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Complexation of cyclic trimeric perfluoro-*o*-phenylenemercury with nitriles. A remarkable sensitivity of the composition and structure of the resulting complexes to the nature of a nitrile

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Abstract

Cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**I**) is capable of reacting with nitriles to form complexes whose composition and structure are dramatically dependent on the nature of the nitrile used. In the case of acrylonitrile, the complex, $[(o\text{-}C_6F_4Hg)_3(CH_2CHCN)]$, containing one nitrile molecule per one molecule of **I** is produced. According to an X-ray structure analysis, the acrylonitrile ligand in this complex is bonded to all Hg atoms of the cycle through the nitrogen atom. The reaction of **I** with acetonitrile gives complex $[(o\text{-}C_6F_4Hg)_3(MeCN)_2]$ which contains two nitrile ligand per one molecule of the macrocycle. This complex has a shape of a spinning top the equatorial girdle of which is the mercury-containing metallacycle, whilst the axis direction is fixed by the linear MeCN ligands located above and below the metallacycle plane. Finally, the isolated complex of **I** with benzonitrile, $[(o\text{-}C_6F_4Hg)_3(PhCN)_3]$, contains three molecules of the coordinated nitrile per one macrocycle molecule. A remarkable structural feature of this complex is that here all the nitrile ligands are located on one side of the metallacycle plane and, in addition, differ from each other in the geometry of coordination with the Hg atoms. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polymercury-containing macrocycles; Nitriles; Complexes; X-ray structure analysis

1. Introduction

During the past decade there has been increasing interest in coordination chemistry of macrocyclic multidentate Lewis acids representing a novel class of promising reagents to the areas of molecular recognition, ion transport and catalysis. A large number of papers on binding of various anionic species by macrocyclic multidentate Lewis acidic hosts has been published [1–4]. The first reports on successful application of such macrocycles in phase transfer catalysis of electrophilic reactions have also appeared [3a,5].

Much less is known on the ability of macrocyclic multidentate Lewis acids to bind neutral Lewis bases [4d,e,f,i,6–8]. In the studies by Wuest et al. [6,7], the complexes of tetramercury-containing macrocycles $[(o\text{-}C_6Me_4HgO(H)Hg)_2]^{2+}$ and $[(o\text{-}C_6Me_4HgOC(O)(CF_2)_3\text{-}C(O)OHg)_2]$ with diethylformamide and 1,2-dimethoxyethane, respectively, have been prepared and structurally characterized. Hawthorne et al. have described the complexes of *o*-carboranylmercury macrocycles with acetonitrile [4e,i], THF [4d] and *o*-phenanthroline [4f].

The complexation with acetonitrile proved to be sensitive to the nature of the starting macrocyclic host. In the case of unsubstituted mercuramacrocycle $(o\text{-}C_2B_{10}H_{10}Hg)_3$, two cocrystallized complexes $[(o\text{-}C_2B_{10}H_{10}Hg)_3(MeCN)_3]$ and $[(o\text{-}C_2B_{10}H_{10}Hg)_3(MeCN)_5]$ have been isolated [4e]. In each of these com-

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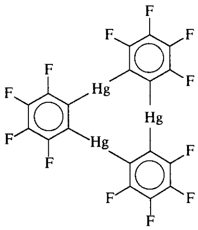
plexes, two acetonitrile ligands are coordinated through the nitrogen atoms with all Hg atoms of the cycle. In contrast to (o-$C_2B_{10}H_{10}Hg)_3$, its hexamethyl derivative (o-$C_2B_{10}H_8Me_2Hg)_3$ gives with acetonitrile the sole complex [(o-$C_2B_{10}H_8Me_2Hg)_3(MeCN)_3$] wherein only one MeCN ligand is simultaneously bonded to all mercury centres of the macrocycle [4i].

Here we wish to report that cyclic trimeric perfluoro-o-phenylenemercury (o-$C_6F_4Hg)_3$ (**I**) [9] which contains three Hg atoms in a planar 9-membered cycle is also capable of reacting with nitriles to form complexes whose composition and structure are dramatically dependent on the nature of the nitrile used.



(I)

A preliminary account of this work has been published in Ref. [10]. For complexing ability of macrocycle **I** towards anionic species, see Refs. [3b,d–g].

2. Results and discussion

The complexes of nitriles (MeCN, PhCN, CH_2=CHCN) with macrocycle **I** are obtained readily under conditions of recrystallization of **I** from the corresponding nitrile as a solvent. The resulting complexes are colourless crystalline solids differing in the amount of nitrile ligands in the molecule. The structure of the complexes has been determined by an X-ray single crystal diffraction study.

In the case of acrylonitrile, the isolated complex is formulated as [(o-$C_6F_4Hg)_3(CH_2CHCN)$] (**II**), i.e. contains one nitrile ligand per one molecule of the macrocycle. In the crystal, complex **II** occupies a special position on a mirror plane passing through all atoms of the acrylonitrile moiety, the Hg(1) atom and the midpoint of the Hg(2)···Hg(2A) line (Fig. 1). The complex has a pyramidal structure with the molecule of acrylonitrile being coordinated to all three Hg atoms of **I** through the nitrogen atom. The Hg–N distances in **II** (see Table 1) are close to each other (2.87(1) and 2.96(1) Å) and are notably smaller than the sum of the Van der Waals radii of the Hg and N atoms (2.1 + 1.6 = 3.7 Å [11]). The N(1)C(10)C(11) bond angle (177(2)°) in the coordinated acrylonitrile is close to 180°. The N(1)–C(10) vector is practically perpendicular to the mean plane of the central 9-membered ring of **I** (the angle between the N(1)–C(10) vector and this plane is 87°).

The IR spectrum of **II** (in Nujol mull) shows not great (6 cm^{-1}) but well reproducible shift of the v_{CN} band to a high-frequency region relatively to the corresponding band (2227 cm^{-1}) in the spectrum of free acrylonitrile. Such 'abnormal' trend of a shift is typical of the complexes of organonitriles with Lewis acids (see, e.g. Refs. [12–15]). The possible reasons of this phenomenon have been discussed in Refs. [12–14].

The crystal packing of **II** is characterized by the short intermolecular Hg···F contacts (Hg(2)···F(6)$_{-1+x,y,z}$ 3.35 Å and Hg(2)···F(9)$_{1+x,y,z}$ 3.42 Å). These contacts being slightly shorter than the sum of the Van der Waals radii of the Hg and F atoms (2.1 + 1.4 = 3.5 Å [11]) are responsible for the association of the molecules of **II** into infinite ladder-like chains along the a-axis of the crystal (Fig. 2). Similar intermolecular Hg···F contacts have been observed previously in the crystal of the chelate complex of 1,2-bis(chloromercurio)tetrafluorobenzene with acetone [16].

Unlike the reaction with acrylonitrile, the reaction of macrocycle **I** with acetonitrile affords complex [(o-

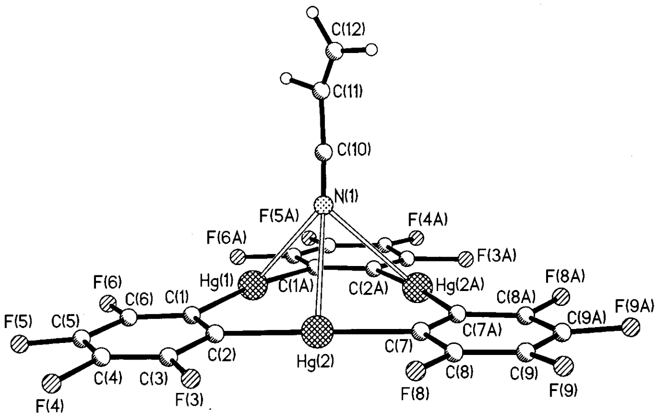


Fig. 1. Molecular structure of complex **II** in the crystal.

Table 1
Selected geometrical parameters for complex **II**

Distances (Å)			
Hg(1)–N(1)	2.87(1)	C(1)–C(2)	1.36(1)
Hg(2)–N(1)	2.96(1)	C(7)–C(7A)	1.34(2)
Hg(1)–C(1)	2.11(1)	C(3)–F(3)	1.37(1)
Hg(2)–C(7)	2.07(1)	C(4)–F(4)	1.36(1)
Hg(2)–C(2)	2.10(1)	C(5)–F(5)	1.32(1)
Hg(1)···Hg(2)	3.614(2)	C(6)–F(6)	1.35(1)
Hg(2)···Hg(2A)	3.571(2)	C(8)–F(8)	1.37(1)
		C(9)–F(9)	1.34(1)
Bond angles (°)			
Hg(1)N(1)C(10)	138(1)	C(2)Hg(2)C(7)	174.3(4)
Hg(2)N(1)C(10)	133(1)	C(2)C(1)Hg(1)	120.9(8)
N(1)C(10)C(11)	177(2)	C(1)C(2)Hg(2)	123.8(8)
C(1)Hg(1)C(1A)	172.8(7)	C(7A)C(7)Hg(2)	122.7(3)
Torsion angles (°)			
Hg(1)C(1)C(2)Hg(2)	0.8	Hg(2)C(7)C(7A)Hg(2A)	0.0

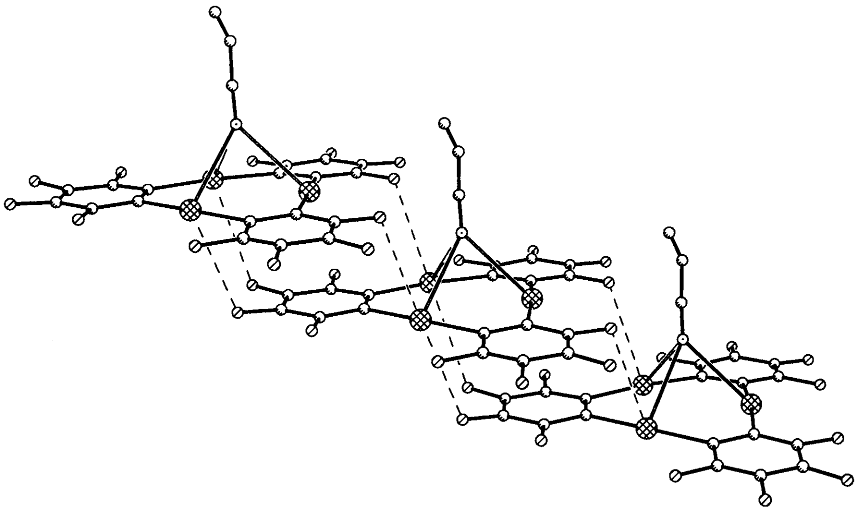


Fig. 2. View of a fragment of the crystal structure of complex **II**, showing the shortest Hg···F contacts between neighbouring molecules of **II**. Hydrogen atoms are omitted for clarity.

$C_6F_4Hg)_3(MeCN)_2]$ (**III**) containing two nitrile ligands per one molecule of **I**. The structure of **III** is shown in Fig. 3. Complex **III** occupies in the crystal a special position on the two-fold axis passing through the Hg(1) atom and the mid-point of the Hg(2)···Hg(2A) line. The complex has a shape of a spinning top, the equatorial girdle of which is the mercury-containing metallacycle, whilst the axis direction is fixed by the MeCN ligands located above and below the metallacycle plane. Each MeCN molecule in **III** is bonded simultaneously through the nitrogen atom to all Hg centres of the cycle. The Hg–N distances in **III** (2.93(1) and 2.99(1) Å; see Table 2) are close to those observed in **II** and again are significantly shorter than the corresponding Van der Waals distance (3.7 Å). The N–C–C fragment in both acetonitrile ligands is practically linear (the N(1)C(10)C(11) bond angle is 179(1)°). The angle between the N(1)–C(10) vector and the mean plane of the central 9-membered cycle of **I** is 88°. The N(1)···N(1A) distance is 4.19(3) Å.

In the crystal of the complex, all intermolecular distances correspond to usual Van der Waals contacts (the shortest distance Hg(1)···F(8) is equal to 3.64 Å). Thus, the crystal of **III**, in contrast to that of **II**, has a true molecular structure built of the isolated molecules of **III** without any specific intermolecular interactions. Interestingly, all macrocyclic planes in the crystal of **III** are normal to the [101] crystallographic direction thus being almost parallel to each other.

Complex **III** is less stable than **II**: on drying in vacuum at r.t. it loses one of the coordinated MeCN molecules to afford mononitrile complex $[(o\text{-}C_6F_4Hg)_3(MeCN)]$ (**IV**). The υ_{CN} band in the IR spectrum of **IV** (Nujol mull) is also shifted to a high-frequency region relatively to the υ_{CN} band for the corresponding free nitrile (2254 cm^{-1}), but in this case the value of the shift is noticeably larger (12 cm^{-1}).

One more type of stoichiometry of complexation is realized in the interaction of **I** with benzonitrile. In this case, the resulting complex, $[(o\text{-}C_6F_4Hg)_3(PhCN)_3]$ (**V**), contains three nitrile ligands per one macrocycle molecule. A remarkable structural feature of **V** is that here all nitrile ligands are located on one side of the metallacycle plane (cf. Ref. [4i]) and, in addition, differ from each other in the geometry of coordination with the Hg atoms (Fig. 4).

One type of the coordination geometry is similar to that in complexes **II** and **III**, being characterized by the simultaneous bonding of the nitrile ligand to all Hg atoms of the cycle. However, as compared to **II** and **III**, this bonding in **V** is more loose and less symmetrical: the Hg(1)–N(1), Hg(2)–N(1) and Hg(3)–N(1) bond lengths are 3.13(1), 3.10(1) and 2.97(1) Å, respectively (Table 3); the angle between the N(1)–C(19) vector and the mean plane of the 9-membered metallacycle (83°) is slightly but significantly different from 90°.

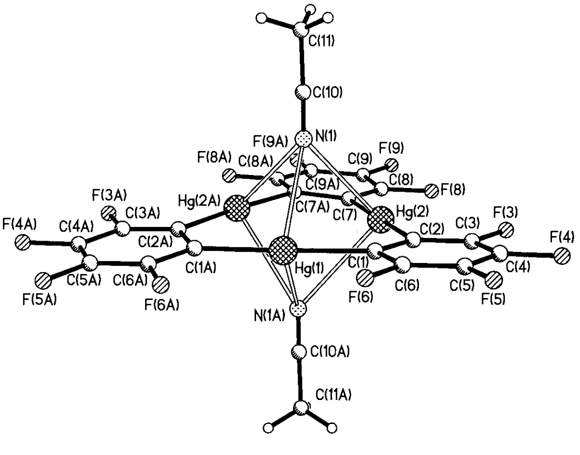


Fig. 3. Molecular structure of complex **III** in the crystal.

Table 2
Selected geometrical parameters for complex **III**

Distances (Å)			
Hg(1)–N(1)	2.99(1)	C(1)–C(2)	1.42(2)
Hg(2)–N(1)	2.93(1)	C(7)–C(7A)	1.40(3)
Hg(1)–C(1)	2.09(1)	C(3)–F(3)	1.36(1)
Hg(2)–C(2)	2.08(1)	C(4)–F(4)	1.37(2)
Hg(2)–C(7)	2.10(1)	C(5)–F(5)	1.35(1)
Hg(1)···Hg(2)	3.605(1)	C(6)–F(6)	1.38(1)
Hg(2)···Hg(2A)	3.573(2)	C(8)–F(8)	1.32(1)
N(1)···N(1A)	4.19(3)	C(9)–F(9)	1.32(1)
Bond angles (°)			
Hg(1)N(1)C(10)	135(1)	C(1)Hg(1)C(1A)	175.8(6)
Hg(2)N(1)C(10)	138(1)	C(2)Hg(2)C(7)	176.9(6)
Hg(2A)N(1)C(10)	133(1)	C(2)C(1)Hg(1)	121.6(10)
N(1)C(10)C(11)	179(1)	C(1)C(2)Hg(2)	121.5(11)
		C(7A)C(7)Hg(2)	121.1(4)
Torsion angles (°)			
Hg(1)C(1)C(2)Hg(2)	3.1	Hg(2)C(7)C(7A)Hg(2A)	5.7

The less symmetrical bonding of the central nitrile ligand in complex **V** than in **II** and **III** can be explained by the presence of the other two benzonitrile ligands in **V**. Each of these is coordinated only to one of the Hg atoms of the macrocycle (Hg(1) and Hg(2), respectively). In the molecule of PhCN attached to the Hg(1) center (see Fig. 4b), the plane of the Ph ring is almost parallel to the corresponding plane of the PhCN ligand bonded to all three Hg atoms of **I** (the dihedral angle between these planes is 5°; the dihedral angles between these planes and the mean plane of 9-membered mercuracarbon ring are 94 and 91°, respectively). The Hg(1)–N(2) bond distance is equal to 2.89(1) Å and the Hg(1)N(2)C(26) bond angle (116°) is much smaller than 180° that might indicate the involvement of p_{π}-electrons of the N(2) atom in the bonding of this PhCN molecule to the macrocycle (cf. Ref. [4e]). Different type of coordination geometry is observed for the PhCN ligand adjacent to the Hg(2) centre. Here, the plane of the Ph ring of the coordinated nitrile is almost parallel to the mean angle of the central 9-membered ring of **I** (the dihedral plane between these planes is 7°). The Hg(2)N(3)C(33) bond angle (105°) deviates even stronger from 180° than the Hg(1)N(2)C(26) angle while the Hg(2)–N(3) bond is elongated up to 3.24(1) Å indicating its considerably smaller strength as compared to other Hg–N bonds in the molecule of **V**. The N(1)C(19)C(20), N(2)C(26)C(27) and N(3)C(33)C(34) bond angles in **V** are close or equal to 180° (177(1), 180(2) and 174(2)°, respectively). The angles between the mean plane of the central 9-membered metallacycle and the N(2)–C(26) and N(3)–C(33) vectors are 51 and 9°, respectively.

The shortest intermolecular contacts in the crystal of **V** are Hg(1)···F(12)$_{x,2.5-y,z}$ 3.19 Å, Hg(3)···F(17)$_{1-x,3-y,2-z}$ 3.26 Å and Hg(3)···F(11)$_{x,2.5-y,-0.5+z}$ 3.53 Å. So short contacts are apparently due to Hg···F attractive interactions leading to the highly networked crystal structure of **V**.

The IR spectrum of **V** is characterized by the υ_{CN} bands at 2221(s) and 2242(sh) cm^{-1}. One of these bands (at 2242 cm^{-1}) is shifted by 11 cm^{-1} to a high-frequency region relatively to the υ_{CN} band of free benzonitrile (2231 cm^{-1}) while the other band (at 2221 cm^{-1}) is shifted by 10 cm^{-1} to a low-frequency region. In contrast to **III**, complex **V** does not change its composition on drying at room temperature (r.t.) in vacuum.

The ^{199}Hg-NMR spectra of **II**, **IV** and **V** in THF solution at r.t. (the initial concentration of **II**, **IV** and **V** is 8×10^{-2} mol l^{-1}) show only negligible differences from the spectrum of starting macrocycle **I** ($[\mathbf{I}]_0 = 8 \times 10^{-2}$ mol l^{-1}; see Ref. [3g]). This may indicate on the displacement of the nitrile ligands from complexes **II**, **IV** and **V** by the molecules of the solvent. The result is quite expectative if one takes into account the Lewis basicity of THF and its very large excess (~ 150:1) with respect to the nitrile complexes. In accordance with this, the addition of the excess of a nitrile to the corresponding nitrile complex in THF solution causes a pronounced downfield shift of the ^{199}Hg-NMR resonance relatively to that of starting **I** (e.g. by 9.1 ppm for **II** at the CH_2CHCN:**II** molar ratio of 38:1, by 9.0 ppm for **IV** at the MeCN:**IV** ratio of 40:1 and by 12.3 ppm for **V** at the PhCN:**V** ratio of 32:1). Such downfield ^{199}Hg-NMR shifts are characteristic of the complexes of multidentate organomercurials with anions and neutral Lewis bases (see e.g. Refs. [3a,g,4d,16,17]).

The central 9-membered mercuramacrocycles in **II**, **III** and **V** are almost planar (maximum displacements from the mean plane are 0.08 Å in **II**, 0.07 Å in **III** and 0.09 Å in **V**) with the HgCCHg torsion angles equal to or smaller than 7° (see Tables 1–3). At the same time, molecules of **I** in **II**, **III** and **V** exibit as a whole, considerable deviations from planarity (up to 0.20, 0.16 and 0.30 Å, respectively), their mercury–carbon frameworks being nonplanar as well (maximum displacements from the mean planes are as large as 0.15 Å in **II**, 0.11 Å in **III** and 0.18 Å in **V**). The Hg–C bond lengths in **II**, **III** and **V** (2.04–2.11 Å) are unexceptional. The CHgC bond angles span the range from 172.8(7) to 177.1(5)°, thus showing the insignificant perturbation of the sp hybridization of the Hg atoms, if any.

3. Conclusions

The results obtained show that macrocycle **I** is able to bind not only various anionic species (see Refs. [3b,d–g]), but also neutral Lewis bases such as nitriles. Depending on the nature of a nitrile used, the isolated complexes (**II**, **III**, **V**) contain one, two and three coordinated molecules of a nitrile, respectively, per one macrocycle molecule.

Complex **II** is the first example of a structurally characterized monomeric 1:1 complex of **I** with a Lewis base. The complex has a symmetrical pyramidal structure. In contrast to **II**, the previously described 1:1 complexes of **I** with bromide and iodide anions form polymeric chains $\{[(o\text{-}C_6F_4Hg)_3X]_n\}^{n-}$ (X = Br, I) in the crystal, which contain pyramidal moieties only as fragments [3b]. A 1:1 complex of **I** with thiocyanate anion is also polymeric in the solid state [3d].

Complex **III** has a symmetrical bipyramidal (spinning top-shaped) structure. Such a type of the coordination geometry is realized in 2:1 complexes of halide anions (Cl^-, Br^-, I^-), *closo*-$B_{10}H_{10}^{2-}$ dianions and diethylformamide with macrocycles $[(CF_3)_2CHg]_5$ [3c,e], $(o\text{-}C_2B_{10}H_8Et_2Hg)_4$ [4f] and $[(o\text{-}C_6Me_4HgO(H)Hg)_2]^{2+}$ [6], respectively. Similar bipyramidal units are present as fragments in the structures of complexes $\{[(o\text{-}C_6F_4Hg)_3X]_n\}^{n-}$ (X = Br, I) [3b] and $[(o\text{-}C_2B_{10}H_{10}Hg)_3(MeCN)_5]$ [4e].

Complex **V** is analogous in its composition to complex $[(o\text{-}C_2B_{10}H_8Me_2Hg)_3(MeCN)_3]$ obtained by Hawthorne et al. [4i]. In both compounds, the RCN ligands are located on one side of the metallacycle plane, with one of them forming a pyramidal structure with the Hg atoms. The unique feature of **V** is that here all three molecules of a nitrile differ from each other in the geometry of coordination with the mercuramacrocycle. In the case of $[(o\text{-}C_2B_{10}H_8Me_2Hg)_3(MeCN)_3]$, two of three RCN ligands are bonded to the metallacycle in the same manner.

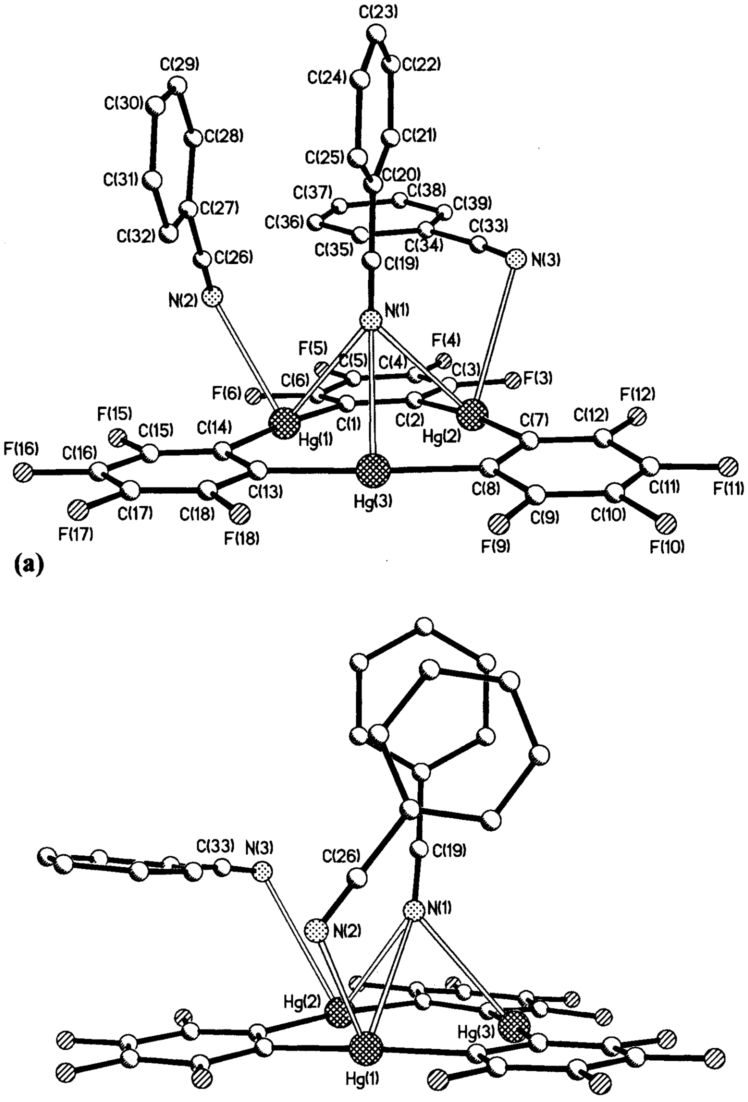


Fig. 4. Two views of the molecule of **V** in the crystal.

Table 3
Selected geometrical parameters for complex **V**

Distances (Å)			
Hg(1)–N(1)	3.13(1)	C(1)–C(2)	1.37(2)
Hg(2)–N(1)	3.10(1)	C(7)–C(8)	1.42(2)
Hg(3)–N(1)	2.97(1)	C(13)–C(14)	1.48(2)
Hg(1)–N(2)	2.89(1)	C(3)–F(3)	1.33(2)
Hg(2)–N(3)	3.24(1)	C(4)–F(4)	1.32(1)
Hg(1)–C(1)	2.06(1)	C(5)–F(5)	1.35(1)
Hg(1)–C(14)	2.07(1)	C(6)–F(6)	1.33(2)
Hg(2)–C(2)	2.07(1)	C(9)–F(9)	1.34(2)
Hg(2)–C(7)	2.07(1)	C(10)–F(10)	1.37(2)
Hg(3)–C(13)	2.04(1)	C(11)–F(11)	1.35(2)
Hg(3)–C(8)	2.05(1)	C(12)–F(12)	1.38(1)
Hg(1)···Hg(2)	3.619(3)	C(15)–F(15)	1.38(1)
Hg(2)···Hg(3)	3.593(3)	C(16)–F(16)	1.33(2)
Hg(1)···Hg(3)	3.574(2)	C(17)–F(17)	1.34(2)
		C(18)–F(18)	1.37(1)
Bond angles (°)			
Hg(1)N(1)C(19)	142(1)	C(1)Hg(1)C(14)	175.4(5)
Hg(2)N(1)C(19)	136(1)	C(2)Hg(2)C(7)	173.7(5)
Hg(3)N(1)C(19)	134(1)	C(8)Hg(3)C(13)	177.1(5)
Hg(1)N(2)C(26)	116(1)	C(2)C(1)Hg(1)	123.0(9)
Hg(2)N(3)C(33)	105(1)	C(1)C(2)Hg(2)	123.0(9)
N(1)C(19)C(20)	177(1)	C(8)C(7)Hg(2)	118.7(9)
N(2)C(26)C(27)	180(2)	C(7)C(8)Hg(3)	124.9(9)
N(3)C(33)C(34)	174(2)	C(14)C(13)Hg(3)	121.3(9)
		C(13)C(14)Hg(1)	120.0(9)
Torsion angles (°)			
Hg(1)C(1)C(2)Hg(2)	0.6	Hg(1)C(14)C(13)Hg(3)	1.4
Hg(2)C(7)C(8)Hg(3)	7.0		

Thus, all of the above nitrile complexes contain at least one fragment wherein a basic nitrogen atom of a nitrile is coordinated simultaneously to all Lewis acidic centres of the macrocycle. This fact impressively illustrates a remarkable property of macrocyclic multidentate Lewis acids to bind cooperatively Lewis basic species.

4. Experimental

The starting macrocycle **I** was prepared by the method described in Ref. [9a]. Commercial acrylonitrile, acetonitrile and benzonitrile were distilled prior to use. The IR spectra were recorded as Nujol mulls on a Specord M-82 instrument. The ^{199}Hg-NMR spectra were taken on a Bruker WP-200 SY spectrometer using Ph_2Hg as an external standard.

*4.1. Synthesis of complex **II***

Compound **I** (0.1 mmol, 105 mg) was dissolved under heating in 3 ml of acrylonitrile and the resulting solution was allowed to stand at r.t. Within 24 h, colourless crystals of complex **II** were precipitated from the solution. The crystals were filtered off and dried at r.t. in vacuum. The yield of **II** was 78 mg (71%). Anal. Calc. for $C_{21}H_3F_{12}NHg_3$: C, 22.91; H, 0.27; F, 20.73; N, 1.27. Found: C, 22.84; H, 0.25; F, 21.15; N, 1.05%. IR (cm^{-1}): 2233(s).

*4.2. Synthesis of complexes **III** and **IV***

Compound **I** (0.1 mmol, 105 mg) was dissolved in 3 ml of acetonitrile under heating and the resulting solution was allowed to stand at r.t. Within 48 h, colourless crystals of complex **III** were formed in the solution. The crystals were filtered off and dried at r.t. in vacuum. Drying of **III** led to loss of one of the coordinated acetonitrile molecules to afford **IV**. The yield of **IV** was 85 mg (78%). Anal. Calc. for $C_{20}H_3F_{12}NHg_3$: C, 22.05; H, 0.27; F, 20.95; N, 1.28. Found: C, 22.13; H, 0.33; F, 20.93; N, 1.26%. IR (cm^{-1}): 2266(s).

*4.3. Synthesis of complex **V***

Complex **V** was obtained, using the same procedure as described above for **II**. The amounts of the reagents were 105 mg (0.1 mmol) of **I** and 3 ml of benzonitrile. Yield of **V** was 71 mg (52%). Anal. Calc. for $C_{39}H_{15}F_{12}N_3Hg_3$: C, 34.51; H, 1.10; F, 16.81; N, 3.10. Found: C, 34.20; H, 1.09; F, 16.75; N, 3.10%. IR (cm^{-1}): 2221(s), 2242(sh).

4.4. X-ray diffraction study

Crystals of **II**, **III** and **V** for an X-ray diffraction study were obtained as described above but were not dried in vacuum. Details of crystal data, data collection and structure refinement parameters for the complexes are given in Table 4. X-ray diffraction experiments were carried out with a Siemens P3/PC diffractometer (graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods. All calculations were performed on IBM PC using SHELXTL PLUS 5 program package [19]. With the exception of carbon atoms in **V**, all non-hydrogen atoms in **II**, **III** and **V** were refined with the anisotropic temperature factors; carbon atoms in **V** were refined isotropically. All H atoms in complexes **II** and **V** were included in the least-squares refinement in the riding model approximation; methyl H atoms in complex **III** were located in the difference map and taken into account as fixed contribution during refinement.

5. Supplementary material

Final positional and thermal parameters for non-hydrogen atoms and full list of bond lengths and angles

Table 4
Crystal data, data collection and structure refinement parameters for **II**, **III** and **V**

Complex	**II**	**III**	**V**
Formula	$C_{21}H_3F_{12}NHg_3$	$C_{22}H_6F_{12}N_2Hg_3$	$C_{39}H_{15}F_{12}N_3Hg_3$
Molecular weight	1099.01	1128.06	1355.31
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$	$C2/c$	$P2_1/c$
a (Å)	7.241(3)	10.384(4)	19.258(13)
b (Å)	15.812(7)	14.536(5)	13.559(9)
c (Å)	9.894(5)	16.527(6)	14.263(10)
β (°)	102.14(4)	99.58(3)	106.34(5)
V (Å^3)	1107.4(9)	2460(2)	3574(4)
Z	2	4	4
D_{calc} (g cm^{-3})	3.296	3.046	2.519
Temperature (K)	293	293	153
Scan mode	ω	$\theta/2\theta$	$\theta/2\theta$
θ_{max} (°)	30	25	25
Absorption coefficient (μ cm^{-1})	208.56	187.82	129.53
Absorption correction	DIFABS [18]	Ψ-scans	DIFABS
Min/max transmission	0.405/1.562	0.082/0.504	0.741/1.513
Unique reflections	3331	2196 [a]	6332
Observed reflections ($I > 2\sigma(I)$)	1757	1521	4224
Parameters	175	177	319
R_1 (on F for observed reflections) [b]	0.0523	0.0464	0.0527
wR_2 (on F^2 for all reflections) [c]	0.1388	0.1206	0.1537
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + F_c^2)/3$		
a,b	0.0360, 0.0000	0.0711, 0.0000	0.0904, 0.0000
Goodness of fit on F^2	0.825	1.043	0.989
Largest difference peak/hole (e Å^{-3})	1.628/−2.100	1.313/−2.129	1.643/−2.265

[a] Due to the deterioration of the crystal check reflections lost half of the initial intensity in the course of the experiment; the correction for crystal decay was successfully applied.

[b] $R_1 = \Sigma |F_o - |F_c|| / \Sigma(F_o)$.

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

for **II**, **III** and **V** have been deposited at the Cambridge Crystallographic Data Centre under registration nos. 138 333, 138 334 and 138 335, respectively. 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).

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