Organometallics **2007,** *26,* 5193−5198

Complexation of [9]Thiacrown-3 and 1,3,5-Trithiane with Cyclic Trimeric Perfluoro-*o*-phenylenemercury. Synthesis and Structures of the First Complexes of Crown Compounds with an Anticrown

Irina A. Tikhonova, Kirill I. Tugashov, Fedor M. Dolgushin, Pavel V. Petrovskii, and
Vladimir B. Shur*

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
Vavilov Street 28, 119991 Moscow, Russia*

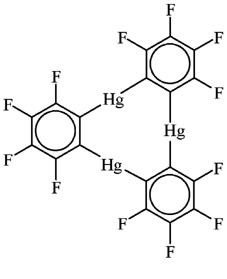
Received May 28, 2007

The interaction of the three-mercury anticrown (o-$C_6F_4Hg)_3$ (**1**) with a 5-fold excess of [9]thiacrown-3 gives a 1:1 complex, $\{[(o\text{-}C_6F_4Hg)_3](C_2H_4S)_3\}$ (**2**), representing a polydecker bent sandwich in the crystal. Every thiacrown ligand in this sandwich is bound to the nearest anticrown units by two sulfur atoms, each of which interacts with a single Hg center of the neighboring molecule of **1**. When the reaction of **1** with [9]thiacrown-3 is conducted at a 2-fold excess of **1**, a complex, $\{[(o\text{-}C_6F_4Hg)_3]_2(C_2H_4S)_3\}$ (**3**), containing two molecules of the mercury anticrown per one thiacrown molecule is produced, and this adduct has a double-decker sandwich structure. Here, all three sulfur atoms of the thiacrown are involved in the bonding to the molecules of the anticrown, two of them being cooperatively coordinated each by all three Lewis acidic Hg sites of the adjacent anticrown molecule, whereas the third sulfur atom interacts again with a single Hg center. From the reaction of **1** with 1,3,5-trithiane, a 1:1 complex, $\{[(o\text{-}C_6F_4Hg)_3](CH_2S)_3\}$ (**4**), has been isolated. This complex, in contrast to **2**, has a discrete, cage structure. The synthesized adducts are the first complexes of crown compounds with an anticrown.

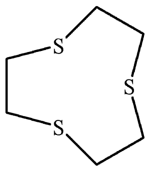
Introduction

Anticrowns,[1] whose coordination and catalytic chemistry has attracted considerable attention over the last two decades (see, for example, reviews[2−7] and recent papers cited in ref 8), are peculiar antipodes of conventional crown compounds. In contrast to crown ethers and their thia and aza analogues, representing macrocyclic multidentate Lewis bases and exhibiting a high affinity for cationic species, the molecules of anticrowns contain several Lewis acidic centers in the macrocyclic chain and so readily coordinate various anions and neutral Lewis bases to form complexes wherein all Lewis acidic sites of a macrocyclic host take part, as a rule, in the binding of a Lewis basic guest. This charge-reverse analogy between crown compounds and anticrowns suggests the possibility of their complexation with one another.

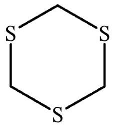
Among presently known anticrowns, particularly efficient are polymercuramacrocycles with the electron-withdrawing perfluorohydrocarbon[2,4,8] and *o*-carborane[3,7,9] backbones. For these macrocycles, a large variety of complexes with different anions and neutral Lewis bases have been prepared and structurally characterized. In the present article, we report the ability of one of such macrocycles, viz., cyclic trimeric perfluoro-*o*-phenylenemercury (o-$C_6F_4Hg)_3$ (**1**),[10] to bind [9]thiacrown-3 (1,4,7-trithiacyclononane) with the formation of complexes $\{[(o\text{-}C_6F_4Hg)_3](C_2H_4S)_3\}$ (**2**) and $\{[(o\text{-}C_6F_4Hg)_3]_2(C_2H_4S)_3\}$ (**3**) containing one and two anticrown molecules, respectively, per one molecule of the thiacrown. The complexation of **1** with the simplest representative of thiacrowns, viz., 1,3,5-trithiane, to afford the corresponding 1:1 adduct $\{[(o\text{-}C_6F_4Hg)_3](CH_2S)_3\}$ (**4**), is also described. The synthesized adducts are the first complexes of crown compounds with an anticrown.



(**1**)



[9]thiacrown-3



1,3,5-trithiane

Results and Discussion

Complex **2** is readily formed in 72% isolated yield in the interaction of **1** at room temperature with a 5-fold excess of [9]thiacrown-3 in CH_2Cl_2. When the reaction of **1** with the thiacrown is conducted at a 2-fold excess of the mercury anticrown, complex **3** is produced in a yield of 79%. Both

---

* Corresponding author. E-mail: vbshur@ineos.ac.ru.

(1) This term was first proposed by Hawthorne et al. in: Yang, X.; Zheng, Z.; Knobler, C. B.; Hawthorne M. W. *J. Am. Chem. Soc.* **1993**, *115*, 193.

(2) Shur, V. B.; Tikhonova, I. A. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Steed, J. W., Eds.; Marcel Dekker: New York, 2004; p 68.

(3) Wedge, T. J.; Hawthorne, M. F. *Coord. Chem. Rev.* **2003**, *240*, 111.

(4) Shur, V. B.; Tikhonova, I. A. *Izv. Akad. Nauk, Ser. Khim.* **2003**, 2401 (*Russ. Chem. Bull., Int. Ed. Engl.* **2003**, *52*, 2539).

(5) Haneline, M. R.; Taylor, R. E.; Gabbaï, F. P. *Chem.*−*Eur. J.* **2003**, *21*, 5188.

(6) Wuest, J. D. *Acc. Chem. Res.* **1999**, *32*, 81.

(7) Hawthorne, M. F.; Zheng, *Z. Acc. Chem. Res.* **1997**, *30*, 267.

(8) Tikhonova, I. A.; Tugashov, K. I.; Dolgushin, F. M.; Yakovenko, A. A.; Petrovskii, P. V.; Furin, G. G.; Zaraisky, A. P.; Shur, V. B. *J. Organomet. Chem.* **2007**, *692*, 953.

(9) Bayer, M. J.; Jalisatgi, S. S.; Smart, B.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1854.

(10) (a) Sartori, P.; Golloch, A. *Chem. Ber.* **1968**, *101*, 2004. (b) Ball, M. C.; Brown, D. S.; Massey, A. G.; Wickens, D. A. *J. Organomet. Chem.* **1981**, *206*, 265.

10.1021/om700526w CCC: $37.00

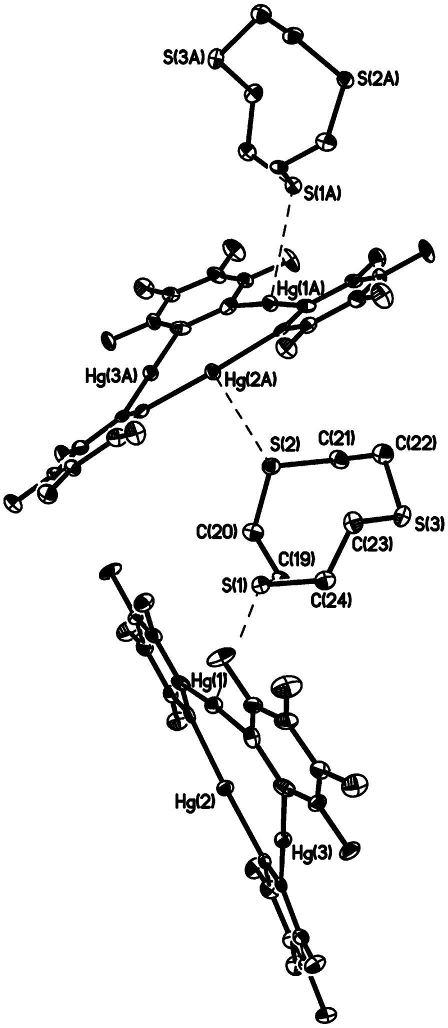


Figure 1. ORTEP representation of the molecular structure of complex **2** with thermal ellipsoids drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Complex 2

Bond Lengths			
Hg(1)−S(1)	3.139(2)	C(20)−S(2)	1.809(8)
Hg(2A)−S(2)[a]	3.194(2)	C(21)−S(2)	1.813(7)
C(24)−S(1)	1.807(8)	C(22)−S(3)	1.812(8)
C(19)−S(1)	1.823(7)	C(23)−S(3)	1.836(7)
Bond Angles			
C(19)−S(1)−C(24)	104.7(3)	C(22)−C(21)−S(2)	114.8(5)
C(20)−S(2)−C(21)	102.2(4)	C(21)−C(22)−S(3)	116.3(6)
C(22)−S(3)−C(23)	104.9(4)	C(24)−C(23)−S(3)	113.1(5)
C(20)−C(19)−S(1)	112.4(5)	C(23)−C(24)−S(1)	115.3(6)
C(19)−C(20)−S(2)	113.6(5)		

[a] Symmetry transformation 1.5−*x*, −0.5+*y*, 0.5−*z* was used to generate equivalent atoms.

complexes are colorless crystalline solids stable to air. The room-temperature ^{199}Hg NMR spectra of **2** and **3** in THF ($[\mathbf{2}]_0 = [\mathbf{3}]_0 = 8 \times 10^{-2}$ M) are characterized by a downfield ^{199}Hg shift of 5 ppm relative to that of free **1**. In the presence of an excess of [9]thiacrown-3 (ca. 20:1), the value of this downfield shift increases to 40 ppm.

The structure of complex **2** is shown in Figure 1. Selected bond lengths and angles for **2** are listed in Table 1. The complex forms in the crystal infinite chains, representing polydecker bent sandwiches wherein the [9]thiacrown-3 molecules alternate with the molecules of the mercury anticrown. Every thiacrown ligand in the sandwich is bound to the nearest anticrown units by two sulfur atoms, each of which interacts with a single Hg center of the neighboring molecule of **1**. The Hg(1)−S(1) and Hg(2A)−S(2) distances in **2** are 3.139(2) and 3.194(2) Å, respectively, which is substantially shorter than the sum of the van der Waals radii of mercury (1.73−2.00 Å,[11a,b]2.1 Å[11c]) and sulfur (2.03 Å[11d]) atoms. These Hg−S distances are comparable to the Hg−S bond length (3.138(4) Å) found in the 1:1 complex of **1** with bis(2-hydroxyethyl)sulfide whose sulfur atom is also coordinated in the adduct only to one Hg atom of the anticrown.[12] Interestingly, the planes of the central Hg_3C_6 rings of the adjacent mercuramacrocycles in **2** are almost perpendicular to each other (the interplane angle is 79.0°). The infinite chains in the crystal structure of **2** are linked with one another through shortened (as compared to the sum of the van der Waals radii) intermolecular Hg···Hg (3.4072(4) Å), Hg···C (3.58(1)−3.74(1) Å), and Hg···F (3.35(1) and 3.56(1) Å) contacts. The previously described 1:1 complexes of **1** with thiocyanate ion[13] and dimethyl sulfide[14] also have polydecker bent sandwich structures in the crystal, but in these sandwiches all six Hg atoms of the juxtaposed molecules of the anticrown take part in the interaction with the sulfur atom of the Lewis basic guest (the Hg−S distances are 3.06(1)−3.87(1) Å in the thiocyanate adduct and 3.543(7)−3.571(3) Å in the dimethyl sulfide adduct).

The unit cell of complex **3** contains two independent molecules (**3A** and **3B**). The structure of one of these molecules (**3A**) is presented in Figure 2. The complex constitutes a double-decker sandwich in which the molecule of [9]thiacrown-3 is located between the mutually parallel planes of two anticrown molecules and is bonded to each of these through Hg−S secondary interactions. A distinctive feature of **3** is that here all three sulfur atoms of the thiacrown are involved in the coordination with the molecules of **1**, two of them being cooperatively bonded each by all three Lewis acidic Hg sites of the adjacent anticrown molecule, whereas the third sulfur atom interacts, as in **2**, with a single Hg center. The resulting Hg−S distances (Table 2) range from 3.181(4) to 3.632(4) Å in **3A** (av 3.38 Å) and from 3.123(4) to 3.590(4) Å in **3B** (av 3.39 Å), and they are all again within the sum of the van der Waals radii of mercury and sulfur atoms. The mutual orientation of the mercuramacrocycles in **3** is close to an eclipsed conformation, and the projections of their centroids onto the plane parallel to these cycles are shifted relative to each other by 1.63 Å. In the previously reported 2:1 complex of **1** with tetrathiafulvalene (TTF), the molecule of a sulfur-containing guest is also sandwiched by two anticrown molecules;[15] however in this adduct only two Hg centers of each molecule of **1** interact with the sulfur atoms (the Hg−S distances span the range 3.467(5)−3.533(5) Å). In the 1:2 complex of **1** with methylparathion, having a bipyramidal structure, the Hg−S bond lengths are in the range 3.278(3)−3.651(3) Å (av 3.42 Å),[12] and in the 1:4 complex of **1** with dimethyl sulfide they are 3.198(7)−3.508(7) Å (av 3.37 Å).[14]

In the crystal, complex **3** forms extended stacks due to shortened intermolecular Hg···Hg and Hg···C contacts between the neighboring molecules of the adduct (**3A**: Hg···Hg 3.642-

---

(11) (a) Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta* **1980**, *45*, L225. (b) Pyykkö, P.; Straka, M. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2489. (c) Batsanov, S. S. *Zh. Neorg. Khim.* **1991**, *36*, 3015. (d) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr., Sect. B* **1985**, *41*, 274.

(12) Tsunoda, M.; Gabbaï, F. P. *Heteroat. Chem.* **2005**, *16*, 292.

(13) Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T.; Gavrilova, A. N.; Saitkulova, L. N.; Shubina, E. S.; Epstein, L. M.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **1996**, *508*, 271.

(14) Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2003**, *125*, 10492.

(15) Haneline, M. R.; Gabbaï, F. P. *C. R. Chim.* **2004**, *7*, 871.

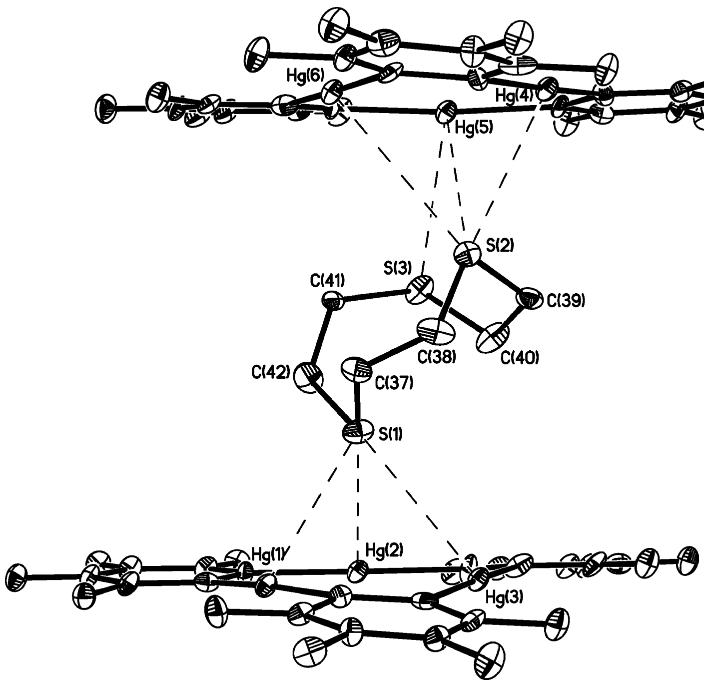


Figure 2. ORTEP representation of the molecular structure of complex **3A** with thermal ellipsoids drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Two Independent Molecules 3A/3B

	Bond Lengths		
Hg(1)−S(1)	3.192(4)/3.211(4)	C(37)−S(1)	1.822(17)/1.846(16)
Hg(2)−S(1)	3.445(4)/3.399(4)	C(42)−S(1)	1.800(17)/1.835(17)
Hg(3)−S(1)	3.337(4)/3.385(4)	C(38)−S(2)	1.804(16)/1.790(16)
Hg(4)−S(2)	3.181(4)/3.123(4)	C(39)−S(2)	1.825(18)/1.837(17)
Hg(5)−S(2)	3.491(4)/3.543(4)	C(40)−S(3)	1.827(19)/1.820(16)
Hg(6)−S(2)	3.632(4)/3.590(4)	C(41)−S(3)	1.884(17)/1.836(16)
Hg(5)−S(3)	3.394(5)/3.500(5)		
	Bond Angles		
C(42)−S(1)−C(37)	104.4(9)/104.3(9)	C(40)−C(39)−S(2)	117.7(13)/114.4(12)
C(38)−S(2)−C(39)	107.2(8)/106.2(9)	C(39)−C(40)−S(3)	116.8(13)/114.5(12)
C(40)−S(3)−C(41)	106.7(8)/106.2(8)	C(42)−C(41)−S(3)	117.5(13)/120.6(13)
C(38)−C(37)−S(1)	116.4(13)/115.2(12)	C(41)−C(42)−S(1)	117.7(13)/119.1(13)
C(37)−C(38)−S(2)	116.1(11)/116.5(12)		

(1) and 3.908(1) Å, Hg···C 3.36(2)−3.86(2) Å; **3B**: Hg···Hg 3.649(1) and 3.900(1) Å, Hg···C 3.34(2)−3.82(2) Å). The stacks are disposed along the *c* crystal axis and are linked with each other through shortened intermolecular Hg···F contacts (3.30(2)−3.45(2) Å). The distances between the mean planes of the central Hg_3C_6 rings of the adjacent mercuramacrocycles in the stack are 3.41 and 3.44 Å for **3A** and 3.39 and 3.43 Å for **3B**. The mutual orientation of these juxtaposed rings corresponds again to an eclipsed conformation. The formation of similar extended stacks (Hg···Hg 3.39−3.91 Å, Hg···C 3.38−3.78 Å) was previously observed in the crystal packing of the double-decker sandwich complexes of **1** with *closo*-$[B_{10}H_{10}]^{2-}$, *closo*-$[B_{12}H_{12}]^{2-}$, *closo*-$[B_{12}H_{11}SCN]^{2-}$, $[Fe(CN)_6]^{3-}$, and $[Fe(CN)_5(NO)]^{2-}$ anions[16−18] as well as with metallocenes[19,20] and *p*-benzoquinone.[21] By contrast, the double-decker sandwich complexes of **1** with TTF[15] and the keto form of acetylacetone[22] do not form extended stacks in the crystal.

The coordinated thiacrown molecule in complexes **2** and **3** loses its crown conformation, but the C−S distances and the C−C−S and C−S−C bond angles in both these adducts remain close to those in free [9]thiacrown-3.[23] The complexation of **1** with [9]thiacrown-3 does not practically affect the geometry of the mercuramacrocycle.

Complex **4** was prepared in 75% isolated yield by the reaction of equimolar amounts of **1** and 1,3,5-trithiane in CH_2Cl_2 at 20°C and also represents a colorless crystalline solid stable to air. The use of an excess of trithiane (5:1) in this reaction has no effect on the composition of the resulting adduct. The room-temperature ^{199}Hg NMR spectrum of **4** in THF ($[\mathbf{4}]_0 = 8 \times 10^{-2}$ M) shows a downfield ^{199}Hg shift of 5 ppm relative to

---

[16] Shubina, E. S.; Tikhonova, I. A.; Bakhmutova, E. V.; Dolgushin, F. M.; Antipin, M. Yu.; Bakhmutov, V. I.; Sivaev, I. B.; Teplitskaya, L. N.; Chizhevsky, I. T.; Pisareva, I. V.; Bregadze, V. I.; Epstein, L. M.; Shur, V. B. *Chem.*−*Eur. J.* **2001**, *7*, 3783.

[17] Tikhonova, I. A.; Shubina, E. S.; Dolgushin, F. M.; Tugashov, K. I.; Teplitskaya, L. N.; Filin, A. M.; Sivaev, I. B.; Petrovskii, P. V.; Furin, G. G.; Bregadze, V. I.; Epstein, L. M.; Shur, V. B. *Izv. Akad. Nauk, Ser. Khim.* **2003**, 570 (*Russ. Chem. Bull., Int. Ed. Engl.* **2003**, *52*, 594).

[18] Tikhonova, I. A.; Dolgushin, F. M.; Tugashov, K. I.; Ellert, O. G.; Novotortsev, V. M.; Furin, G. G.; Antipin, M. Yu.; Shur, V. B. *J. Organomet. Chem.* **2004**, *689*, 82.

[19] Haneline, M. R.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 5471.

[20] Tikhonova, I. A.; Dolgushin, F. M.; Tugashov, K. I.; Petrovskii, P. V.; Antipin, M. Yu.; Shur, V. B. *Izv. Akad. Nauk, Ser. Khim.* **2004**, 2754 (*Russ. Chem. Bull., Int. Ed. Engl.* **2004**, *53*, 2871).

[21] Tikhonova, I. A.; Dolgushin, F. M.; Yakovenko, A. A.; Tugashov, K. I.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *Organometallics* **2005**, *24*, 3395.

[22] Tikhonova, I. A.; Yakovenko, A. A.; Tugashov, K. I.; Dolgushin, F. M.; Novikov, V. V.; Antipin, M. Yu.; Shur, V. B. *Organometallics* **2006**, *25*, 6155.

[23] Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068.

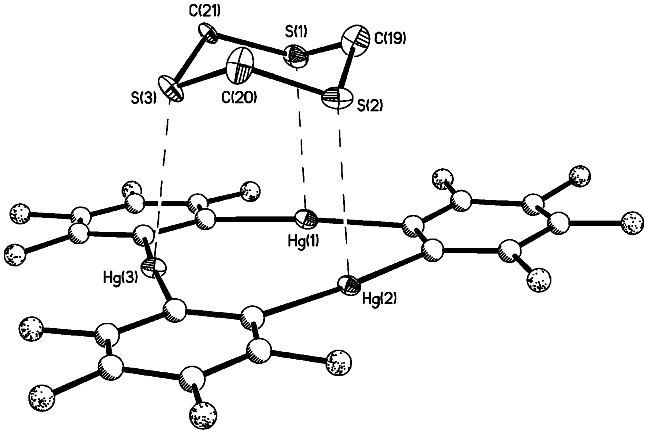


Figure 3. Molecular structure of complex **4A** with thermal ellipsoids for the sulfur and carbon atoms of trithiane and the mercury atoms of the macrocycle drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Four Independent Molecules 4A−4D

	4A	4B	4C	4D
Bond Lengths				
Hg(1)−S(1)	3.112(6)	3.132(6)	3.148(6)	3.186(7)
Hg(2)−S(2)	3.244(6)	3.300(7)	3.168(6)	3.190(7)
Hg(3)−S(3)	3.246(6)	3.259(6)	3.197(7)	3.230(6)
C(19)−S(1)	1.80(2)	1.82(2)	1.75(3)	1.76(3)
C(21)−S(1)	1.78(2)	1.79(3)	1.81(3)	1.81(4)
C(19)−S(2)	1.80(2)	1.83(2)	1.81(3)	1.79(3)
C(20)−S(2)	1.80(2)	1.79(2)	1.83(3)	1.83(3)
C(20)−S(3)	1.82(2)	1.84(2)	1.80(3)	1.77(2)
C(21)−S(3)	1.82(2)	1.81(2)	1.76(3)	1.77(3)
Bond Angles				
C(19)−S(1)−C(21)	102(1)	102(1)	99(1)	99(2)
C(19)−S(2)−C(20)	102(1)	101(1)	99(1)	101(2)
C(20)−S(3)−C(21)	101(1)	101(1)	99(1)	100(2)
S(1)−C(19)−S(2)	116(1)	116(1)	118(2)	119(2)
S(2)−C(20)−S(3)	114(1)	115(1)	115(1)	116(1)
S(1)−C(21)−S(3)	117(1)	117(2)	118(1)	118(2)

that of neat **1**. On the introduction of an excess of trithiane with respect to **4** (1.5:1), the value of this downfield shift is enhanced to 17 ppm.

An X-ray diffraction study of complex **4** has shown that the unit cell of **4** contains four independent molecules (**4A**−**4D**), and the complex itself, in contrast to complex **2**, analogous in its composition, has a discrete, cage structure (Figure 3). Both **1** and the trithiane molecule in **4** behave as tridentate ligands and are coordinated to each other in a face-on fashion. The Hg−S distances in **4A**−**4D** are in the range 3.112(6)−3.300(7) Å (av 3.20 Å; Table 3). The trithiane ligand in the complex retains its chair conformation,[24] and the geometry of **1** does not change essentially upon its complexation. The plane formed by the sulfur atoms of the coordinated trithiane in **4** is practically parallel to the mean plane of the central nine-membered cycle of **1** (the average interplane angle in **4A**−**4D** is 1.7°). In the crystal, complex **4** is associated into centrosymmetric cofacial dimers due to shortened intermolecular Hg···Hg (3.737(3)−3.939(3) Å) and Hg···C (3.44(3)−3.62(2) Å) contacts between the adjacent molecules of **4**. The previously reported 1:1 complexes of **1** with nitrobenzene,[8] *n*-butyronitrile,[25] and acetone[26] also form cofacial dimers in the crystal (Hg···Hg 3.372−3.512 Å, Hg···C 3.402−3.617 Å), but intermolecular Hg···Hg contacts in these dimers are considerably shorter than in the case of **4**.

The formation of **4** from 1,3,5-trithiane and **1** can be considered as a peculiar neutralization reaction of a cyclic multidentate Lewis acid with a cyclic multidentate Lewis base.

Conclusion

Macrocycle **1** is able to bind [9]thiacrown-3 in a CH_2Cl_2 solution with the formation of complexes whose composition and structure depend on the reagent ratio. The use of a large excess of [9]thiacrown-3 in the reaction with **1** affords 1:1 complex **2**, having a polydecker bent sandwich structure in the crystal. However, when a 2-fold excess of **1** with respect to [9]thiacrown-3 is used, 2:1 complex **3**, having a double-decker sandwich structure, is produced. A quite different behavior in the reaction with **1** in CH_2Cl_2 is demonstrated by 1,3,5-trithiane. Here, 1:1 complex **4** is formed both at the equimolar reagent ratio and at an excess of a thiacrown, and this adduct, in contrast to **2**, has a discrete, cage structure. In the case of **2**, only two of three sulfur atoms of the thiacrown and only two of three Hg centers of the anticrown take part in the bonding. By contrast, in the case of **3** and **4**, all three sulfur atoms of the thiacrown molecule and all three Hg sites of the anticrown are involved in the complexation.

The ^{199}Hg NMR data show that the downfield shift of the ^{199}Hg resonance of complexes **2**−**4** in THF relative to free **1** is very small (5 ppm; $[\mathbf{2}]_0 = [\mathbf{3}]_0 = [\mathbf{4}]_0 = 8 \times 10^{-2}$ M), thus indicating that the overwhelming part of the dissolved adducts is destroyed here as a result of the displacement of the coordinated thiacrown species by a large excess (∼150:1) of THF. However, when an excess of the corresponding thiacrown is present in a THF solution of **2**−**4**, the value of this downfield shift is significantly augmented (to 40 ppm for **2** and **3** at the thiacrown/adduct molar ratio of 20:1 and to 17 ppm for **4** at the thiacrown/adduct ratio of 1.5:1), which is evidence of a considerable enhancement in the thiacrown adduct concentration under such conditions. As is known, CH_2Cl_2 is a much weaker Lewis base than THF, and therefore the equilibriums of the reactions between **1** and thiacrowns in this solvent should be shifted toward the thiacrown complexes to a significantly greater extent than in THF, particularly in the presence of an excess of a thiacrown.

The above-discussed behavior of **2**−**4** in THF is typical of complexes of **1** with comparatively weak neutral Lewis basic species such as nitriles,[25,27] esters,[28] and nitro compounds.[8] All these adducts are characterized by a small value of the downfield ^{199}Hg shift (0−10 ppm), which, as a rule, substantially increases on the introduction of an excess of a free Lewis base in the system. However, when a neutral donor guest markedly exceeds THF in its Lewis basicity, the resulting adducts with **1** show considerable downfield ^{199}Hg shifts in THF (e.g., 35.5 ppm in the case of the 2:1 HMPA complex[28]) even in the absence of an excess of the corresponding free Lewis base. Still greater downfield ^{199}Hg NMR shifts in a THF solution are observed for adducts of **1** with anionic species. Thus, in the case of the sandwich complex of **1** with the $[Fe(CN)_5(NO)]^{2-}$ ion the value

---

[24] Edema, J. J. H.; Buter, J.; Bolhuis, F. van; Meetsma, A. *Inorg. Chim. Acta* **1993**, *207*, 263.

[25] Tikhonova, I. A.; Dolgushin, F. M.; Tugashov, K. I.; Furin, G. G.; Petrovskii, P. V.; Shur, V. B. *Izv. Akad. Nauk, Ser. Khim.* **2001**, 1595 [*Russ. Chem. Bull., Int. Ed. Engl.* **2001**, *50*, 1673].

[26] King, J. B.; Haneline, M. R.; Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2002**, *124*, 9350.

[27] Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Starikova, Z. A.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **2000**, *613*, 60.

[28] Tikhonova, I. A.; Dolgushin, F. M.; Tugashov, K. I.; Petrovskii, P. V.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **2002**, *654*, 123.

Table 4. Crystal Data and Data Collection and Structure Refinement Parameters for 2−4

	2	**3**	**4**
formula	$C_{24}H_{12}F_{12}Hg_3S_3$	$C_{42}H_{12}F_{24}Hg_6S_3$	$C_{21}H_6F_{12}Hg_3S_3$
molecular wt	1226.29	2272.24	1184.21
cryst color, habit	colorless needle	colorless prism	colorless prism
cryst size, mm	0.20 × 0.06 × 0.03	0.42 × 0.14 × 0.10	0.38 × 0.10 × 0.08
T (K)	120(2)	120(2)	100(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	5.0886(3)	19.213(2)	10.572(1)
b (Å)	19.953(1)	40.352(4)	21.781(2)
c (Å)	25.919(1)	12.327(1)	21.997(2)
α (deg)	90	90	98.782(2)
β (deg)	95.094(1)	107.742(1)	103.749(2)
γ (deg)	90	90	90.145(2)
V (Å^3)	2621.1(2)	9102(1)	4858.5(8)
Z	4	8	8
D_{calcd} (g cm^{-3})	3.107	3.316	3.238
$2\theta_{max}$ (deg)	58	52	56
μ(Mo Kα, $\lambda = 0.71073$ Å) (cm^{-1})	178.70	204.36	192.75
transmn factors, min./max.	0.171/0.532	0.006/0.094	0.051/0.308
no. of collected reflns	28 632	63 879	89 649
no. of unique reflns (R_{int})	6938 (0.0617)	17 678 (0.0675)	23 028 (0.0890)
no. of obsd reflns ($I > 2\sigma(I)$)	5097	12 222	17 093
no. of params	379	1351	806
R_1 (on *F* for obsd reflns)[a]	0.0359	0.0596	0.0653
wR_2 (on F^2 for all reflns)[b]	0.0759	0.1419	0.1697

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

of this downfield shift amounts to 51 ppm,[18] and in the case of the sandwich complex of **1** with the *closo*-$[B_{10}H_{10}]^{2-}$ dianion it reaches 163 ppm.[16]

The formation of **3** and **4** impressively illustrates a charge-reverse analogy between crown compounds and anticrowns.

Experimental Section

The starting macrocycle **1** was prepared according to the published procedure.[10a] Commercial [9]thiacrown-3 (Aldrich) and 1,3,5-trithiane (Merck) were used without an additional purification. Solvents were purified by conventional methods and were distilled prior to use. The ^{199}Hg NMR spectra were recorded on a Bruker WP-200 SY instrument using a 0.2 M solution of Ph_2Hg in pyridine ($\delta = -791.1$ ppm[29]) as an external standard.

Synthesis of {[(*o*-C_6F_4Hg)$_3$](C_2H_4S)$_3$} (2). To a solution of **1** (0.1050 g, 0.1 mmol) in CH_2Cl_2 (15 mL) was added at room temperature a solution of [9]thiacrown-3 (0.0901 g, 0.5 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was allowed to slowly evaporate to dryness. After 2 days, the resulting colorless crystalline solid was washed with hot *n*-hexane (3 × 5 mL) and dried at 20 °C in vacuo for 6 h. Yield of **2**: 0.887 g (72%). Anal. Calcd for $C_{24}H_{12}F_{12}S_3Hg_3$: C, 23.51; H, 0.99; F, 18.59. Found: C, 23.59; H, 0.96; F, 18.73.

Synthesis of {[(*o*-C_6F_4Hg)$_3$]$_2$(C_2H_4S)$_3$} (3). To a solution of **1** (0.1048 g, 0.1 mmol) in CH_2Cl_2 (15 mL) was added at room temperature a solution of [9]thiacrown-3 (0.0090 g, 0.05 mmol) in CH_2Cl_2 (3 mL), and the reaction mixture was allowed to slowly evaporate to 0.5 mL at 20 °C. Then, the precipitated colorless, fine crystalline complex **3** was filtered, washed with diethyl ether (3 × 0.5 mL), and dried at 20 °C in vacuo for 2 h. Yield: 0.0892 g (79%). Anal. Calcd for $C_{42}H_{12}F_{24}S_3Hg_6$: C, 22.20; H, 0.53; F, 20.07. Found: C, 22.15; H, 0.56; F, 20.00. Single crystals of **3** for the X-ray diffraction study were grown from CH_2Cl_2.

Synthesis of {[(*o*-C_6F_4Hg)$_3$](CH_2S)$_3$} (4). To a solution of **1** (0.1048 g, 0.1 mmol) in CH_2Cl_2 (15 mL) was added at room temperature a solution of 1,3,5-trithiane (0.0141 g, 0.1 mmol) in CH_2Cl_2 (5 mL). After 5−10 min, the reaction solution became turbid and the white flaky precipitate began to form. Then, the mixture was allowed to evaporate for 3 days to 1 mL at 20 °C, and the resulting colorless, fine crystalline powder of complex **4** was filtered off, washed with CH_2Cl_2 (3 × 0.5 mL), and dried at 20 °C in vacuo for 6 h. Yield: 0.0893 g (75%). Anal. Calcd for $C_{21}H_6F_{12}S_3Hg_3$: C, 21.30; H, 0.51; F, 19.25. Found: C, 20.93; H, 0.71; F, 19.29. Single crystals of **4** for the X-ray diffraction study were grown by a slow evaporation of its solution in CH_2Cl_2.

X-ray Diffraction Study. Details of the crystal data and data collection and structure refinement parameters for complexes **2**−**4** are given in Table 4. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD diffractometer[30] for **2** and **3** and a Bruker SMART APEX II[31] for **4** (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, ω-scans). The semiempirical method SADABS[32] for complexes **2** and **3** and a numerical from crystal shape for complex **4** were applied for absorption correction. The structures of **2**−**4** were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic displacement parameters (in the case of **2** and **3**) for all non-hydrogen atoms. The crystals of complex **4** are twins with a very small off-orientation angle between twinning components. Repeated attempts of crystal growth from different solvent systems did not result in single crystals of **4** of good quality. All attempts (four data collection of various crystal samples) to resolve twinning by means of reciprocal space analysis (RLATT and CELLNOW programs incorporated in the APEX II program package) failed. The best result, which allowed the satisfactory description of the structure of the complex, was obtained when we treat **4** as a merohedrical twin with twinning law 1 0 0, 0 −1 0, −1 0 −1 (BASF = 0.31). However, as a consequence of the above twinning as well as a high absorption, it was impossible to obtain correct values of the anisotropic displacement parameters for the carbon and fluorine atoms of the mercuramacrocycle in **4** (all these atoms were refined here isotropically) and accurate bond lengths. The hydrogen atoms in **2**−**4** were placed geometrically and included

---

(29) Grishin, Yu. K.; Strelenko, Yu. A.; Margulis, L. A.; Ustynyuk, Yu. A.; Golovchenko, L. S.; Peregudov, A. S.; Kravtsov, D. N. *Dokl. Akad. Nauk SSSR* **1979**, *249*, 892.

(30) *SMART V5.051* and *SAINT V5.00*, Area detector control and integration software; Bruker AXS Inc.: Madison, WI 53719, 1998.

(31) *APEX II* software package; Bruker AXS Inc.: Madison, WI 53719, 2005.

(32) Sheldrick, G. M. *SADABS*; Bruker AXS Inc.: Madison, WI 53719, 1997.

(33) Sheldrick, G. M. *SHELXTL-97, V5.10*; Bruker AXS Inc.: Madison, WI 53719, 1997.

in the structure factor calculation in the riding motion approximation. All calculations were performed using SHELXTL-97 program packages.[33]

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (project code 05-03-32891) and the Russian Science Support Foundation (K.I.T.).

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2**−**4**. This material is available free of charge via the Internet at http://pubs.asc.org.

OM700526W