

Organometallic Chemistry

Coordination chemistry of macrocyclic multidentate Lewis acids.

Synthesis and structures of complexes of cyclic trimeric perfluoro-*o*-phenylenemercury with *N,N*-dimethylacetamide and *n*-butyronitrile

I. A. Tikhonova,^a F. M. Dolgushin,^a K. I. Tugashov,^a G. G. Furin,^b P. V. Petrovskii,^a and V. B. Shur^{a*}

^aA. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: vbshur@ineos.ac.ru

^bNovosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 35 4747

Cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄Hg)₃ readily reacts with *N,N*-dimethylacetamide and *n*-butyronitrile to form the complexes {[*o*-C₆F₄Hg)₃](MeCONMe₂)₂} and {[*o*-C₆F₄Hg)₃](PrⁿCN)}₂, respectively. According to X-ray diffraction data, the amide ligands are located above and below the plane of the macrocycle, each being coordinated to all Hg atoms of the macrocycle through the O atom. The nitrile ligand is bound to the macrocycle through the N atom, all Hg atoms being also involved in this bonding.

Key words: polymercury-containing macrocycles, Lewis acids, carboxamides, nitriles, complexes, X-ray diffraction analysis.

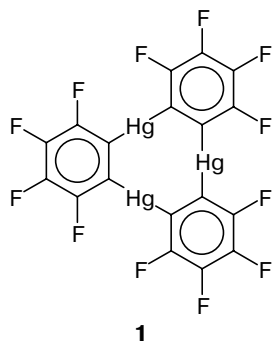
The coordination chemistry of macrocyclic multidentate Lewis acids, which represent a new class of promising reagents for organic synthesis, ion transport, and catalysis, has attracted growing interest in the last decade (see Refs. 1–3 and references cited therein).

Macrocyclic multidentate Lewis acids are peculiar antipodes of crown ethers and their thia and aza analogs. Owing to the presence of several Lewis-acidic centers in the macrocyclic chain, these compounds efficiently bind various anions giving rise to lipophilic anionic complexes, which is successfully used in phase

transfer catalysis of electrophilic reactions.^{4–7} The complexation of macrocyclic multidentate Lewis acids with neutral Lewis bases, particularly, with carbonyl compounds and nitriles, is also of considerable interest^{1–3} because cooperative binding of the C=O and C≡N groups by several Lewis-acidic centers of the macrocycle could lead to efficient activation of the carbonyl and nitrile groups in nucleophilic addition reactions.

Previously, we have found^{8–12} that cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄Hg)₃ (**1**) containing three Hg atoms in the planar nine-membered ring^{13,14}

exhibits high affinity for various anions at $\sim 20^\circ\text{C}$ to form unusual complexes in which the anionic species is coordinated to all Hg atoms.



The complexation of macrocycle **1** with acetonitrile, benzonitrile, and acrylonitrile has also been investigated; it has been shown that the composition and the structure of the resulting complexes are highly sensitive to the nature of the nitrile used.¹ Taking into account this fact, we carried out further examination of the reactions of compound **1** with nitriles. In the present paper, we describe the synthesis and the structure of complex **1** with *n*-butyronitrile as well as the first com-

plex of this macrocycle with a carbonyl compound, viz., with *N,N*-dimethylacetamide.

Results and Discussion

The complexes of macrocycle **1** with *N,N*-dimethylacetamide or *n*-butyronitrile are readily obtained upon recrystallization of **1** from *N,N*-dimethylacetamide and *n*-butyronitrile, respectively. The resulting compounds are air-stable colorless crystalline substances. The structures of the complexes were established by X-ray diffraction analysis.

The complex of **1** with *N,N*-dimethylacetamide, $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3(\text{MeCONMe}_2)_2]\}$ (**2**), contains two amide ligands per macrocycle. X-ray diffraction study of the complex demonstrated that it has a virtually bipyramidal structure. The amide ligands in molecule **2** (Fig. 1) are located above and below the plane of the macrocycle, each being coordinated to all Hg atoms through the O atom. The Hg—O distances are in the range of 2.777–2.988(4) Å (the average is 2.855 Å; Table 1), which are substantially smaller than the sum of the van der Waals radii of the Hg and O atoms ($2.1 + 1.5 = 3.6$ Å).¹⁵ The C=O bonds in the amide ligands are somewhat elongated due to coordination to the Hg atoms

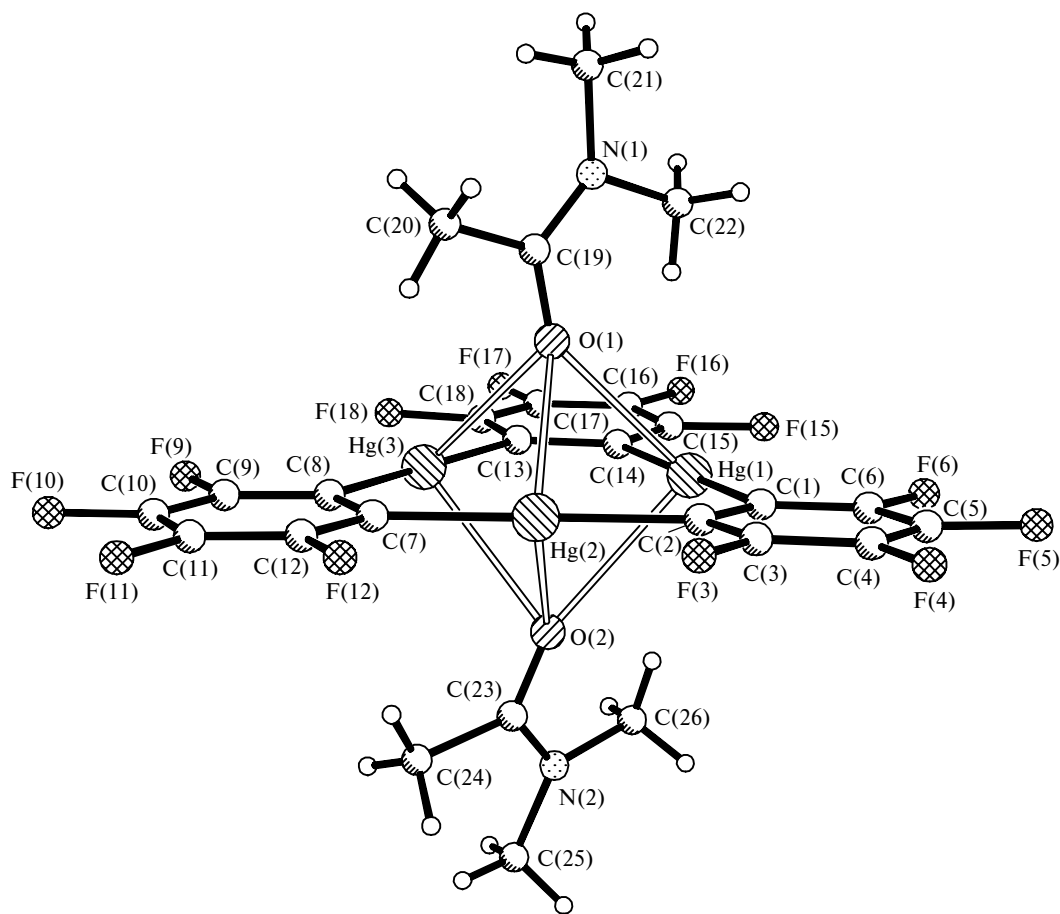


Fig. 1. Molecular structure of complex **2**.

Table 1. Selected bond lengths (*d*), bond angles (ω), and torsion angles (ϕ) in complex **2**

Bond	<i>d</i> /Å	Bond angle	ω /deg
Hg(1)—O(1)	2.777(4)	Hg(1)—O(1)—C(19)	146.5(4)
Hg(2)—O(1)	2.899(4)	Hg(2)—O(1)—C(19)	122.4(3)
Hg(3)—O(1)	2.777(4)	Hg(3)—O(1)—C(19)	127.0(3)
Hg(1)—O(2)	2.848(4)	Hg(1)—O(2)—C(23)	152.8(4)
Hg(2)—O(2)	2.988(4)	Hg(2)—O(2)—C(23)	130.0(4)
Hg(3)—O(2)	2.842(4)	Hg(3)—O(2)—C(23)	115.1(4)
Hg(1)—C(1)	2.079(5)	C(1)—Hg(1)—C(14)	176.8(2)
Hg(1)—C(14)	2.082(5)	C(2)—Hg(2)—C(7)	178.2(2)
Hg(2)—C(2)	2.075(5)	C(8)—Hg(3)—C(13)	176.9(2)
Hg(2)—C(7)	2.081(5)	C(2)—C(1)—Hg(1)	120.5(4)
Hg(3)—C(8)	2.076(5)	C(1)—C(2)—Hg(2)	121.3(4)
Hg(3)—C(13)	2.080(5)	C(8)—C(7)—Hg(2)	122.0(4)
Hg(1)...Hg(2)	3.547(1)	C(7)—C(8)—Hg(3)	120.0(4)
Hg(1)...Hg(3)	3.603(1)	C(14)—C(13)—Hg(3)	121.4(4)
Hg(2)...Hg(3)	3.572(2)	C(13)—C(14)—Hg(1)	121.8(4)
C(1)—C(2)	1.412(7)	C(19)—N(1)—C(22)	117.7(5)
C(7)—C(8)	1.431(8)	C(19)—N(1)—C(21)	123.8(5)
C(13)—C(14)	1.420(7)	C(22)—N(1)—C(21)	116.8(5)
O(1)—C(19)	1.254(6)	O(1)—C(19)—N(1)	121.1(5)
N(1)—C(19)	1.335(7)	O(1)—C(19)—C(20)	119.4(5)
N(1)—C(22)	1.468(7)	N(1)—C(19)—C(20)	119.6(5)
N(1)—C(21)	1.465(7)	C(23)—N(2)—C(26)	119.3(5)
C(19)—C(20)	1.512(8)	C(23)—N(2)—C(25)	122.3(6)
O(2)—C(23)	1.269(7)	C(26)—N(2)—C(25)	117.8(6)
N(2)—C(23)	1.323(8)	O(2)—C(23)—N(2)	120.6(6)
N(2)—C(26)	1.473(8)	O(2)—C(23)—C(24)	121.4(6)
N(2)—C(25)	1.470(8)	N(2)—C(23)—C(24)	118.0(6)
C(23)—C(24)	1.525(8)	Torsion angle ϕ /deg	
		Hg(1)—C(1)—C(2)—Hg(2)	2.8
		Hg(2)—C(7)—C(8)—Hg(3)	0.1
		Hg(3)—C(13)—C(14)—Hg(1)	−1.9

(C(19)—O(1), 1.254(6) Å; C(23)—O(2), 1.269(7) Å), whereas the N—C(O) bonds are slightly shortened (N(1)—C(19), 1.335(7) Å; N(2)—C(23), 1.323(8) Å) compared to the corresponding distances (1.23 and 1.35 Å) in free tertiary carboxamides.¹⁶

In the IR spectrum of complex **2**, the $\nu(\text{CO})$ band (1605 cm^{-1}) is shifted to the low-frequency region by 43 cm^{-1} with respect to the analogous band in the spectrum of noncoordinated *N,N*-dimethylacetamide ($\nu(\text{CO})$ 1648 cm^{-1}). These data are indicative of substantial weakening of the C=O bonds in both amide ligands upon complex formation with the macrocycle.

An interesting structural feature of complex **2** is the essential deviation of both C=O bonds from the perpendicular to the plane of the central nine-membered metallacycle. This deviation attains 22.2° and 12.3° for the C(23)—O(2) and C(19)—O(1) bonds, respectively. In the bipyramidal complex of the $[(o\text{-C}_6\text{Me}_4\text{HgO}(\text{H})\text{Hg})_2]^{2+}$ macrocycle with two *N,N*-diethylformamide molecules studied previously,³ both C=O bonds deviate from the perpendicular to the plane of the central ten-membered ring by ~17°. The ability of macrocyclic multidentate Lewis acids to form bipyramidal structures with Lewis bases has been exemplified for the first time¹⁷ by the

complex of the macrocycle $[(\text{CF}_3)_2\text{CHg}]_5$ with the chloride anion.

All non-hydrogen atoms in each of the amide ligands in complex **2**, like those in free carboxamides, are in a single plane. One of these planes, *viz.*, O(1)C(19)C(20)N(1)C(21)C(22), is virtually perpendicular to the plane of the nine-membered ring (the dihedral angle between these planes is 88.2°), whereas another plane, *viz.*, O(2)C(23)C(24)N(2)C(25)C(26), deviates substantially from the perpendicular to this plane (the dihedral angle is 74.1°). Therefore, the amide ligands in complex **2** differ noticeably in orientation with respect to the mercury-containing macrocycle.

The ^{199}Hg NMR spectrum of an $8 \cdot 10^{-2}$ M solution of complex **2** in THF at 20 °C has a triplet of triplets ($\delta = -307.2$, $^3J(^{199}\text{Hg}-^{19}\text{F}) = 446$ Hz, $^4J(^{199}\text{Hg}-^{19}\text{F}) = 139$ Hz, $^5J(^{199}\text{Hg}-^{19}\text{F}) = 26$ Hz), which is shifted downfield by 10.7 ppm relative to the analogous signal of the free macrocycle ($^3J(^{199}\text{Hg}-^{19}\text{F}) = 446$ Hz, $^4J(^{199}\text{Hg}-^{19}\text{F}) = 125$ Hz, $^5J(^{199}\text{Hg}-^{19}\text{F}) = 27$ Hz). Such downfield shifts in the ^{199}Hg NMR spectra are characteristic of complexes of mercury-containing multidentate Lewis acids with anions and neutral Lewis bases.^{4,11,18}

In the crystal, molecules **2** are linked in layers parallel to the crystallographic plane (100) through shortened intermolecular Hg...F contacts (Hg(2)...F(17)_{*x*,−1+*y*,*z*}, 3.33 Å; Hg(3)...F(9)_{−*x*,3−*y*,2−*z*}, 3.38 Å; the Hg...F van der Waals distance is 2.1 + 1.4 = 3.5 Å¹⁵).

The reaction of compound **1** with *n*-butyronitrile afforded the complex $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3](\text{Pr}^n\text{CN})\}$ (**3**) containing one nitrile ligand per macrocycle. According to the X-ray diffraction data, complex **3** has a pyramidal structure (Fig. 2). In this complex, the nitrile ligand is bound to the macrocycle through the N atom, which is

Table 2. Selected bond lengths (*d*), bond angles (ω), and torsion angles (ϕ) in complex **3**

Bond	<i>d</i> /Å	Bond angle	ω /deg
Hg(1)—N(1)	2.945(15)	Hg(1)—N(1)—C(19)	128(1)
Hg(2)—N(1)	2.909(16)	Hg(2)—N(1)—C(19)	141(1)
Hg(3)—N(1)	2.913(14)	Hg(3)—N(1)—C(19)	135(1)
Hg(1)—C(1)	2.07(2)	C(1)—Hg(1)—C(14)	176.1(7)
Hg(1)—C(14)	2.08(2)	C(7)—Hg(2)—C(2)	176.5(7)
Hg(2)—C(7)	2.05(2)	C(8)—Hg(3)—C(13)	175.6(6)
Hg(2)—C(2)	2.11(2)	C(2)—C(1)—Hg(1)	124.2(12)
Hg(3)—C(8)	2.04(2)	C(1)—C(2)—Hg(2)	120.2(11)
Hg(3)—C(13)	2.05(2)	C(8)—C(7)—Hg(2)	120.8(11)
Hg(1)...Hg(2)	3.608(1)	C(7)—C(8)—Hg(3)	121.3(12)
Hg(1)...Hg(3)	3.588(1)	C(14)—C(13)—Hg(3)	122.3(11)
Hg(2)...Hg(3)	3.585(1)	C(13)—C(14)—Hg(1)	120.1(12)
C(1)—C(2)	1.38(2)	N(1)—C(19)—C(20)	179(2)
C(7)—C(8)	1.48(3)	C(21)—C(20)—C(19)	117(2)
C(13)—C(14)	1.44(2)	C(20)—C(21)—C(22)	119(4)
N(1)—C(19)	1.12(2)	Torsion angle ϕ /deg	
C(19)—C(20)	1.44(3)	Hg(1)—C(1)—C(2)—Hg(2)	−4.5
C(20)—C(21)	1.36(4)	Hg(2)—C(7)—C(8)—Hg(3)	−1.6
C(21)—C(22)	1.55(5)	Hg(3)—C(13)—C(14)—Hg(1)	3.7

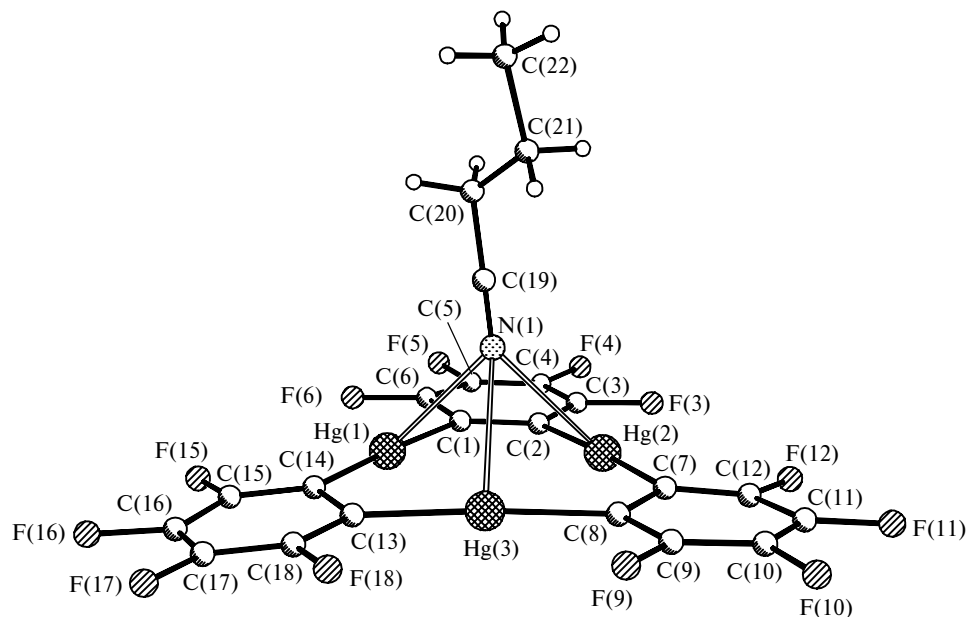


Fig. 2. Molecular structure of complex **3**.

almost symmetrically coordinated to all Hg atoms. The Hg(1)—N(1), Hg(2)—N(1), and Hg(3)—N(1) distances (2.95(2), 2.91(2), and 2.91(1) Å, respectively; Table 2) are substantially shorter than the corresponding van der Waals distance ($2.1 + 1.6 = 3.7$ Å).¹⁵ The C(19)—N(1) bond vector deviates from the perpendicular to the plane of the nine-membered ring by 6.4°. The N(1)—C(19)—C(20) bond angle, like those in free ni-

triles, is close to 180°. Unfortunately, rather low accuracy of the determination of the geometric parameters of the coordinated nitrile ligand in compound **3** does not allow us to discuss the changes in the C≡N bond length.

The IR spectrum of complex **3** is characterized by a small (6 cm⁻¹) but well reproducible shift of the ν(CN) band to the high-frequency region relative to the corresponding band (2251 cm⁻¹) in the spectrum of free

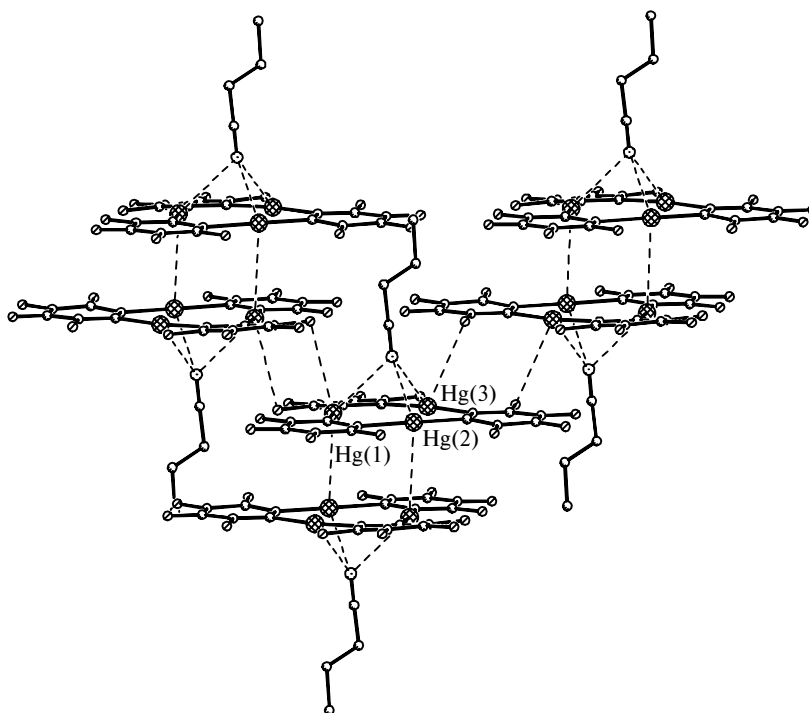


Fig. 3. Fragment of the crystal structure of complex **3**; the shortest Hg...F contacts between the adjacent molecules **3** are shown. The hydrogen atoms of the nitrile ligands are omitted for clarity.

n-butyronitrile. This unusual direction of the shift of the $\nu(\text{CN})$ band is typical of nitrile complexes with Lewis acids. Possible reasons for this phenomenon have been discussed previously.^{19,20}

The ^{199}Hg NMR spectrum of an $8 \cdot 10^{-2} \text{ M}$ solution of compound **3** in THF differs only insignificantly from the spectrum of the initial macrocycle, which indicates that the *n*-butyronitrile ligand is displaced from the complex by the solvent molecules. This result is quite expected if one takes into account that nitriles possess substantially lower basicity than THF²¹ and that a large excess of THF with respect to the nitrile complex was used ($\sim 150 : 1$). In accordance with the aforesaid, the addition of an excess of *n*-butyronitrile to a solution of complex **3** in THF leads to a noticeable downfield shift of the signal in the ^{199}Hg NMR spectrum (by 9.3 ppm for the ratio $\text{Pr}^{\text{n}}\text{CN} : \mathbf{3} = 40 : 1$). Hence, the ^{199}Hg NMR spectral data provide evidence that complex **3**, unlike complex **2**, is labile in THF and can exist in solution only in the presence of an excess of the nitrile ligand. This difference in the behavior of complexes **2** and **3** is quite understandable taking into account that *N,N*-dimethylacetamide is superior not only to nitriles but also to THF in Lewis basicity.²¹

Previously, we have prepared an analogous pyramidal complex $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3](\text{CH}_2\text{CHCN})\}$ (**4**) by the reaction of macrocycle **1** with acrylonitrile.¹ However, in this complex, the C—N bond vector of the nitrile ligand virtually coincides with the perpendicular to the plane of the nine-membered ring. Complex **4** differs also from complex **3** in crystal structure. In the crystal, molecules **4** are linked in infinite ladder-like chains through shortened intermolecular Hg...F contacts (3.35 and 3.42 Å),¹ whereas molecules **3** are linked in centrosymmetric dimers with the free planes of the macrocycles facing each other (Fig. 3). The dimers are characterized by unusually short intermolecular Hg...Hg contacts (Hg(1)...Hg(2)_{2-x,1-y,-2-z}, 3.372 Å) compared to twice the van der Waals radius of the mercury atom (4.2 Å). The occurrence of such shortened Hg...Hg contacts has been observed previously;²² however, the nature of this phenomenon remains unclear. The macrocyclic fragments in the dimer are in the staggered orientation and their centers are shifted with respect to each other by 2.25 Å. In the dimer, the distance between the mean planes of the macrocycles is 3.26 Å. In the crystal, the dimers are linked in layers parallel to the crystallographic plane (100) through shortened intermolecular Hg...F contacts (Hg(1)...F(15)_{2-x,2-y,-2-z}, 3.44 Å; Hg(3)...F(9)_{2-x,1-y,-3-z}, 3.28 Å).

The central nine-membered mercury-containing metallacycle in complexes **2** and **3** is virtually planar (the maximum deviations from the mean plane are 0.04 and 0.05 Å, respectively; the Hg—C—C—Hg torsion angles are smaller than 5°; see Tables 1 and 2). However, macrocycle **1** as a whole is noticeably nonplanar both in compounds **2** and **3** (the deviations are up to 0.13 and 0.21 Å, respectively). The external 21-membered

mercuracarbon ring is also nonplanar (the maximum deviations from the mean plane are 0.07 and 0.15 Å, respectively). The Hg—C bond lengths in complexes **2** and **3** have standard values (2.04–2.11 Å). The C—Hg—C bond angles are in the range of 175.6–178.2°, which indicates that the sp hybridization of the Hg atoms of the macrocycles is retained in compounds **2** and **3**.

To summarize, the data obtained in the present study demonstrate that macrocycle **1** readily forms complexes with *N,N*-dimethylacetamide and *n*-butyronitrile. *N,N*-Dimethylacetamide is bound to the macrocycle through the O atom, whereas binding of *n*-butyronitrile occurs through the N atom. In both cases, all Hg atoms of the metallacycle are involved in complexation with the Lewis basic center, which is characteristic of macrocyclic multidentate Lewis acids and is indicative of enhanced strength of this type of cooperative binding.

Experimental

Compound **1** was synthesized according to a procedure described previously.¹³ *N,N*-Dimethylacetamide and *n*-butyronitrile were purified by distillation. The IR spectra were mea-

Table 3. Crystallographic data, details of X-ray data collection, and parameters of the structure refinement for compounds **2** and **3**

Parameter	2	3
Molecular formula	C ₂₆ H ₁₈ F ₁₂ Hg ₃ N ₂ O ₂	C ₂₂ H ₇ F ₁₂ Hg ₃ N
Molecular weight	1220.19	1115.06
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>T</i> /K	100.0(2)	228(2)
<i>a</i> /Å	9.4232(3)	10.137(4)
<i>b</i> /Å	10.6904(4)	10.294(4)
<i>c</i> /Å	16.2990(6)	12.142(5)
α /deg	87.336(1)	104.23(3)
β /deg	75.821(1)	99.40(3)
γ /deg	65.440(1)	95.91(3)
<i>V</i> /Å ³	1445.03(9)	1198.0(8)
<i>Z</i>	2	2
<i>d</i> _{calc} /g cm ⁻³	2.804	3.091
Diffractometer	SMART 1000 CCD	Syntex P2 ₁
Radiation (λ)	Mo-Kα (0.71073 Å)	
μ/cm ⁻¹	160.04	192.81
Absorption correction	SADABS	DIFABS
<i>T</i> _{min} / <i>T</i> _{max}	0.273/0.996	0.487/1.400
Scan mode	ω—φ	θ—2θ
2θ _{max} /deg	61	60
Number of independent reflections (<i>R</i> _{int})	8734 (0.0407)	6884 (0.1372)
<i>R</i> ₁ (based on <i>F</i> for reflections with <i>I</i> > 2σ(<i>I</i>)) (7430 reflections)	0.0351	0.0727
<i>wR</i> ₂ (based on <i>F</i> ² for all reflections)	0.0888	0.1767
Number of parameters in the refinement	406	343
Weighting scheme, <i>w</i> ⁻¹	σ ² (<i>F</i> _o ²) + (<i>aP</i>) ² + <i>bP</i> , where <i>P</i> = 1/3(<i>F</i> _o ² + 2 <i>F</i> _c ²)	
<i>a</i>	0.0620	0.0957
<i>b</i>	0.0000	0.0000

sured on a Specord M-82 instrument in Nujol mulls. The ^{199}Hg NMR spectra were recorded on a Bruker WP-200 SY spectrometer with Ph_2Hg as the external standard.

Synthesis of complex 2. Compound **1** (0.1046 g, 0.1 mmol) was dissolved in *N,N*-dimethylacetamide (3 mL) with gentle heating and kept at room temperature for 1–2 days. Colorless crystals of complex **2** that precipitated were filtered off and dried *in vacuo*; the yield was 0.0875 g (72%). Found (%): C, 25.74; H, 1.37; F, 18.47; N, 2.38. $\text{C}_{26}\text{H}_{18}\text{F}_{12}\text{N}_2\text{O}_2\text{Hg}_3$. Calculated (%): C, 25.55; H, 1.47; F, 18.67; N, 2.29. IR, v/cm^{-1} : 1605 (C=O).

Synthesis of complex 3 was carried out analogously; the yield was 0.096 g (86%). Found (%): C, 23.56; H, 0.79; F, 20.40; N, 1.14. $\text{C}_{22}\text{H}_7\text{F}_{12}\text{NHg}_3$. Calculated (%): C, 23.66; H, 0.62; F, 20.43; N, 1.25. IR, v/cm^{-1} : 2257 (C \equiv N).

X-ray diffraction study of complexes 2 and 3. The crystallographic data and details of the refinement of compounds **2** and **3** are given in Table 3. Both structures were solved by the direct method. The positional and thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method first isotropically and then anisotropically. The hydrogen atoms were placed in geometrically calculated positions and were included in the refinement using the riding model. All calculations were carried out on a personal computer using known program packages.^{23–26}

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