ with aqueous solutions of K₃[Fe(CN)₆] and Na₂[Fe(CN)₅NO] · 2H₂O, respectively, and were characterized by elemental analyses and IR spectra. Macrocycle **1** was synthesized by the method described in [1]. The IR spectra were recorded as Nujol mulls on a Specord M-82 instrument. The electronic spectra were taken on a Specord M-40 spectrophotometer in CH₂Cl₂. The ¹⁹⁹Hg NMR spectrum was recorded on a Bruker WP-200 SY instrument using Ph₂Hg as an external standard. Magnetic susceptibility was measured by the Faraday method at 295 K.

3.1. Synthesis of complex **2**

To a solution of **1** (0.1047 g, 0.1 mmol) in ethanol (3 ml) was added at room temperature a solution of [PPN]₃[Fe(CN)₆] (0.0910 g, 0.05 mmol) in ethanol (4 ml). Immediately, a yellow powder of complex **2** began to precipitate. Within 3 days, this yellow powder turned into bright yellow needles of **2** which were filtered, washed with EtOH (2 × 2 ml) and dried at 20 °C in vacuum. The yield of **2** is 0.1404 g (72%). *Anal. Calc.* for C₁₅₀H₉₀F₂₄FeHg₆N₉P₆: C, 45.94; H, 2.30; F, 11.64. *Found:* C, 45.45; H, 2.62; F, 11.17%.

3.2. Synthesis of complex **3**

To a solution of **1** (0.1046 g, 0.1 mmol) in ethanol (2 ml) was added at room temperature a solution of [PPN]₂[Fe(CN)₅NO] (0.0648 g, 0.05 mmol) in ethanol (6 ml) and the reaction mixture was kept overnight at 20 °C. After 14 h, precipitated grey-brown crystals of complex **3** were filtered, washed with EtOH (2 × 2 ml) and dried at 20 °C in vacuum. The yield of **3** is 0.1238 g (74%). *Anal. Calc.* for C₁₁₃H₆₀F₂₄FeHg₆N₈OP₄: C, 40.07; H, 1.77; N, 3.31. *Found:* C, 40.48; H, 1.97; N, 3.22%.

3.3. X-ray diffraction study

Crystals of **2** · Et₂O · 3Me₂CO (0.45 × 0.25 × 0.10 mm, C₁₆₃H₁₁₈F₂₄FeHg₆N₉O₄P₆, *M* = 4167.87) are triclinic, space group *P*-1, *a* = 16.729(1), *b* = 21.716(2), *c* = 22.049(2) Å, α = 110.878(1), β = 90.124(2), γ = 92.634(2), *V* = 7474.9(9) Å³, *Z* = 2, *d*_{calc} = 1.852 g cm⁻³, μ (Mo K α) = 63.85 cm⁻¹. Intensities of 43,365 independent reflections were measured at 110(1) K with a Bruker SMART 1000 CCD diffractometer ($2\theta < 60^\circ$, semiempirical absorption correction from equivalents, min/max transmission factors 0.143/0.568). The refinement converged to *wR*₂ = 0.1045 and GOF = 0.994 for all independent reflections (*R*₁ = 0.0455 was calculated against *F*_{hkl} for 29,293 reflections with *I* > 2 σ (*I*). Crys-

tals of **3** ($0.22 \times 0.20 \times 0.12$ mm, $C_{113}H_{60}F_{24}FeHg_6N_8OP_4$, $M = 3384.96$) are monoclinic, space group $P2_1/n$, $a = 12.636(1)$, $b = 13.782(1)$, $c = 29.668(3)$ Å, $\beta = 94.501(2)^\circ$, $V = 5151.0(9)$ Å³, $Z = 2$, $d_{\text{calc}} = 2.182$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 92.06$ cm⁻¹. Intensities of 15,070 independent reflections were measured at 110(1) K with a Bruker SMART 1000 CCD diffractometer ($2\theta < 60^\circ$, semiempirical absorption correction from equivalents, min/max transmission factors 0.277/0.493). The refinement converged to $wR_2 = 0.1076$ and GOF = 0.866 for all independent reflections $R_1 = 0.0487$ was calculated against F_{hkl} for 8519 reflections with $I > 2\sigma(I)$. Both structures were solved by direct methods and refined by the full-matrix least-squares technique against F_{hkl}^2 in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were fixed in idealized positions and refined isotropically as the riding model. All calculations were carried out using SHELXTL-97 program [10].

4. 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 208193 (**2**·Et₂O·3Me₂CO) and CCDC 208194 (**3**). 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](http://www.ccdc.cam.ac.uk)).

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