Crown Compounds for Anions: Sandwich and Half-Sandwich Complexes of Cyclic Trimeric Perfluoro-*o*-phenylenemercury with Polyhedral *closo*-$[B_{10}H_{10}]^{2-}$ and *closo*-$[B_{12}H_{12}]^{2-}$ Anions

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Abstract: It has been shown by IR and NMR spectroscopy that cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) is capable of binding *closo*-$[B_{10}H_{10}]^{2-}$ and *closo*-$[B_{12}H_{12}]^{2-}$ anions to form complexes $[\{(o\text{-}C_6F_4Hg)_3\}(B_{10}H_{10})]^{2-}$ (**2**), $[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{10}H_{10})]^{2-}$ (**3**), $[\{(o\text{-}C_6F_4Hg)_3\}(B_{12}H_{12})]^{2-}$ (**4**), and $[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{12}H_{12})]^{2-}$ (**5**). According to IR data, the bonding of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ ions to the macrocycle in these complexes is accomplished through the formation of B-H-Hg bridges. Complexes **2**, **3**, and **5** have been isolated in analytically pure form and have been characterized by spectroscopic means. X-ray diffraction studies of **3** and **5** have revealed that these compounds have unusual sandwich structures, in which the polyhedral dianion is located between the planes of two molecules of **1** and is bonded to each of them through two types of B-H-Hg bridges. One type is the simultaneous coordination of a B−H group to all three Hg atoms of the macrocycle. The other type is the coordination of a B−H group to a single Hg atom of the cycle. According to X-ray diffraction data, complex **2** has an analogous but half-sandwich structure. The obtained complexes **2**–**5** are quite stable; their stability constants in THF/acetone (1:1) at 20 °C have been determined as $1.0 \times 10^2\,L\,mol^{-1}$, $2.6 \times 10^3\,L^2\,mol^{-2}$, $0.7 \times 10^2\,L\,mol^{-1}$, and $0.98 \times 10^3\,L^2\,mol^{-2}$, respectively.

Keywords: anions · boranes · mercury · polymercuramacrocycles · structure elucidation

Introduction

Recent investigations have revealed a remarkable ability of polymercuramacrocycles to effectively bind various anions and neutral Lewis bases with the formation of complexes in which the Lewis basic species is simultaneously coordinated to all Hg atoms of the cycle.[1–3] This unusual property of polymercuramacrocycles is reminiscent of the behavior of crown ethers and their thia and aza analogues in metal cation binding and may find useful applications in organic synthesis, ion transport, and catalysis (see, for example, refs. [1a, 4]).

In the majority of complexes of polymercuramacrocycles with anions, the bonding to the mercury atoms is accomplished through the lone electron pairs of the anionic guest, but anions lacking unshared electron pairs can also form complexes with these macrocycles. The first example of a reaction of this type was found by Hawthorne et al., who described a complex of the *o*-carboranylmercury macrocycle $(o\text{-}C_2B_{10}H_8Et_2Hg)_4$ with two *closo*-$[B_{10}H_{10}]^{2-}$ anions.[2f] The isolated complex $[\{(o\text{-}C_2B_{10}H_8Et_2Hg)_4\}(B_{10}H_{10})_2]^{4-}$ was found to have a bipyramidal structure, in which the $[B_{10}H_{10}]^{2-}$ ions were located above and below the metallacycle plane and each of them was coordinated to the Hg atoms of the cycle through B-H-Hg bridges. Interestingly, in the case of the $[B_{12}H_{12}]^{2-}$ ion, no complexation with $(o\text{-}C_2B_{10}H_8Et_2Hg)_4$ was observed.

Recently, we have found[1g] that cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**), which contains three Hg atoms in a planar nine-membered cycle,[5] is capable of binding borohydride anions in THF solution to form complexes $[\{(o\text{-}C_6F_4Hg)_3\}(BH_4)]^-$, $[\{(o\text{-}C_6F_4Hg)_3\}(BH_4)_2]^{2-}$, and $[\{(o\text{-}C_6F_4Hg)_3\}_2(BH_4)]^-$. The bonding of the BH_4^- ions to the macrocycle is also accomplished here through B-H-Hg bridges. Unfortunately, these complexes could not be obtained as crystals suitable for X-ray diffraction studies. The results of quantum-chemical calculations suggested that they should have the unique half-sandwich, bipyramidal, and sandwich structures, respectively.

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Herein, the complexation reactions of macrocycle **1** with $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions are described in detail. It has been found that the reaction of **1** with $[B_{10}H_{10}]^{2-}$ ions affords two complexes, $[\{(o\text{-}C_6F_4Hg)_3\}(B_{10}H_{10})]^{2-}$ (**2**) and $[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{10}H_{10})]^{2-}$ (**3**), which have been isolated in analytically pure form and characterized by spectroscopic means. According to X-ray diffraction data, the complexes have an unusual half-sandwich and a sandwich structure, respectively. Similar complexes, $[\{(o\text{-}C_6F_4Hg)_3\}(B_{12}H_{12})]^{2-}$ (**4**) and $[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{12}H_{12})]^{2-}$ (**5**), are formed in the reaction of **1** with $[B_{12}H_{12}]^{2-}$ ions. An X-ray analysis of **5** has revealed that this compound, like **3**, also has a sandwich structure.

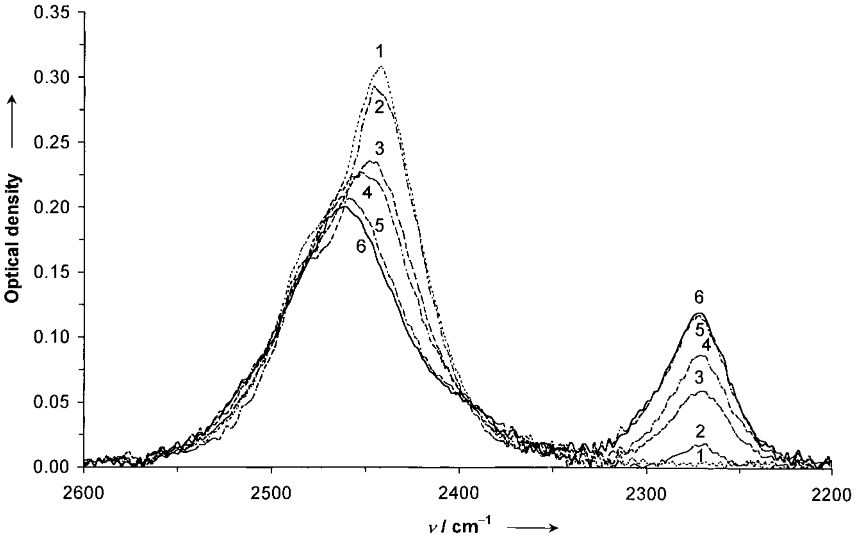
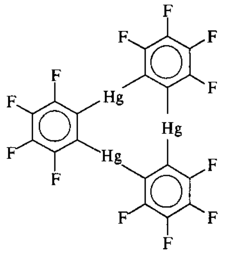


Figure 1. IR spectra in the ν(BH) range: 1) $(nBu_4N)_2[B_{10}H_{10}]$ in THF/acetone (1:1); 2)–6) reaction solutions in THF/acetone with $[B_{10}H_{10}]^{2-}$:**1** molar ratios of 1:0.5 (2); 1:0.8 (3); 1:1 (4); 1:1.3 (5); 1:1.5 (6).



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Results and Discussion

The complexation of macrocycle **1** with $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ ions was first studied by means of IR and NMR spectroscopy. These studies allowed us to detect the aforementioned complexes **2**–**5** in solution and to determine their compositions and stability constants. Furthermore, the solid complexes isolated from the reaction mixtures were investigated by analytical and spectroscopic means, as well as by X-ray structure analyses. The results of these investigations showed the isolated complexes to be identical in their compositions and spectral characteristics to the species detected in solution by IR and NMR spectroscopy.

Complexes 2 and 4

IR spectroscopic data: When **1** is gradually added to an excess of $(nBu_4N)_2[B_{10}H_{10}]$ in THF/acetone (1:1) solution ($[B_{10}H_{10}{}^{2-}]_o = 4\times10^{-3}$ M) at room temperature, the intensities of the ν(BH) bands of free $[B_{10}H_{10}]^{2-}$ anions (at 2443 and 2480 cm^{-1}[6]) decrease, and new absorption bands appear in the spectrum at 2280 and 2464 cm^{-1} indicating a complexation of $[B_{10}H_{10}]^{2-}$ with the Hg atoms of **1**. The decrease in the intensities of the initial ν(BH) bands and the increase in those of new bands occurs with an isobestic point (Figure 1). When the $[B_{10}H_{10}]^{2-}$:**1** molar ratio becomes equal to 1:1–1:1.5, the ν(BH) bands of free $[B_{10}H_{10}]^{2-}$ ions practically disappear and the spectrum shows only the aforementioned absorption bands at 2280 and 2464 cm^{-1} attributable to complex **2**. The band at 2280 cm^{-1}, shifted by 163 and 200 cm^{-1}, respectively, to the low-frequency region relative to the ν(BH) bands of free $[B_{10}H_{10}]^{2-}$ anion, can be attributed to stretching vibrations of the B–H bonds coordinated to the Hg atoms of the macrocycle through B-H-Hg bridges (ν(BH)^b). We assign the high-frequency absorption band at 2464 cm^{-1} to stretching vibrations of the terminal B–H bonds (ν(BH)^t).

Analogous spectral changes in the ν(BH) region occur when **1** is gradually added to an excess of $(nBu_4N)_2[B_{12}H_{12}]$ in THF/acetone (1:1) solution ($[B_{12}H_{12}]_o = 4\times10^{-3}$ M) at 20 °C. Here, practically complete disappearance of the ν(BH) band of the free $[B_{12}H_{12}]^{2-}$ ion (at 2466 cm^{-1}[6]) is again observed at a 1:1–1:1.5 molar ratio of the reagents. A decrease in intensity of the initial ν(BH) band is accompanied by the appearance of two new absorption bands at 2292 (ν(BH)^b) and 2478 cm^{-1} (ν(BH)^t) attributable to complex **4**. Thus, the complexation of the $[B_{12}H_{12}]^{2-}$ anions with macrocycle **1** also leads to a very large shift (174 cm^{-1}) of the ν(BH)^b band to the low-frequency region relative to the ν(BH) band of the free $[B_{12}H_{12}]^{2-}$ ion. Similarly large low-frequency shifts of the ν(BH)^b bands have previously been reported for complexes of **1** with borohydride anions.[1g]

A study of the compositions of complexes **2** and **4** by the mole ratio and continuous variation (Job) methods[7] showed that they contain one anionic species per molecule of **1**, and consequently they can be formulated as $[\{(o\text{-}C_6F_4Hg)_3\}(B_{10}H_{10})]^{2-}$ and $[\{(o\text{-}C_6F_4Hg)_3\}(B_{12}H_{12})]^{2-}$, respectively. The complexes are quite stable: their stability constants (THF/acetone, 20 °C) were determined from the IR spectra as 1.0×10^2 and 0.7×10^2 L mol^{-1}, respectively.

Complex **2** was isolated as a colorless crystalline solid by treating **1** with an equimolar amount of $(nBu_4N)_2[B_{10}H_{10}]$ in acetone, followed by addition of MeOH to the resulting material. According to elemental analysis and X-ray diffraction data (see below), the complex does indeed have a 1:1 composition, but also contains one molecule of MeOH per molecule of **2**. The IR spectrum of solid **2** (as a Nujol mull) shows practically the same ν(BH) absorption bands (at 2287 and 2454 cm^{-1}) as those observed in THF/acetone solution (see above). Unfortunately, our attempts to obtain analytically pure complex **4** failed, but the IR spectrum of the isolated product is again very similar [$\nu(BH) = 2300$ and 2484 cm^{-1}] to the solution spectrum.

NMR spectroscopic studies: The room-temperature ^{199}Hg NMR spectrum of macrocycle **1** in [D$_6$]acetone is characterized by a broad signal at $\delta = -314.8$. The ^{199}Hg NMR spectrum (295 K) of complex **2** obtained by mixing **1** with an equimolar amount of $(nBu_4N)_2[B_{10}H_{10}]$ in the same solvent shows a poorly resolved signal at $\delta = -108$. Thus, the interaction of **1** with $[B_{10}H_{10}]^{2-}$ anions to form **2** leads to a downfield shift of the ^{199}Hg resonance by more than 200 ppm. On lowering the temperature to 180 K, the position of the ^{199}Hg line in the spectrum of **2** is displaced to $\delta = -89$.

Similar changes in the room temperature ^{199}Hg NMR spectrum are observed in the course of the formation of complex **4**. On addition of $(nBu_4N)_2[B_{12}H_{12}]$ to a solution of **1** in [D$_6$]acetone until a $[B_{12}H_{12}]^{2-}$:**1** ratio of 1:1 is reached, the ^{199}Hg resonance is strongly broadened and is shifted to $\delta = -176.1$. Thus, the magnitude of the downfield displacement of the ^{199}Hg line on going from **1** to **4** is around 139 ppm. Cooling of the solution (to 200 K) again leads to a noticeable change in the position of the signal ($\delta = -188$).

The $^{11}B\{^1H\}$ NMR spectrum of $(nBu_4N)_2[B_{10}H_{10}]$ in [D$_6$]acetone (295 K) features two broad resonances (in a 1:4 ratio) at $\delta = -0.93$ and -29.2, corresponding to the apical and equatorial boron atoms, respectively. In the spectrum of **2**, these signals are shifted downfield to $\delta = 2.37$ and -23.9, thus suggesting that both types of B–H groups of the $[B_{10}H_{10}]^{2-}$ anion (apical and equatorial) are involved in the complexation. The positions of the ^{11}B resonances at 180 K are $\delta = 1.97$ and -26.0, respectively.

The ^1H NMR spectra of **2** and **4** proved to be uninformative due to strong broadening of the B–H resonances.

Table 1. Selected bond lengths [Å] and angles [°] in complex **2**.

Hg(1)–H(2)	2.5(1)	Hg(1)–B(2)	3.26(2)
Hg(2)–H(2)	2.8(1)	Hg(2)–B(2)	3.32(2)
Hg(3)–H(2)	2.8(1)	Hg(3)–B(2)	3.50(2)
Hg(1)–H(1)	2.6(1)	Hg(1)–B(1)	3.24(2)
Hg(2)–H(6)	2.8(1)	Hg(2)–B(6)	3.43(2)
Hg(1)–C(14)	2.09(1)	Hg(3)–C(8)	2.07(1)
Hg(1)–C(1)	2.09(1)	C(1)–C(2)	1.41(2)
Hg(2)–C(2)	2.05(1)	C(7)–C(8)	1.41(2)
Hg(2)–C(7)	2.09(1)	C(13)–C(14)	1.38(2)
Hg(3)–C(13)	2.07(2)		
C(14)-Hg(1)-C(1)	173.2(5)	C(13)-Hg(3)-C(8)	172.4(6)
C(2)-Hg(2)-C(7)	172.3(5)		

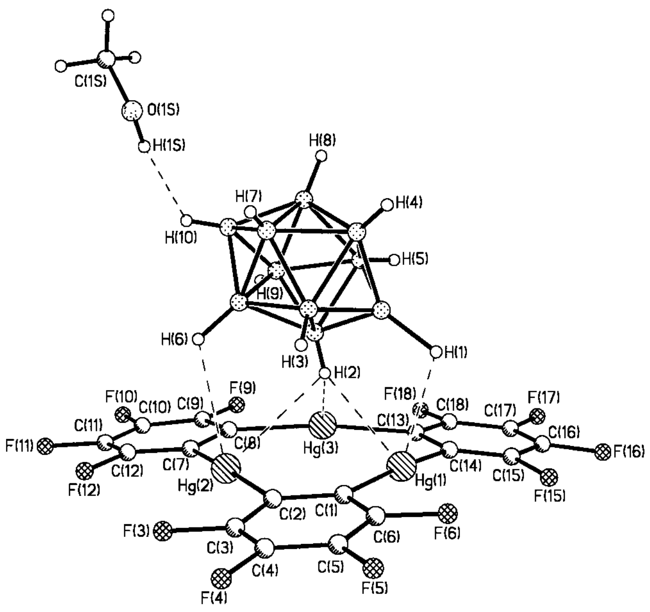

Figure 2. Molecular structure of complex **2**·MeOH in the crystal.

*X-ray crystallographic study of complex **2**·MeOH*: Figure 2 shows the structure of **2**·MeOH. Selected bond lengths and angles are listed in Table 1. The complex has an unusual half-sandwich structure, in which the *closo*-$[B_{10}H_{10}]^{2-}$ anion is coordinated to **1** through two types of B-H-Hg bridges. One type is the simultaneous bonding of the equatorial B(2)–H(2) group of the $[B_{10}H_{10}]^{2-}$ ion to all three Hg atoms of the cycle. The Hg(1)–H(2), Hg(2)–H(2), and Hg(3)–H(2) distances in **2** are 2.5(1), 2.8(1), and 2.8(1) Å and the Hg(1)–B(2), Hg(2)–B(2), and Hg(3)–B(2) distances are 3.26(2), 3.32(2), and 3.50(2) Å, respectively. All these distances are notably shorter than the sums of the van der Waals radii of mercury and hydrogen atoms (2.1 + 1.2 = 3.3 Å[8]), and mercury and boron atoms (2.1 + 1.75 = 3.85 Å[8]). The latter feature may indicate that the boron atom of the B(2)–H(2) group is also involved in the bonding to the Hg centers of the macrocycle (cf. ref. [1g]). Different types of B-H-Hg bridges are found in complex **2** as a result of coordination of the apical B(1)–H(1) and equatorial B(6)–H(6) groups of the $[B_{10}H_{10}]^{2-}$ ion to **1**. Each of these, in contrast to the B(2)–H(2) group, is bonded only to one Hg atom of the macrocycle (Hg(1) and Hg(2), respectively). The Hg(1)–H(1) and Hg(2)–H(6) distances are 2.6(1) and 2.8(1) Å, while the Hg(1)–B(1) and Hg(2)–B(6) distances are 3.24(2) and 3.43(2) Å, respectively, which are again noticeably shorter than the corresponding sums of the van der Waals radii.

The complexation of the $[B_{10}H_{10}]^{2-}$ anion by **1** leads to some distortion of the polyhedral borane cage. This is manifested in notable differences in the B_{ap}–B_{eq} bond lengths for the coordinated B(1) and non-coordinated B(10) apical vertices (the average values are 1.70 and 1.64 Å, respectively; 1.690 Å for the free $[B_{10}H_{10}]^{2-}$ anion[9]). The geometry of the polymercuramacrocycle in **2** is also somewhat distorted. The Hg atoms of the macrocycle deviate from the mean plane of the central nine-membered ring of **1** towards the $[B_{10}H_{10}]^{2-}$ ion [the maximum displacement is 0.10 Å for Hg(3)], whereas the perfluorophenylene rings are displaced in the opposite direction [the maximum displacement from this plane is 0.31 Å for C(16)]. As a result, the C-Hg-C fragments in the cycle deviate slightly from linearity (the C-Hg-C bond angles are 172.4(6), 172.3(5), and 173.2(5)°), thus showing some perturbation of the sp hybridization of the Hg atoms.

The methanol solvate molecule is bonded to the apical B(10)–H(10) group through an O–H···H–B dihydrogen bond (see Figure 2). The H(1S)$\cdots$H(10) and O(1S)$\cdots$B(10) distances are 2.2(2) and 3.55(2) Å, and the O(1S)-H(1S)-H(10) and H(1S)-H(10)-B(10) angles are 171(18) and 116(12)°, respectively. The results of the spectroscopic and theoretical study of the O–H$\cdots$H–B dihydrogen bonding of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions with proton donors are discussed in ref. [10].

Complexes 3 and 5

IR and NMR spectroscopic data: When a solution of complex **2** in THF ($[\mathbf{2}]_o = 4 \times 10^{-2}$ M) is treated with additional amounts of the macrocycle, the gradual disappearance of the ν(BH) bands of **2** (at 2280 and 2464 cm^{-1}) is observed and three new absorption bands (at 2300, 2410, and 2479 cm^{-1}) attributable to complex **3** appear in the spectrum. The decrease in intensities of the IR bands of **2** and increase in intensities of those of **3** also occurs with isobestic points (Figure 3). When the **1**:**2** molar ratio reaches 2:1, the spectrum shows the sole presence of complex **3** in the solution. The aforementioned low-frequency bands (at 2300 and 2410 cm^{-1}) in the IR spectrum of **3** can be assigned to $\nu(BH)^b$ stretching modes. The high-frequency band of **3** (at 2479 cm^{-1}) can be attributed to the corresponding $\nu(BH)^t$ absorption.

Similar changes in the IR spectrum are observed upon gradual addition of **1** to a solution of complex **4** in THF. This reaction leads to complex **5**, which is also characterized by three ν(BH) absorption bands [at 2313 ($\nu(BH)^b$), 2435 ($\nu(BH)^b$), and 2483 ($\nu(BH)^t$) cm^{-1}] in its IR spectrum. Practically complete conversion of **4** to complex **5** is achieved at a **1**:**4** molar ratio of 2:1.

It should be noted that the relative intensities of the $\nu(BH)^b$ bands in the spectra of **3** and **5** are noticeably greater than those of the corresponding bands in the spectra of **2** and **4**. This indicates an increase in the number of BH groups involved in the complexation on going from **2** and **4** to **3** and **5**, respectively. One may assume that two $\nu(BH)^b$ absorption bands observed in the IR spectra of complexes **3** and **5** correspond to two different types of B-H-Hg bonding.

The room-temperature ^{199}Hg NMR spectra of solutions of **3** and **5** in [D$_8$]THF (obtained by treating $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, respectively, with a threefold excess of **1**) feature broad signals at $\delta = -160.7$ and -284.3, respectively ($\delta = -323.9$ for **1** in [D$_8$]THF[1g]). Unfortunately, all attempts to measure the low-temperature ^{199}Hg NMR spectra of **3** and **5** failed because of the low solubilities of the complexes.

Using the mole ratio and Job methods, we established that complexes **3** and **5** have compositions of $[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{10}H_{10})]^{2-}$ and $[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{12}H_{12})]^{2-}$, respectively. Thus, they contain two molecules of the macrocycle per one anionic species. These complexes are even more stable than **2** and **4**: their stability constants (determined by the mole ratio method) amount to 2.6×10^3 and 9.8×10^2 L^{2}mol^{-2}, respectively. However, they are considerably less stable than the previously described complex of macrocycle **1** with the borohydride anion of similar composition $[\{(o\text{-}C_6F_4Hg)_3\}_2(BH_4)]^-$ ($K = 10^7$ L^{2}mol^{-2}).[1g]

Solid complexes **3** and **5** were isolated in analytically pure form by treating **1** in ethanol with 0.5 equivalents of $(PPN)_2[B_{10}H_{10}]$ and $(nBu_4N)_2[B_{12}H_{12}]$, respectively (PPN = $(PPh_3)_2N$). The IR spectra of the isolated complexes **3** and **5** (in Nujol mulls) also feature three absorption bands in the ν(BH) region. The positions of these bands (2309, 2408, and 2485 cm^{-1} for **3**; 2328, 2433, and 2486 cm^{-1} for **5**) are very close to those observed in solution (see above).

X-ray study of complex $3 \cdot Et_2O$: Crystals of the complex suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of diethyl ether into a solution of **3** in acetone at 20 °C. The crystals were found to contain one molecule of Et$_2$O per molecule of **3**. The structure of **3** is shown in Figure 4. Selected bond lengths and angles are given in Table 2.

The complex has a bent sandwich structure, in which the $[B_{10}H_{10}]^{2-}$ anion is located between the planes of two molecules of the macrocycle and is coordinated to each of these in the same manner as in the half-sandwich complex **2** described above. The B(2)–H(2) and B(8)–H(8) equatorial groups of the $[B_{10}H_{10}]^{2-}$ ion in **3** are simultaneously bonded to all three Hg atoms of the neighboring molecule of **1**. The Hg–H(2) and Hg–H(8) bond lengths in **3** are in the range 2.41(4)–2.60(4) Å (average 2.52 Å), while the corresponding Hg–B(2) and Hg–B(8) distances are in the range 3.154(5)–3.489(6) Å (average 3.28 Å). An additional contribution to the bonding of the $[B_{10}H_{10}]^{2-}$ ion to **1** in complex **3** involves the B(1)–H(1), B(6)–H(6), B(4)–H(4), and

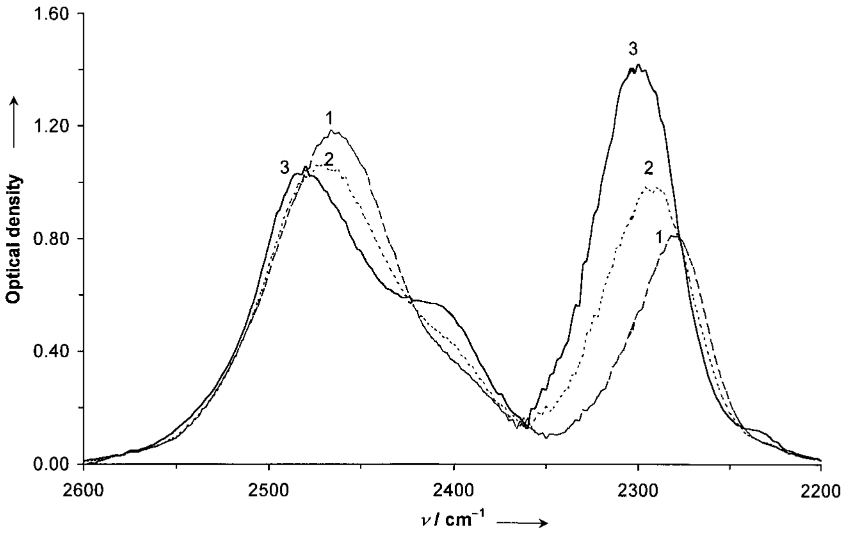

Figure 3. IR spectra in the ν(BH) range: 1) complex **2** in THF; 2) and 3) reaction solutions in THF with **2**:**1** molar ratios of 1:1 (2) and 1:2 (3).

B(10)–H(10) groups, each of which is coordinated to a single Hg atom of the macrocycle. The Hg–H distances for these groups (2.54(6)–2.75(4) Å; average 2.67 Å) are notably longer than those for the equatorial B(2)–H(2) and B(8)–H(8) groups. The Hg–B distances are in the range 3.152(6)–3.442(6) Å (average 3.26 Å). Thus, six of the ten vertices of the $[B_{10}H_{10}]^{2-}$ anion in **3** are involved in the coordination to the macrocycle (three to each molecule of **1**).

Due to the symmetrical bonding of the $[B_{10}H_{10}]^{2-}$ ion to two macrocyclic units in complex **3**, all B–B bond lengths at the B(1) and B(10) apical vertices in this complex are close to each other. The average B_{ap}–B_{eq} distance is 1.69 Å, which is close to the corresponding value for the B(1) apical vertex in **2**.

In contrast to the situation in complex **2**, in **3** only one Hg atom, namely Hg(1A), is displaced (by 0.19 Å) from the mean plane of the central nine-membered ring of **1** towards the $[B_{10}H_{10}]^{2-}$ ion; this leads to a noticeable deviation of the C(1A)-Hg(1A)-C(14A) bond angle (170.8(2)°) from the ideal value of 180°. Other C-Hg-C fragments in **3** deviate from linearity to a lesser extent (the average C-Hg-C angle is 175°). The mutual orientation of the macrocyclic units in **3** is close to an eclipsed conformation (the Hg(3A)-X(1A)-X(1B)-Hg(3B) torsion angle is 4°; X(1A) and X(1B) are the centers of the corresponding macrocycles). The dihedral angle between the planes of the macrocycles is 19°.

X-ray study of complex **5**: Suitable crystals of **5** were also grown by slow vapor diffusion of diethyl ether into a solution of the complex in acetone. The structures of the two crystallographically independent molecules of **5** (conformers **5a** and **5b**) are presented in Figure 5. Selected bond lengths and angles for **5a** and **5b** are listed in Tables 3 and 4.

As can be seen in Figure 5, conformers **5a** and **5b** both have bent sandwich structures like that of **3**, in which the polyhedral anion is coordinated to the molecules of **1** through two types of B-H-Hg bridges. In each conformer, the B(1)–H(1) and B(7)–H(7) groups are simultaneously bonded to all the Hg atoms of the neighboring macrocycle. The Hg–H

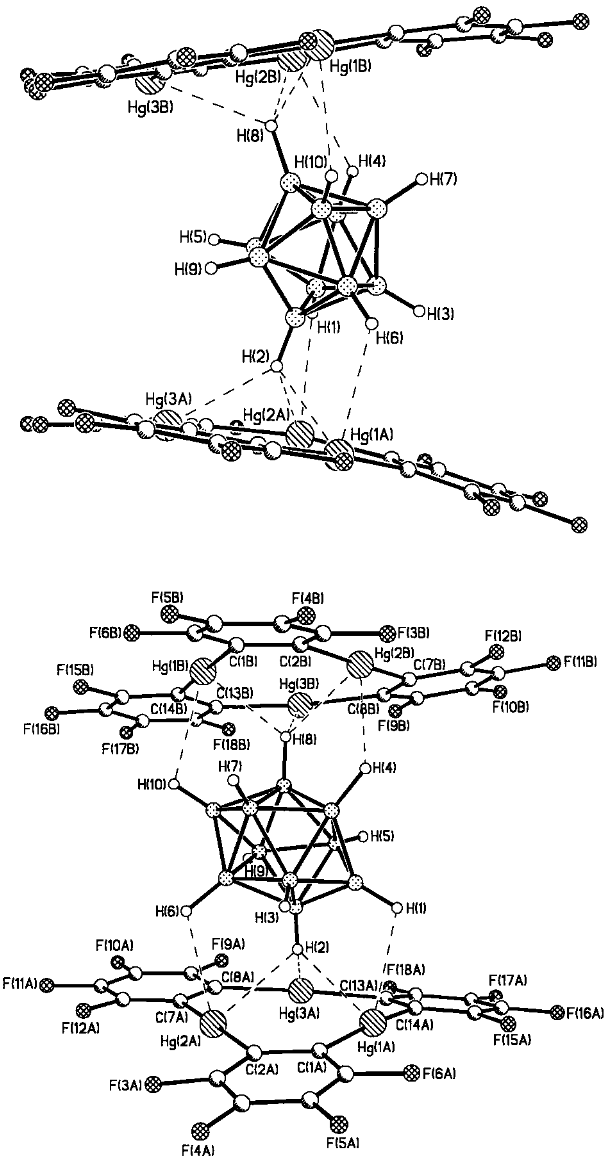

Figure 4. Two views of complex **3** in the crystal.

Table 2. Selected bond lengths [Å] and angles [°] in complex **3**.

Hg(1A)–H(2)	2.51(4)	Hg(1A)–B(2)	3.154(5)
Hg(2A)–H(2)	2.60(4)	Hg(2A)–B(2)	3.213(6)
Hg(3A)–H(2)	2.54(4)	Hg(3A)–B(2)	3.385(6)
Hg(1A)–H(1)	2.66(5)	Hg(1A)–B(1)	3.152(6)
Hg(2A)–H(6)	2.65(4)	Hg(2A)–B(6)	3.291(5)
Hg(1B)–H(8)	2.41(4)	Hg(1B)–B(8)	3.182(6)
Hg(2B)–H(8)	2.48(4)	Hg(2B)–B(8)	3.246(5)
Hg(3B)–H(8)	2.59(5)	Hg(3B)–B(8)	3.489(6)
Hg(1B)–H(10)	2.64(6)	Hg(1B)–B(10)	3.167(5)
Hg(2B)–H(4)	2.75(4)	Hg(2B)–B(4)	3.442(6)
Hg(1A)–C(1A)	2.083(5)	Hg(1B)–C(1B)	2.078(5)
Hg(1A)–C(14A)	2.090(6)	Hg(1B)–C(14B)	2.092(5)
Hg(2A)–C(2A)	2.078(5)	Hg(2B)–C(7B)	2.076(5)
Hg(2A)–C(7A)	2.091(5)	Hg(2B)–C(2B)	2.085(6)
Hg(3A)–C(13A)	2.078(4)	Hg(3B)–C(8B)	2.075(5)
Hg(3A)–C(8A)	2.089(5)	Hg(3B)–C(13B)	2.076(5)
C(1A)–C(2A)	1.416(7)	C(1B)–C(2B)	1.404(7)
C(7A)–C(8A)	1.397(8)	C(7B)–C(8B)	1.434(7)
C(13A)–C(14A)	1.423(7)	C(13B)–C(14B)	1.391(8)
C(1A)-Hg(1A)-C(14A)	170.8(2)	C(1B)-Hg(1B)-C(14B)	176.5(2)
C(2A)-Hg(2A)-C(7A)	175.5(2)	C(2B)-Hg(2B)-C(7B)	174.4(2)
C(8A)-Hg(3A)-C(13A)	175.6(2)	C(8B)-Hg(3B)-C(13B)	173.3(2)

Table 3. Selected bond lengths [Å] and angles [°] in complex **5a**.

Hg(1A)–H(1A)	2.57(5)	Hg(1A)–B(1A)	3.381(8)
Hg(2A)–H(1A)	2.42(6)	Hg(2A)–B(1A)	3.342(9)
Hg(3A)–H(1A)	2.44(5)	Hg(3A)–B(1A)	3.193(9)
Hg(1A)–H(5A)	2.81(7)	Hg(1A)–B(5A)	3.527(9)
Hg(3A)–H(3A)	2.94(6)	Hg(3A)–B(3A)	3.529(10)
Hg(1B)–H(7A)	2.54(6)	Hg(1B)–B(7A)	3.369(9)
Hg(2B)–H(7A)	2.67(6)	Hg(2B)–B(7A)	3.346(8)
Hg(3B)–H(7A)	2.65(6)	Hg(3B)–B(7A)	3.326(9)
Hg(2B)–H(11A)	2.86(5)	Hg(2B)–B(11A)	3.448(8)
Hg(1A)–C(1A)	2.078(7)	Hg(1B)–C(14B)	2.067(8)
Hg(1A)–C(14A)	2.097(7)	Hg(1B)–C(1B)	2.073(8)
Hg(2A)–C(7A)	2.054(8)	Hg(2B)–C(2B)	2.066(8)
Hg(2A)–C(2A)	2.077(7)	Hg(2B)–C(7B)	2.078(8)
Hg(3A)–C(13A)	2.053(8)	Hg(3B)–C(8B)	2.062(8)
Hg(3A)–C(8A)	2.077(7)	Hg(3B)–C(13B)	2.088(9)
C(1A)–C(2A)	1.419(11)	C(1B)–C(2B)	1.411(11)
C(7A)–C(8A)	1.386(10)	C(7B)–C(8B)	1.419(11)
C(13A)–C(14A)	1.393(10)	C(13B)–C(14B)	1.416(12)
C(1A)-Hg(1A)-C(14A)	174.4(3)	C(14B)-Hg(1B)-C(1B)	174.1(3)
C(7A)-Hg(2A)-C(2A)	174.1(3)	C(2B)-Hg(2B)-C(7B)	172.4(3)
C(13A)-Hg(3A)-C(8A)	172.7(3)	C(8B)-Hg(3B)-C(13B)	174.7(3)

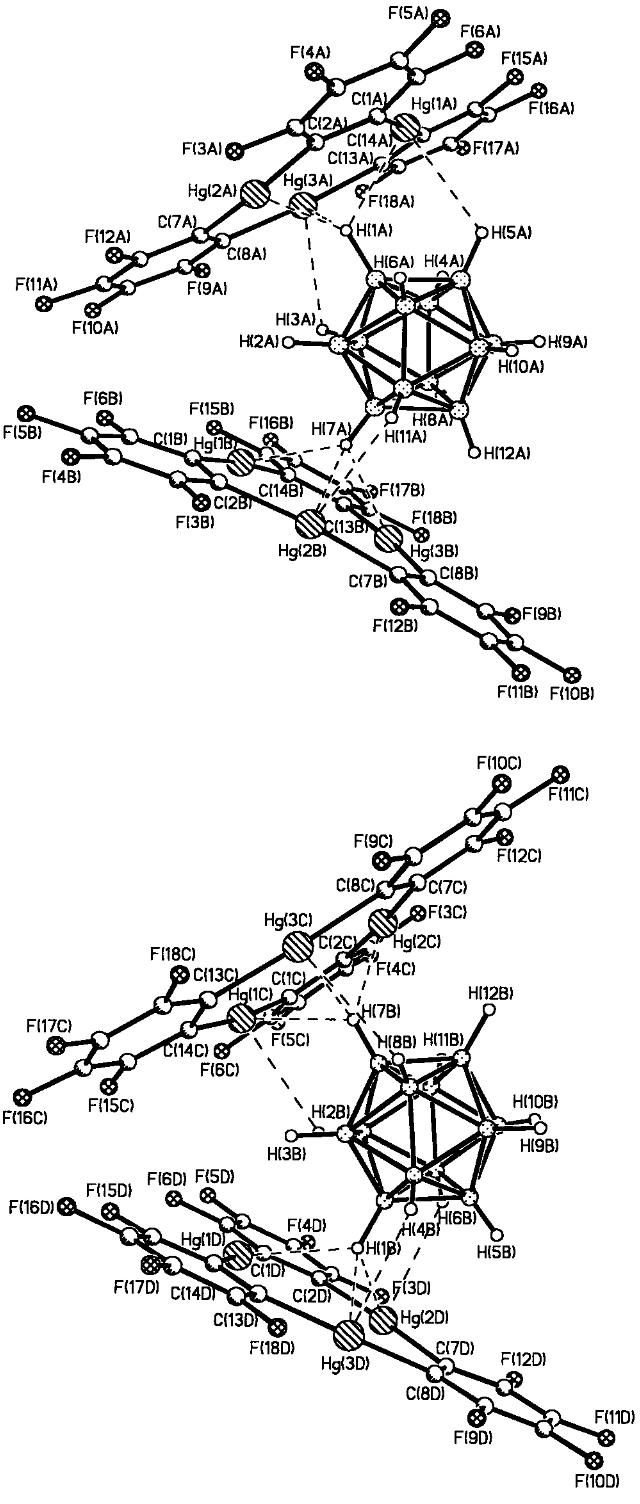

Figure 5. Molecular structures of **5a** (top) and **5b** (bottom) in the crystal.

and Hg–B distances for this type of coordination are in the ranges 2.41(6) – 2.72(7) Å (average 2.55 Å) and 3.193(9) – 3.381(8) Å (average 3.31 Å), respectively. Additionally, there are several B-H-Hg bridges (three in **5a** and four in **5b**) that arise through bonding of a B–H group to a single Hg atom of **1**. Here, the Hg–H and Hg–B distances are in the ranges 2.81(7) – 3.06(8) Å (average 2.91 Å) and 3.442(9) – 3.550(9) Å (average 3.50 Å), respectively.

Table 4. Selected bond lengths [Å] and angles [°] in complex **5b**.

Hg(1D)–H(1B)	2.59(6)	Hg(1D)–B(1B)	3.360(8)
Hg(2D)–H(1B)	2.51(6)	Hg(2D)–B(1B)	3.244(8)
Hg(3D)–H(1B)	2.41(6)	Hg(3D)–B(1B)	3.203(8)
Hg(3D)–H(4B)	2.92(7)	Hg(3D)–B(4B)	3.442(9)
Hg(2D)–H(6B)	2.86(6)	Hg(2D)–B(6B)	3.491(9)
Hg(1C)–H(7B)	2.72(7)	Hg(1C)–B(7B)	3.360(8)
Hg(2C)–H(7B)	2.52(6)	Hg(2C)–B(7B)	3.282(8)
Hg(3C)–H(7B)	2.53(6)	Hg(3C)–B(7B)	3.300(8)
Hg(1C)–H(2B)	2.92(6)	Hg(1C)–B(2B)	3.532(9)
Hg(3C)–H(8B)	3.06(8)	Hg(3C)–B(8B)	3.550(9)
Hg(1C)–C(1C)	2.071(8)	Hg(1D)–C(14D)	2.061(7)
Hg(1C)–C(14C)	2.080(8)	Hg(1D)–C(1D)	2.074(8)
Hg(2C)–C(2C)	2.061(8)	Hg(2D)–C(7D)	2.080(8)
Hg(2C)–C(7C)	2.074(8)	Hg(2D)–C(2D)	2.081(7)
Hg(3C)–C(8C)	2.070(9)	Hg(3D)–C(13D)	2.064(8)
Hg(3C)–C(13C)	2.073(9)	Hg(3D)–C(8D)	2.087(7)
C(1C)–C(2C)	1.450(11)	C(1D)–C(2D)	1.418(11)
C(7C)–C(8C)	1.404(11)	C(7D)–C(8D)	1.399(10)
C(13C)–C(14C)	1.427(11)	C(13D)–C(14D)	1.417(10)
C(1C)-Hg(1C)-C(14C)	173.3(3)	C(14D)-Hg(1D)-C(1D)	176.6(3)
C(2C)-Hg(2C)-C(7C)	175.2(3)	C(7D)-Hg(2D)-C(2D)	176.2(3)
C(8C)-Hg(3C)-C(13C)	174.7(3)	C(13D)-Hg(3D)-C(8D)	173.6(3)

The distortions of the macrocyclic units in **5a** and **5b** are not systematic. The C-Hg-C bond angles lie in the range 172.4(3) – 176.6(3)° (average 174.3°). The mutual orientation of the macrocycles in **5a** is close to a staggered conformation, whereas in **5b** they are almost in an eclipsed conformation. The dihedral angles between the mean planes of the central nine-membered rings of the macrocycles in **5a** and **5b** are 58.7 and 59.1°, respectively, which is considerably greater than that in **3** (19°, see above).

Experimental Section

The starting macrocycle **1** was synthesized according to the published procedure.[5a] The other starting reagents, $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{B}_{10}\mathrm{H}_{10}]$ and $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{B}_{12}\mathrm{H}_{12}]$, were obtained as described in refs. [11, 12]; $(\mathrm{PPN})_2[\mathrm{B}_{10}\mathrm{H}_{10}]$ was prepared by an exchange reaction of $\mathrm{K}_2[\mathrm{B}_{10}\mathrm{H}_{10}]$ with $[\mathrm{PPN}]^+\mathrm{Cl}^-$ in aqueous solution and was characterized by its ^{1}H and ^{11}B NMR spectra. Reaction solvents were purified by conventional methods and were distilled prior to use. THF was distilled from sodium benzophenone under Ar.

IR spectra were measured on a Specord M-82 instrument (Carl Zeiss Jena) with a resolution of 2 cm^{-1}. IR spectra of the reaction solutions were recorded in the ν(BH) region (1500 – 2500 cm^{-1}) at various concentrations ($0.4 - 4 \times 10^{-3}$ M) and ratios of the reagents in CaF_2 cells ($d = 0.0125 - 0.0612$ cm). IR spectra of the solid samples were recorded in Nujol mulls over the range 400 – 4000 cm^{-1}. The compositions of the complexes in solution were determined by the molar ratio and continuous variation (Job) methods[7] (see also ref. [1g]).

Variable-temperature NMR data were acquired on Bruker AMX400 and WP200 spectrometers. The ^{11}B and ^{199}Hg chemical shifts were determined with $\mathrm{BF}_3 \cdot \mathrm{Et}_2\mathrm{O}$ and $\mathrm{Ph}_2\mathrm{Hg}$, respectively, as external standards. All the NMR spectra were recorded starting at low temperatures (180 K). The solutions to be studied were prepared in 5 mm NMR tubes in a cold *i*PrOH bath and transferred to precooled NMR probes.

$(n\mathrm{Bu}_4\mathrm{N})_2[\{(o\text{-}\mathrm{C}_6\mathrm{F}_4\mathrm{Hg})_3\}(\mathrm{B}_{10}\mathrm{H}_{10})]$ (2): At room temperature, a solution of **1** (0.1046 g, 0.1 mmol) in acetone (5 mL) was added to a solution of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{B}_{10}\mathrm{H}_{10}]$ (0.0604 g, 0.1 mmol) in acetone (5 mL), and after 5 min the reaction mixture was concentrated to dryness in vacuo at 20 °C. The oily residue was treated with methanol (2 mL) to give colourless crystals of **2** $\cdot$ $\mathrm{CH}_3\mathrm{OH}$, which were dried at room temperature. Yield: 0.158 g (94 %);

elemental analysis calcd (%) for $C_{51}H_{86}F_{12}ON_2B_{10}Hg_3$: C 36.36, H 5.10, F 13.54, B 6.53, Hg 35.82; found: C 36.88, H 5.05, F 13.49, B 6.30, Hg 35.03; IR (Nujol): ν(BH) = 2287 (s), 2454 cm^{-1} (s).

$(PPN)_2[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{10}H_{10})]$ (3): A hot solution of $(PPN)_2[B_{10}H_{10}]$ (0.120 g, 0.1 mmol) in ethanol (15 mL) was added to a stirred solution of **1** (0.209 g, 0.2 mmol) in ethanol (5 mL). After 5 min, colorless crystals of complex **3** had precipitated, which were collected by filtration, washed with EtOH, and dried at 20°C in vacuo. Yield: 0.253 g (77%); elemental analysis calcd (%) for $C_{108}H_{70}F_{24}N_2P_4B_{10}Hg_6$: C 39.37, H 2.12, F 13.85, P 3.91, B 3.34, Hg 36.63; found: C 39.40, H 2.26, F 13.13, P 3.81, B 3.31, Hg 36.80; IR (Nujol): ν(BH) = 2309 (s), 2408 (w), 2485 cm^{-1} (m).

$(nBu_4N)_2[\{(o\text{-}C_6F_4Hg)_3\}_2(B_{12}H_{12})]$ (5): A hot solution of $(nBu_4N)_2[B_{12}H_{12}]$ (0.031 g, 0.05 mmol) in ethanol (3 mL) was added to a stirred solution of **1** (0.105 g, 0.1 mmol) in ethanol (5 mL). A colorless crystalline precipitate of complex **5** was immediately formed. After 10 min, the complex was collected by filtration, washed with EtOH, and dried in vacuo at room temperature. Yield: 0.112 g (83%); elemental analysis calcd (%) for $C_{68}H_{84}F_{24}N_2B_{12}Hg_6$: C 29.97, H 3.08, F 16.75, N 1.02; found: C 30.09, H 3.10, F 16.49, N 0.97; IR (Nujol): ν(BH) = 2328 (s), 2433 (w), 2486 cm^{-1} (m).

X-ray diffraction study: Details of the crystal data, data collections, and structure refinement parameters for **2** · MeOH, **3** · Et_2O, and **5** are given in Table 5. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 using anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms of the borate anions as well as the hydroxyl hydrogen of the methanol solvate molecule in **2** were located from the Fourier synthesis and refined in the isotropic approximation. Other hydrogen atoms in **2**, **3**, and **5** were placed in geometrical positions and were included in the structure factor calculation in the riding motion approximation. Data reduction and further calculations were performed with SAINT[13] and SHELXTL-97[14] (for **3** and **5**), and SHELXTL-PLUS 5[15] (for **2**) on an IBM PC AT. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154788 (**2**), CCDC-154789 (**3**), and CCDC-154790 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 5. Crystal data, data collection, and structure refinement parameters for **2**, **3**, and **5**

	2	**3**	**5**
formula	$C_{51}H_{86}B_{10}F_{12}N_2OHg_3$	$C_{112}H_{80}B_{10}F_{24}N_2OP_4Hg_6$	$C_{68}H_{84}B_{12}F_{24}N_2Hg_6$
M_r	1681.09	3361.30	2718.63
crystal system	orthorhombic	monoclinic	triclinic
space group	*Pbca*	$P2_1/n$	$P\bar{1}$
a [Å]	16.728(9)	19.4290(7)	16.7970(2)
b [Å]	23.082(12)	21.5690(7)	18.7592(2)
c [Å]	32.046(12)	26.492(1)	28.5834(4)
α [°]	90	90	98.336(1)
β [°]	90	91.183(1)	103.447(1)
γ [°]	90	90	108.252(1)
V [Å^3]	12373(10)	11099.6(7)	8084.3(2)
Z	8	4	4
ρ_{calcd} [gcm^{-3}]	1.805	2.011	2.234
T [K]	173(2)	100.0(2)	110.0(2)
diffractometer	Siemens P3/PC	SMART 1000 CCD	SMART 1000 CCD
scan mode	ω	ω and φ	ω and φ
θ_{max} [°]	22.5	31.5	29
μ ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å) [cm^{-1}]	75.00	84.17	114.49
absorption correction	Ψ-scans	semiempirical from equivalents	
transmission factors, min/max	0.055/0.499	0.653/0.984	0.389/0.947
unique reflections (R_{int})	6932	33954 (0.0640)	39076 (0.0699)
observed reflections [$I > 2\sigma(I)$]	4763	18936	24079
parameters	756	1472	2113
R_1 [$I > 2\sigma(I)$] [a]	0.0516	0.0350	0.0427
wR_2 (all data))[b]	0.1332	0.0664	0.0936

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

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