Crown compounds for anions. Sandwich complex of cyclic trimeric perfluoro-*o*-phenylenemercury with $[B_{12}H_{11}SCN]^{2-}$ anion*

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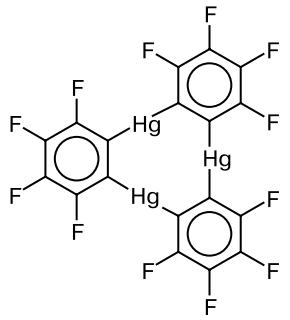
The reaction of cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) with the polyhedral $[B_{12}H_{11}SCN]^{2-}$ anion in THF at 20 °C affords the $\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{11}SCN)\}^{2-}$ (**4**) and $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}^{2-}$ (**5**) complexes. Complex **5** was isolated as the tetrabutylammonium salt. X-ray diffraction analysis showed that this complex has a bent-sandwich structure in which the $[B_{12}H_{11}SCN]^{2-}$ anion is located between the planes of two molecules **1** and is coordinated to both these molecules through B—H—Hg bridges and S—Hg bonds. The stability constants of complexes **4** and **5** in THF (20° C), which were determined from the IR spectroscopic data, are 16 L mol^{-1} and 992 L^2 mol^{-2}, respectively.

Key words: polymercuramacrocycles, polyhedral boron-containing anions, complexes, IR spectra, X-ray diffraction analysis.

Abundant data on the bonding of anions and neutral Lewis bases by polymercuramacrocycles are available in the literature (see Refs. 1—6 and references cited therein). These macrocycles containing several Lewis acidic centers in the macrocyclic chain are peculiar antipodes of crown ethers and their thia and aza analogs. Detailed investigation of the coordination chemistry of such polymetallamacrocycles can lead to the development of a new class of reagents, which hold promise for the organic synthesis, ion transport, and catalysis.

In earlier studies (see Refs. 1—3 and references cited therein), we have described the complexing and catalytic properties of cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) in which three Hg atoms are involved in the planar nine-membered ring.[7,8]

In particular, it was found that this macrocycle can efficiently bind the polyhedral $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ dianions to form unusual complexes, such as $\{[(o\text{-}C_6F_4Hg)_3](B_{10}H_{10})\}^{2-}$, $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{10}H_{10})\}^{2-}$, $\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{12})\}^{2-}$ (**2**), and $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{12})\}^{2-}$ (**3**), having half-sandwich and sandwich structures.[2] In these complexes, the anionic species is bound to molecules **1** through B—H—Hg bridges.



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In the present study, we examined the reaction of macrocycle **1** with the $[B_{12}H_{11}SCN]^{2-}$ ion in THF. Two complexes, *viz.*, $\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{11}SCN)\}^{2-}$ (**4**) and $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}^{2-}$ (**5**), were detected in the reaction solution by IR spectroscopy and their stability constants were determined. X-ray diffraction study of complex **5**, which was isolated in the individual form as the tetrabutylammonium salt, revealed that this complex, like compound **3**, has a sandwich structure. However, the anionic species in complex **5**, unlike that in complex **3**, is

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bound to the mercury atoms not only by the BH groups but also by the thiocyanate group.

Results and Discussion

As macrocycle **1** is gradually added to an excess of $[n\text{-}Bu_4N]_2[B_{12}H_{11}SCN]$ in THF at 20 °C ($[B_{12}H_{11}SCN^{2-}]_o = 2 \cdot 10^{-2}$ mol L^{-1}), the intensity of the ν(BH) band of the free $[B_{12}H_{11}SCN]^{2-}$ ion (at 2489 cm^{-1}) in the IR spectrum decreases and new absorption bands at 2332 and 2492 cm^{-1} appear. These changes indicate that the $[B_{12}H_{11}SCN]^{2-}$ anion is coordinated to the mercury atoms of the macrocycle to form a complex. The curves for the decreasing intensity of the initial ν(BH) band and increasing intensities of new ν(BH) bands pass through an isobestic point. When the **1** : $[B_{12}H_{11}SCN]^{2-}$ molar ratio becomes equal to 1 : 1, the ν(BH) band of the uncoordinated $[B_{12}H_{11}SCN]^{2-}$ anion virtually disappears, and the spectrum of the reaction solution in the region of 2100—2600 cm^{-1} has only the above-mentioned absorption bands at 2332 and 2492 cm^{-1}. Further experiments demonstrated that these bands belong to complex **4** (Table 1).

The band at 2332 cm^{-1}, which is shifted to a low-frequency region by 157 cm^{-1} with respect to the ν(BH) band of the free $[B_{12}H_{11}SCN]^{2-}$ ion, can be assigned to stretching vibrations of the B—H bonds (ν(BH)^b) coordinated to the mercury atoms of the macrocycle through the B—H—Hg bridges. The high-frequency band at 2492 cm^{-1} can be assigned to stretching vibrations of the terminal B—H bonds (ν(BH)^t), *i.e.*, the bonds, which are not involved in coordination to the macrocycle. The ν(CN) band is shifted to a high-frequency region by 5 cm^{-1} (from 2132 to 2137 cm^{-1}) upon the formation of complex **4**. Such a small shift of the ν(CN) band indicates that the thiocyanate group in compound **4** is bound to the mercury atoms of the macrocycle very weakly, if at all.

Table 1. Stretching frequencies of the B—H and C—N bonds in the IR spectra of the $[B_{12}H_{11}SCN]^{2-}$ ion and complexes **4** and **5** in Nujol mulls and in THF

Compound	ν/cm^{-1}		
	Nujol mull	THF	Assignment
$[B_{12}H_{11}SCN]^{2-}$	2479 s	2489 s	ν(BH)
	2131 m	2132 m	ν(CN)
Complex **4**	—	2492 s	ν(BH)^t
	—	2332 s	ν(BH)^b
	—	2137 m	ν(CN)
Complex **5**	2498 s	2498 s	ν(BH)^t
	2372 s	2372 sh	ν(BH)^b
	2366 s	2366 s	ν(BH)^b
	2155 m	2164 w	ν(CN)

Investigation of the stoichiometry of the formation of complex **4** by the molar ratio and continuous variation methods[9] demonstrated that this complex contains one $[B_{12}H_{11}SCN]^{2-}$ ion per molecule **1** and, consequently, its composition can be described by the formula $\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{11}SCN)\}^{2-}$. The stability constant (K_1) of complex **4** determined from the IR spectroscopic data is 16 L mol^{-1} (THF, 20 °C), which is considerably lower than the corresponding value (70 L mol^{-1}) found[2] for compositionally similar complex **2** with the unsubstituted $[B_{12}H_{12}]^{2-}$ ion.

Treatment of the reaction solution, which was obtained after the formation of complex **4**, with an additional amount of the macrocycle leads to further changes in the IR spectrum: the ν(BH) bands of compound **4** (at 2332 and 2492 cm^{-1}) gradually disappear and new absorption bands belonging to complex **5** appear at 2366, 2372, and 2498 cm^{-1} (see Table 1). When the **1** : $[B_{12}H_{11}SCN]^{2-}$ molar ratio reaches (3—4) : 1, the spectrum of the solution in the ν(BH) vibration region ceases to change and the reaction mixture contains only complex **5** (together with excess macrocycle).

The low-frequency bands at 2366 and 2372 cm^{-1} in the IR spectrum of compound **5** can be assigned to ν(BH)^b vibrations and the corresponding high-frequency band (at 2498 cm^{-1}) can be assigned to ν(BH)^t vibrations. The formation of complex **5** causes a more substantial high-frequency shift of the ν(CN) band (from 2132 to 2164 cm^{-1}) than that observed in the case of compound **4**, which indicates that the thiocyanate group of the $[B_{12}H_{11}SCN]^{2-}$ ion is involved in coordination to the mercury atoms of the macrocycle. Judging from the observed shift (32 cm^{-1}) and based on the published data,[10] this coordination in compound **5** occurs through the sulfur atom.

Investigation with the use of the molar ratio and continuous variation methods demonstrated that complex **5** has the composition $\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}^{2-}$,

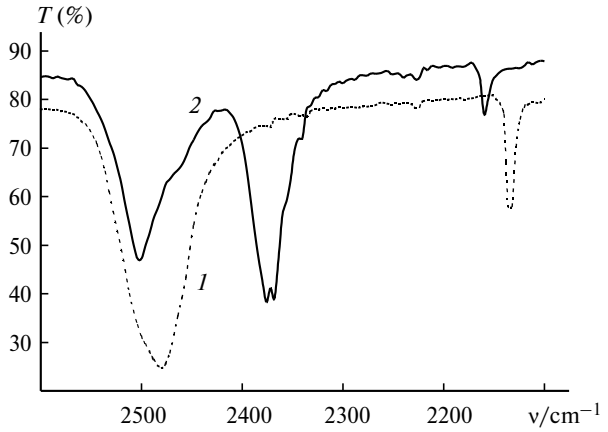

Fig. 1. IR spectra of the $[B_{12}H_{11}SCN]^{2-}$ ion (*1*) and complex **5** (*2*) in Nujol mulls.

i.e., contains one $[B_{12}H_{11}SCN]^{2-}$ ion per two molecules of the macrocycle. The stability constant of complex **5** (K_2) is 992 L^2 mol^{-2} (THF, 20 °C), which is close to the corresponding constant (980 L^2 mol^{-2}) found[2] for sandwich complex **3** with an analogous composition. Hence, in this case, unlike compounds **2** and **4**, the replacement of the hydride hydrogen atom in the $[B_{12}H_{12}]^{2-}$ ion by the thiocyanate group does not lead to a weakening of the bond between the polyhedral boron-containing anion and the macrocycle.

Complex **5** was prepared in the individual form by the reaction of $[n\text{-}Bu_4N]_2[B_{12}H_{11}SCN]$ with a twofold molar excess of macrocycle **1** in a solution in acetone. According to the elemental analysis data, this complex contains one $[B_{12}H_{11}SCN]^{2-}$ ion per two molecules of compound **1**. The IR spectrum of complex **5** in Nujol mull (Fig. 1) is characterized by the ν(BH) (2366, 2372, 2498 cm^{-1}) and ν(CN) (2155 cm^{-1}) bands analogous to those observed in the IR spectrum in THF (see Table 1). The ^{199}Hg NMR spectrum of complex **5** in THF

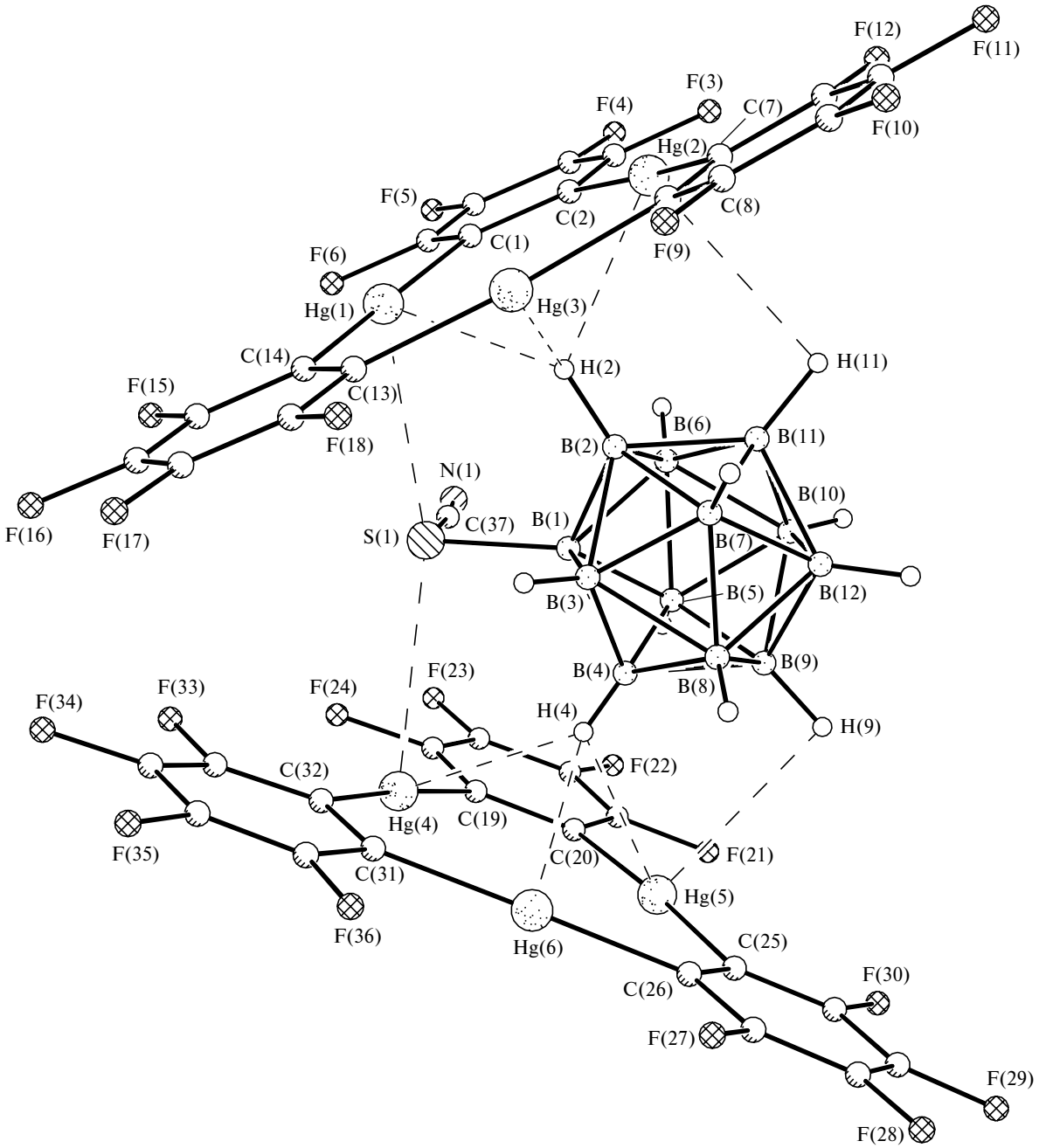

Fig. 2. Molecular structure of complex **5**.

($8 \cdot 10^{-2}$ mol L^{-1}) at 20 °C shows a triplet of triplets of triplets (δ = −253.9, $^{3}J(^{199}Hg—^{19}F)$ = 456 Hz, $^{4}J(^{199}Hg—^{19}F)$ = 132 Hz, $^{4(5)}J(^{199}Hg—^{19}F)$ = 27 Hz) shifted downfield by 64 ppm with respect to the analogous signal of the free macrocycle ($^{3}J(^{199}Hg—^{19}F)$ = 446 Hz, $^{4}J(^{199}Hg—^{19}F)$ = 125 Hz, $^{4(5)}J(^{199}Hg—^{19}F)$ = 27 Hz). The ^{11}B NMR spectrum of complex **5** in acetone-d_6 is virtually identical with that of the free $[B_{12}H_{11}SCN]^{2-}$ ion. According to the IR spectroscopic data, dissolution of complex **5** in THF is accompanied by its partial dissociation to give complex **4**. Cooling of the solution to −73 °C leads to the reverse transformation of **4** into **5**. Attempts to isolate complex **4** failed.

The structure of complex **5** was established by X-ray diffraction analysis (Fig. 2). The selected bond lengths and bond angles are given in Table 2. As can be seen from Fig. 2, complex **5** has a bent-sandwich structure in which the polyhedral $[B_{12}H_{11}SCN]^{2-}$ dianion is located between the planes of two macrocycles and is coordinated to each of them through the B—H—Hg bridges and S—Hg bonds. This agrees with the conclusions made based on the IR spectroscopic data. Like the above-mentioned sandwich complex **3**, molecule **5** contains the bridging B—H—Hg bonds of two types. One type of the B—H—Hg bonds is characterized by the simultaneous coordination of the BH group to all three mercury atoms of the macrocycle. The B(2)—H(2) and B(4)—H(4) groups of the polyhedral dianion are involved in this mode of coordination. The Hg—H(2) and Hg—H(4) distances in compound **5** are in the range of 2.56—2.75 Å (aver. 2.65 Å), and the Hg—B(2) and Hg—B(4) distances are in the range of 3.317(10)—3.539(10) Å (aver. 3.42 Å). All these distances are substantially shorter than the sum of the van der Waals radii of the mercury and hydrogen atoms (2.1 + 1.2 = 3.3 Å)[11] and, correspondingly, of the mercury and boron atoms (2.1 + 1.75 = 3.85 Å).[11] The latter fact may indicate that the boron atoms of the B(2)—H(2) and B(4)—H(4) groups are also involved in coordination to the mercury centers of the macrocycle (*cf.* Ref. 12).

The coordination of the B(11)—H(11) and B(9)—H(9) groups gives rise to another type of B—H—Hg bridges in molecule **5**. Each of these groups, unlike the B(2)—H(2) and B(4)—H(4) groups, in complex **5** is coordinated to only one mercury atom of the macrocycle (Hg(2) and Hg(5), respectively). This mode of coordination is characterized by somewhat longer Hg—H distances (Hg(2)—H(11), 3.09 Å; Hg(5)—H(9), 3.18 Å). The Hg(2)—B(11) and Hg(5)—B(9) distances are 3.489(10) and 3.546(11) Å, respectively. Interestingly, two crystallographically independent molecules of sandwich complex **3** contain three and four B—H—Hg bridges of this type,[2] in contrast to compound **5** containing two such bridges.

The thiocyanate group in complex **5** is coordinated only to one mercury atom (Hg(1) and Hg(4)) of each macrocycle through the sulfur atom. The Hg(1)—S(1) and Hg(4)—S(1) distances are 3.257(2) and 3.225(2) Å, respectively, which are substantially smaller than the sum of the van der Waals radii of the mercury and sulfur atoms (2.1 + 1.85 = 3.95 Å).[11] The complexation of $[B_{12}H_{11}SCN]^{2-}$ with macrocycle **1** leads to a slight elongation of both the C—N bond (from 1.13(1)[13] to 1.166(12) Å) and the B—S bond (from 1.893(8)[13] to 1.921(11) Å) and to a shortening of the S—C bond (from 1.684(9)[13] to 1.655(11) Å). The B(1)—S(1)—C(37), S(1)—B(1)—B(2), S(1)—B(1)—B(3), S(1)—B(1)—B(4), S(1)—B(1)—B(5), and S(1)—B(1)—B(6) bond angles in compound **5** are close to the corresponding values found[13]

Table 2. Selected bond lengths (d/Å) and bond angles (ω/deg) in complex **5**

Bond	d/Å	Bond	d/Å	Angle	ω/deg
Hg(1)—H(2)	2.56	Hg(4)—S(1)	3.225(2)	C(14)—Hg(1)—C(1)	173.8(4)
Hg(2)—H(2)	2.66	S(1)—B(1)	1.921(11)	C(7)—Hg(2)—C(2)	174.5(4)
Hg(3)—H(2)	2.62	S(1)—C(37)	1.655(11)	C(13)—Hg(3)—C(8)	175.2(4)
Hg(2)—H(11)	3.09	C(37)—N(1)	1.166(12)	C(19)—Hg(4)—C(32)	176.2(4)
Hg(4)—H(4)	2.63	Hg(1)—C(1)	2.096(9)	C(20)—Hg(5)—C(25)	175.2(4)
Hg(5)—H(4)	2.75	Hg(1)—C(14)	2.080(9)	C(31)—Hg(6)—C(26)	175.1(4)
Hg(6)—H(4)	2.66	Hg(2)—C(2)	2.062(10)	B(1)—S(1)—C(37)	101.5(5)
Hg(5)—H(9)	3.18	Hg(2)—C(7)	2.057(9)	S(1)—C(37)—N(1)	174(1)
Hg(1)—B(2)	3.387(11)	Hg(3)—C(8)	2.080(11)	S(1)—B(1)—B(2)	118.4(7)
Hg(2)—B(2)	3.346(10)	Hg(3)—C(13)	2.059(10)	S(1)—B(1)—B(3)	116.9(7)
Hg(3)—B(2)	3.539(10)	Hg(4)—C(19)	2.091(9)	S(1)—B(1)—B(4)	120.5(7)
Hg(2)—B(11)	3.489(10)	Hg(4)—C(32)	2.065(10)	S(1)—B(1)—B(5)	124.3(7)
Hg(4)—B(4)	3.472(11)	Hg(5)—C(20)	2.073(10)	S(1)—B(1)—B(6)	123.0(7)
Hg(5)—B(4)	3.317(10)	Hg(5)—C(25)	2.071(10)		
Hg(6)—B(4)	3.476(11)	Hg(6)—C(26)	2.081(11)		
Hg(5)—B(9)	3.546(11)	Hg(6)—C(31)	2.048(12)		
Hg(1)—S(1)	3.257(2)				

in the free $[B_{12}H_{11}SCN]^{2-}$ ion. The S(1)—C(37)—N(1) group, like that in the uncoordinated $[B_{12}H_{11}SCN]^{2-}$ anion, is virtually linear.

The Hg—C bond lengths in complex **5** have standard values (2.05—2.10 Å). The C—Hg—C bond angles are in the range of 173.8—176.2°, which indicates that the sp-hybridization of the mercury atoms is retained in molecule **5**. The mutual orientation of the macrocycles in complex **5** corresponds to an eclipsed conformation. The dihedral angle between the mean planes of the central nine-membered rings of the macrocycles is 50.5°, which is 8—9° smaller than the corresponding angles in sand-

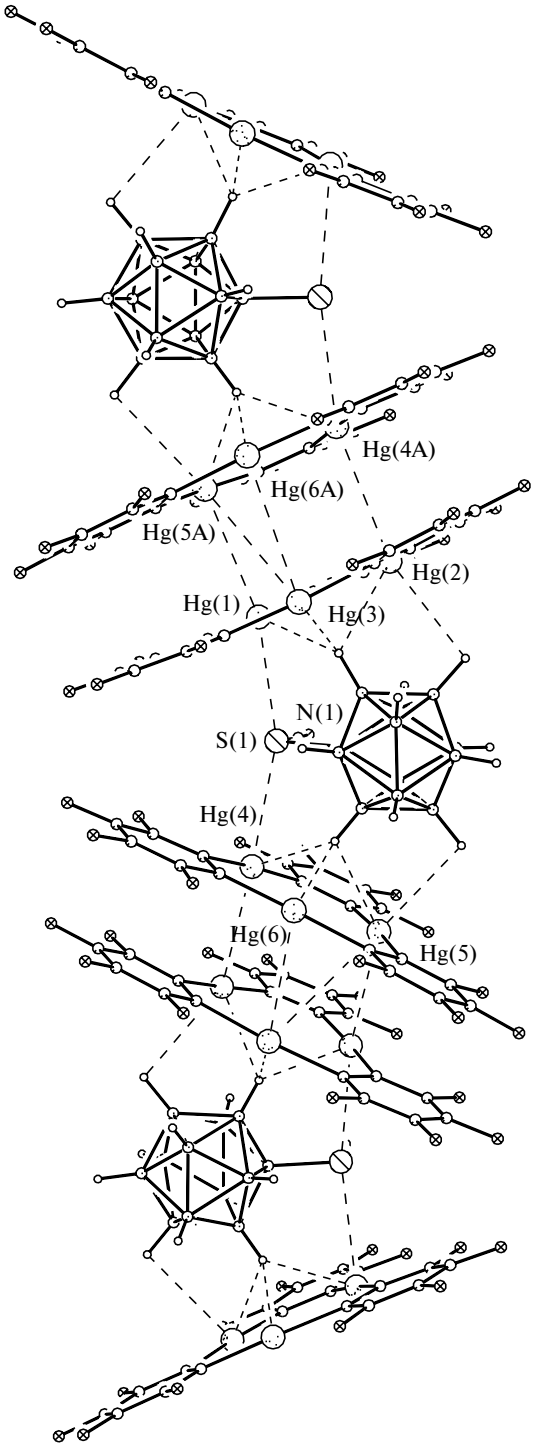

Fig. 3. Fragment of the crystal packing of complex **5.**

wich complex **3**. Presumably, complex **4** has a half-sandwich structure.

In the crystal, sandwich molecules **5** are linked in zigzag chains along the [101] crystallographic direction. The fragment of the crystal packing of complex **5** is shown in Fig. 3. In the chain, each two neighboring molecules **5** are oriented in such a way that the sides of their mercury-containing macrocycles, which are not involved in coordination with the dianion, face each other (the distance between their mean planes is 3.56 Å). The mutual orientation of the neighboring macrocycles in the chain also corresponds to an eclipsed conformation, the macrocycles being shifted with respect to each other by 1.77 Å. An interesting feature of the crystal structure of complex **5** is the presence of somewhat shortened (compared to the sum of the van der Waals radii) Hg···Hg contacts between the adjacent molecules **1** (H(1)···Hg(5A), 3.888 Å; Hg(2)···Hg(4A), 3.913 Å; Hg(3)···Hg(5A), 3.910 Å; Hg(3)···Hg(6A), 4.123 Å). The formation of such infinite chains has been observed earlier[2] in the crystal structures of sandwich complexes of macrocycle **1** with the unsubstituted $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ dianions. In spite of slight differences in the geometric characteristics (staggered or eclipsed orientation of the adjacent macrocycles, the distances between their mean planes, the shortest intermolecular distances, *etc.*), the overall structure of the zigzag chain with shortened Hg···Hg contacts is retained in all three structures regardless of the nature of the polyhedral dianion.

Experimental

Macrocycle **1** and $[n\text{-}Bu_4N]_2[B_{12}H_{11}SCN]$ were synthesized according to known procedures.[7,13] The solvents were purified according to standard procedures and distilled before use.

The IR spectra were recorded on a Specord M-82 instrument (resolution was 2 cm^{-1}), The spectra of the reaction solutions were measured in CaF_2 cells (d = 0.0125—0.12 cm) at different concentrations (10^{-3}—10^{-1} mol L^{-1}) and reagent ratios. The IR spectra of solid samples were recorded in Nujol mulls in the range of 400—4000 cm^{-1}. The low-temperature IR spectra of solutions were measured using a Carl Zeiss Jena cryostat. The ^{199}Hg and ^{11}B NMR spectra were recorded on Bruker WP-200 SY and Bruker AMX-400 spectrometers with the use of Ph_2Hg and $BF_3 \cdot Et_2O$, respectively, as the external standards.

The compositions of the resulting complexes were determined from the IR spectroscopic data by the molar ratio and continuous variation methods.[9] In the case of the molar ratio method, the optical densities of the ν(BH) bands at 2332 cm^{-1} (complex **4**) and 2366 cm^{-1} (complex **5**) were measured for a series of solutions with equal starting concentrations of the $[B_{12}H_{11}SCN]^{2-}$ ions ($2 \cdot 10^{-2}$ mol L^{-1}) and different concentrations of the macrocycle (10^{-2}–10^{-1} mol L^{-1}). The compositions of the complexes were determined from the point of inflection in the dependence of the optical density on the $[\mathbf{1}]_o/[B_{12}H_{11}SCN^{2-}]_0$ concentration ratio. In the case of the continuous variation method, the optical densities of the above-mentioned bands were measured for a series of solutions with different concentrations ($2 \cdot 10^{-3}$—$1.8 \cdot 10^{-2}$ mol L^{-1}) of the macrocycle and the $[B_{12}H_{11}SCN]^{2-}$ ion, but with the same overall concentration ($2 \cdot 10^{-2}$ mol L^{-1}). In this case, the compositions of the complexes were determined from the position of the maximum in the dependence of the optical density on the $[\mathbf{1}]_o/([\mathbf{1}]_o + + [B_{12}H_{11}SCN^{2-}]_o)$ concentration ratio. The results obtained by both methods are consistent with each other.

The stability constants of complexes **4** and **5** for the equilibria

$$(o\text{-}C_6F_4Hg)_3 + [B_{12}H_{11}SCN]^{2-} \overset{K_1}{\rightleftharpoons} \{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{11}SCN)\}^{2-},$$

$$2\,(o\text{-}C_6F_4Hg)_3 + [B_{12}H_{11}SCN]^{2-} \overset{K_2}{\rightleftharpoons} \{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}^{2-},$$

$$\{[(o\text{-}C_6F_4Hg)_3](B_{12}H_{11}SCN)\}^{2-} + (o\text{-}C_6F_4Hg)_3 \overset{K_3}{\rightleftharpoons} \{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}^{2-}$$

were calculated by the equations

$$K_1 = [C_{SCN} - D_{SCN}/(\varepsilon_{SCN}\, d)]/ /\{[D_{SCN}/(\varepsilon_{SCN}\, d)] \cdot [C_{Hg} - (C_{SCN} - D_{SCN}/(\varepsilon_{SCN}\, d))]\},$$

$$K_2 = K_1 \cdot K_3,$$

$$K_3 = [C_{SCN} - D_{SCN}/(\varepsilon_{SCN}\, d) - D_{\mathbf{4}}/(\varepsilon_{\mathbf{4}}\, d)]/ /\{[D_{\mathbf{4}}/(\varepsilon_{\mathbf{4}}\, d)] \cdot [C_{Hg} - (C_{SCN} - D_{SCN}/(\varepsilon_{SCN}\, d) - D_{\mathbf{4}}/(\varepsilon_{\mathbf{4}}\, d))]\},$$

where C_{SCN} and C_{Hg} are the initial concentrations of the $[B_{12}H_{11}SCN]^{2-}$ ion and macrocycle **1**, respectively; D_{SCN} is the optical density of the ν(BH) band of the free $[B_{12}H_{11}SCN]^{2-}$ ion at 2489 cm^{-1}; $D_{\mathbf{4}}$ is the optical density of the ν(BH) band of complex **4** at 2332 cm^{-1}; ε_{SCN} and $\varepsilon_{\mathbf{4}}$ are the extinction coefficients of the ν(BH) bands at 2489 and 2332 cm^{-1}, respectively; d is the thickness of the cell.

Synthesis of bis{cyclotris[μ-(3,4,5,6-tetrafluoro-1,2-diphenylene)]trimercury} tetrabutylammonium 1,2,3,4,5,6,7,8,9,10,11-undecahydro-12-thicyanatododecaborate(2–), $[n\text{-}Bu_4N]_2\{[(o\text{-}C_6F_4Hg)_3]_2(B_{12}H_{11}SCN)\}$ (5). A solution of $[n\text{-}Bu_4N]_2[B_{12}H_{11}SCN]$ (0.0343 g, 0.05 mmol) in acetone (2 mL) was added to a solution of compound **1** (0.1044 g, 0.1 mmol) in acetone (2 mL). The reaction mixture was kept at 20 °C for 1 h and then concentrated to ~0.5 mL, after which methanol (2 mL) was added. Yellowish crystals of complex **5** that formed were filtered off and dried *in vacuo*. The yield was 0.1116 g (80%). Found (%): C, 29.85; H, 3.04; F, 16.57; B, 4.78. $C_{69}H_{83}F_{24}Hg_6N_3B_{12}S$. Calculated (%): C, 29.81; H, 2.98; F, 16.42; B, 4.75. IR (Nujol mull), ν/cm^{-1}: 2155 m (C≡N); 2366 s (B—H), 2372 s (B—H), 2498 s (BH).

X-ray diffraction study of complex 5. The crystals of complex **5** are monoclinic, space group $P2_1/n$, at 110 K a = 16.273(2), b = 27.920(3), c = 18.379(2) Å, β = 99.172(3)°, V = 8243(2) $Å^3$, Z = 4, M = 2775.70, d_{calc} = 2.237 g cm^{-3}, μ(Mo-Kα) = 112.55 cm^{-1}, $F(000)$ = 5160. The intensities of 18011 independent reflections (R_{int} = 0.0854) were measured on an automated Bruker SMART 1000 CCD diffractometer equipped with a co-

ordinate detector[14,15] (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, T = 110 K, ω scanning mode with a scan step of 0.3° and a counting time of 15 s per step, 2θ < 54°). The semiempirical absorption correction was applied by repeated scanning of the intensities of equivalent reflections with the use of the SADABS program[16] (T_{min}/T_{max} = 0.145/0.261). The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms of the $[B_{12}H_{11}SCN]^{2-}$ ion were located from difference Fourier syntheses and included in the subsequent refinement with fixed geometric parameters. The hydrogen atoms of the butyl groups of the $[n\text{-}Bu_4N]^+$ cations were placed in geometrically calculated positions and refined using the riding model. The final reliability factors were as follows: wR_2 = 0.0882 and GOOF = 0.803 for all independent reflections (R_1 = 0.0428 calculated based on F for 9382 reflections with $I > 2\sigma(I)$). All calculations were carried out using the SHELXTL PLUS 5.0 program package.[17] The complete tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

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