www.elsevier.nl/locate/jorganchem
Journal of Organometallic Chemistry 585 (1999) 201–210

Crown compounds for anions. Spectroscopic and theoretical studies of complexation of borohydride anions with cyclic trimeric perfluoro-*o*-phenylenemercury

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Received 3 February 1999; received in revised form 8 April 1999

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 borohydride anions in THF and 1,2-dichloroethane solutions to form complexes $\{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-}$ (**2**) and $\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$ (**3**). According to the IR data, complex **2** contains both terminal and coordinated B–H bonds while all four B–H bonds of the BH_4^- ion are coordinated with the mercury atoms in complex **3**. The use of NMR spectroscopy provided the identification of one more complex of **1** with BH_4^-, which can be formulated as $\{[(o\text{-}C_6F_4Hg)_3](BH_4)\}^-$ (**4**). The stability constants of complexes **2** and **3** have been determined by IR spectroscopy. Quantum-chemical calculations of **2**–**4** by the AM1 method suggest that the complexes have the unusual bipyramidal, sandwich and half-sandwich structures, respectively. In contrast to **1**, the interaction of $(C_6F_5)_2Hg$ with BH_4^- anions in THF gives a single complex $\{[(C_6F_5)_2Hg](BH_4)\}^-$ (**5**) independently of the reagent ratio. This complex is much less stable than **2** and **3**.

Keywords: Borohydride complexes; IR spectroscopy; NMR spectroscopy; Polymercury-containing macrocycles; Quantum-chemical calculations

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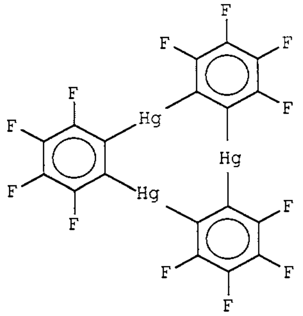
1. Introduction

During the past decade, a large number of papers on complexation of anions with polymetallamacrocycles have been published (see e.g. Refs. [1–4]). These macrocycles contain several Lewis acidic centres in the macrocyclic chain and, therefore, can be considered as the peculiar antipodes of crown ethers and their thia and aza analogues. Most of the results were obtained for polymercury-containing macrocycles [3,4], which proved to be very efficient hosts for binding various anionic species.

In our previous work on the complexing and catalytic properties of polymetallamacrocycles [3a–m], we have described the complexes of chloride [3b], bromide [3b], iodide [3c], thiocyanate [3j], 4-nitrophenolate and 4-nitrothiophenolate [3l] anions with cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**1**) [5], which contains three Hg atoms in a planar nine-membered cycle.



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PII: S0022-328X(99)00200-4

It has been shown that in the case of bromide and iodide anions, the resulting complexes of the composition $[(o\text{-}C_6F_4Hg)_3X]^-$ (X = Br, I) have (in the solid state) an unusual structure of polydecker bent sandwiches $[(\cdots\mathbf{1}\cdots X\cdots)_n]^{n-}$ wherein every halide anion is coordinated to six mercury atoms of two neighbouring molecules of **1** [3b,c]. An analogous polymeric structure has been established for a 1:1 complex of **1** with the thiocyanate anion [3j]. The nature of chemical bonds in the complexes of halide anions with **1** and some other polymercury-containing macrocycles has been investigated by quantum-chemical methods and it has been shown that a uniform description of the bonding in such complexes, not depending on the number of mercury atoms in the macrocycle, can be reached within the framework of the concept of generalised chemical bonds [3h,i,k].

In the present paper, we report on the ability of macrocycle **1** to bind effectively borohydride anions in solution with formation of complexes whose composition is strongly dependent on the reagent ratio. The resulting complexes are the first examples of host–guest complexes of polymetallamacrocycles with BH_4^- ions. For preliminary communication see Ref. [3m]. The complexes of *o*-carboranylmercury macrocycles with *closo*-$[B_{10}H_{10}]^{2-}$ dianions were described previously by Hawthorne et al. [4c,f].

2. Results and discussion

The complexation of macrocycle **1** with borohydride anions was studied by the IR and NMR spectroscopy methods. The reactions were carried out in THF and 1,2-dichloroethane (DCE) solutions at room temperature in an Ar atmosphere. Under such conditions, macrocycle **1** reacted rapidly with BH_4^- ions to afford three complexes **2**–**4** with different BH_4^-:**1** ratios.

Complex **2** of composition $\{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-}$ is formed at a two to four-fold excess of borohydride anions with respect to **1** and contains two BH_4^- ions per macrocycle molecule. The formation of another complex $\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$ (**3**) occurs at a two- to five-fold excess of **1** with respect to BH_4^-; this complex contains one BH_4^- anion per two molecules of the macrocycle. Finally, the third complex (**4**), formulated as $\{[(o\text{-}C_6F_4Hg)_3](BH_4)\}^-$, is produced at an equimolar ratio of the reagents. Unfortunately, our attempts to obtain the resulting complexes as crystals suitable for the X-ray analysis failed. Nevertheless, the detailed spectroscopic studies together with the quantum-chemical calculations revealed a number of the essential peculiarities of their structures.

2.1. IR spectroscopy data

The IR spectroscopy turned out to be very informative in studying the complexation of borohydride anions with macrocycle **1**. As is known, the IR spectra of the BH_4^- ion and its metal complexes exhibit characteristic ν(BH) bands in the 2000–2600 cm^{-1} region [6], and these bands proved to be very convenient for monitoring the process of the complexation. By means of the IR method, complexes **2** and **3** were detected and their compositions and stability constants determined. This method was also successfully employed for detecting the terminal and coordinated B–H bonds in the complexes. Unlike **2** and **3**, complex **4** could not be fixed unambiguously in the IR spectra however its formation is proved by the results of the NMR studies which will be considered in detail after discussing the IR data.

2.1.1. Complex 2

When **1** is gradually added to an excess of *n*-Bu_4NBH_4 in THF (BH_4^-:**1** = 4–2:1, $[BH_4^-]_o = 8 \times 10^{-2}$ M), the intensity of the ν(BH) band of free borohydride anions (at 2201 cm^{-1}) [7] decreases and three new bands (at 2300, 2080 and 2015 cm^{-1}), shifted to high-frequency and low-frequency regions, appear in the spectrum indicating a complexation of BH_4^- with the Hg atoms of **1**[1]. A decrease in intensity of the initial ν(BH) band and an increase in those of new bands occur with the isosbestic points (Fig. 1(a)). When the BH_4^-:**1** molar ratio becomes equal to 2:1, the ν(BH) band of free BH_4^- ions practically disappears and the spectrum shows only the above-mentioned bands at 2300 (s), 2080 (w) and 2015 (s) cm^{-1} belonging to complex **2**. Analogous spectral changes are observed when the reaction is carried out in DCE solution.

In accordance with the literature data [6,8–12], a high-frequency band of **2** (2300 cm^{-1}) can be assigned to stretching vibrations of the terminal B–H bonds ($\nu(BH)^t$) in the complex. The increase in the $\nu(BH)^t$ frequency by about 100 cm^{-1} (relatively to ν(BH) for free BH_4^- ion) is typical of the metal complexes with borohydride anions [6,8–12]. A low-frequency strong and broad band at 2015 cm^{-1}, shifted by 186 cm^{-1} relatively to the initial BH_4^- band, can be attributed to stretching vibrations ($\nu(BH)^b$) of the B–H bonds coordinated to the Hg atoms of the macrocycle through the hydrogen atoms. When *n*-Bu_4NBH_4 is substituted by $NaBD_4$ in the reaction with **1**, the ν(BH) bands of **2** at 2300 and 2015 cm^{-1} undergo an isotopic shift to 1730

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[1] Besides the main intense band at 2201 cm^{-1}, high (2269 cm^{-1}) and low (2129 cm^{-1}) frequency bands of low intensity are also observed in the spectra of BH_4^- anion. These bands are assigned to combined vibration ($\delta_s(BH) + \delta_{as}(BH)$) and to overtone $2\delta_{as}(BH)$, respectively.

and 1510 cm^{-1}, respectively. The isotopic ν(BH)/ν(BD) ratio for both bands is 1.33, which is characteristic for bands of the same nature. The additional weak band at 2080 cm^{-1} in the spectrum of **2** could be assigned to the overtone of the δ_{as}(BH) mode.

The IR spectra of the solid films of complex **2**, recorded in the 1500–400 cm^{-1} region, revealed the ν(HgHB) and δ_{as}(BH) vibrations. A band of **2** at 1304 cm^{-1}, which is absent in the spectrum of free BH_4^- anion, can be assigned to the ν(HgHB) mode on the basis of the literature data for stretching vibrations of the bridged M–H–B groups [6]. The δ_{as}(BH) band observed for the free BH_4^- anion at 1072 cm^{-1} is shifted to 1054 cm^{-1} in complex **2**. Such a low-frequency shift demonstrates the peculiarity of the resulting complex because usually the increase in the $\delta_{as(}$BH) frequency occurs as a result of complexation [6,9,14,15].

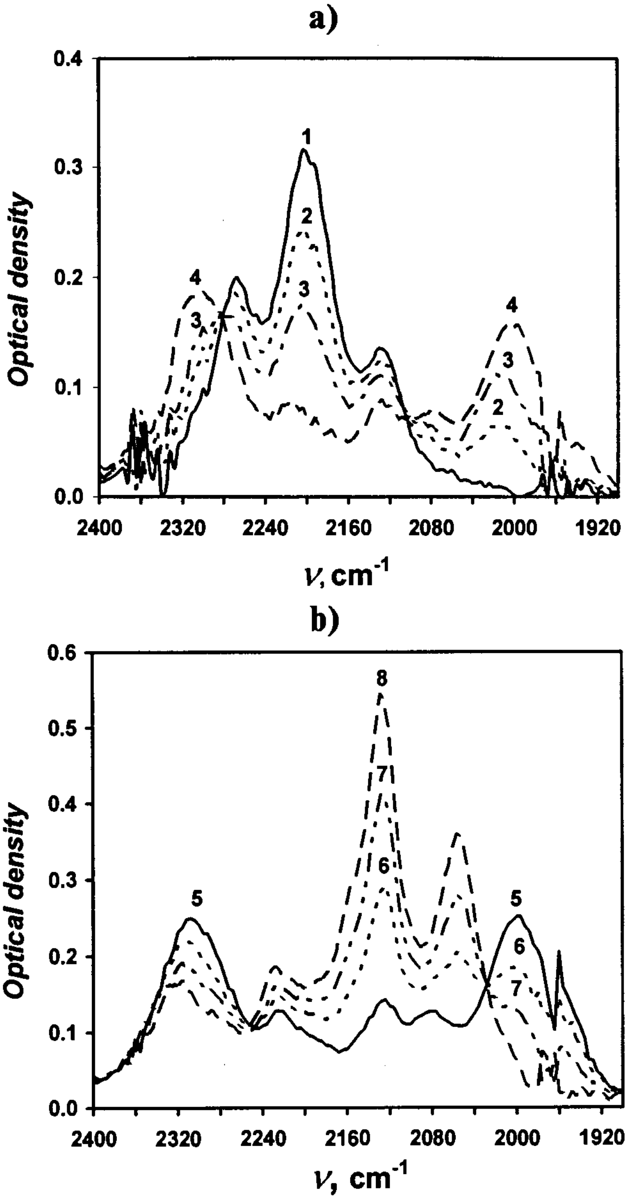

Fig. 1. IR spectra in the ν(BH) range: (1) n-Bu_4NBH_4 in THF; (2)–(8) reaction solutions in THF with different BH_4^-:**1** molar ratios: (2) 1:4; (3) 1:3; (4) 1:2; (5) 1:1.5; (6) 1:1; (7) 1.5:1; (8) 2:1.

A study of the composition of complex **2** by the mole ratio and continuous variation (Job) methods [13] has shown that it contains two BH_4^- ions per molecule of **1**, and consequently **2** can be formulated as $[(o\text{-}C_6F_4Hg)_3(BH_4)_2]^{2-}$. The complex is quite stable: its stability constant (K_1) in THF (determined by the mole ratio method) amounts to 10^4 l^2 mol^{-2} at room temperature.

2.1.2. Complex 3

If the solution of complex **2** (formed at the BH_4^-:**1** molar ratio of 2:1) is treated by additional amounts of the macrocycle, the gradual disappearance of the ν(BH) bands of **2** (at 2300 and 2015 cm^{-1}) is observed and two new intense ν(BH) bands (at 2129 and 2057 cm^{-1}) belonging to complex **3** appear in the spectrum. In addition, a weak high-frequency band at 2230 cm^{-1} arises, which can be assigned to the combination δ_s(BH) + δ_{as}(BH) vibration of **3**. It should be noted that a decrease in intensities of the IR bands of **2** and an increase in intensities of those of **3** occur with the isobestic points as well (Fig. 1(b)). When the BH_4^-:**1** molar ratio reaches a value of 1:5 the IR spectrum shows only complex **3** together with an excess of unreacted **1**. On replacement of n-Bu_4NBH_4 by $NaBD_4$ in the reaction with **1**, the $\nu(BH)^b$ bands of **3** at 2129 and 2057 cm^{-1} are shifted to 1610 and 1554 cm^{-1}, respectively. The isotopic ν(BH)/ν(BD) ratio for both bands is again equal to 1.32, confirming their assignment.

The ν(HgHB) band in the spectrum of the solid films of **3** is manifested at 1300 cm^{-1}. The intensity of this band is greater than that of the corresponding band in the spectrum of **2**. The bending δ_{as}(BH) band of **3** is observed even at lower frequency (1037 cm^{-1}) than that of **2**.

Using the Job method, it has been established that complex **3** has a composition $\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$, i.e. contains two molecules of the macrocycle per one BH_4^- anion. Since in the case of **3**, both ν(BH) bands are shifted to a low-frequency region (relatively to the corresponding band of free BH_4^- ion) one may conclude that all four B–H bonds of BH_4^- anion in this complex are coordinated to the mercury atoms. Complex **3** is even more stable than **2**: its stability constant (K_3) (determined by the mole ratio method) reaches 10^7 l^2 mol^{-2}. So the high stability of **3** and **2** is quite unusual for complexes of BH_4^- anions and other boron hydrides with mercury compounds.

As mentioned above, the attempts to detect complex **4** by the IR spectroscopy were unsuccessful. At the BH_4^-:**1** molar ratio of 1:1, the IR spectra of the solution show the presence of only complexes **2** and **3**. However some broadening and small low-frequency shift of the $\nu(BH)^b$ bands (by 15 cm^{-1}) are observed under these conditions. It is interesting that a lowering in temperature (to 200 K) causes an additional broadening (rather than narrowing) of the $\nu(BH)^b$ band of complex **2**. Thus, the failure in detection of complex **4** in the IR spectra is apparently due to the overlapping of its $\nu(BH)^b$ bands with those of complex **2**.

2.1.3. *Complexation of $(C_6F_5)_2Hg$ with BH_4^- ions*

To reveal the cooperative effect of the Hg atoms in macrocycle **1** on the binding of BH_4^- anions, the complexation of BH_4^- with monomeric acyclic analogue of **1**, viz. $(C_6F_5)_2Hg$ has been studied.

After addition of $(C_6F_5)_2Hg$ to a THF solution of *n*-Bu_4NBH_4, both high- and low-frequency $\nu(BH)$ bands (at 2330 and 2115 cm^{-1}) of the coordinated BH_4^- ion appear in the spectrum (Fig. 2). An increase in intensities of these bands and a decrease in intensity of the $\nu(BH)$ band of free BH_4^- anion occur again with the isosbestic points. When the $BH_4^-:(C_6F_5)_2Hg$ molar ratio becomes equal to 1:6, the $\nu(BH)$ band of free BH_4^- anion practically disappear and the IR spectrum exhibits the above bands at 2330 and 2115 cm^{-1}, belonging to the terminal and coordinated B–H bonds respectively in the resulting complex. Thus, $(C_6F_5)_2Hg$, in contrast to **1**, reacts with BH_4^- anions to give only one complex (**5**) independently of the reagent ratio. The composition of this complex (determined by the Job method) corresponds to the formula $\{[(C_6F_5)_2Hg](BH_4)\}^-$. Complex **5** is much less stable than **2** and **3**: its stability constant (K_4) is 10^2 l mol^{-1}.

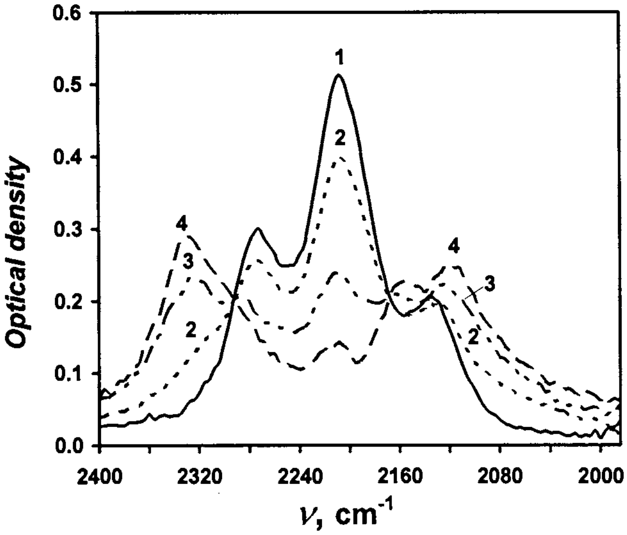

Fig. 2. IR spectra in the $\nu(BH)$ range: (1) *n*-Bu_4NBH_4 in THF; (2)–(4) reaction solutions in THF with different $BH_4^-:Hg(C_6F_5)_2$ molar ratios: (2) 1:0.5; (3) 1:1; (4) 1:6.

2.2. *NMR studies*

The room-temperature ^1H-NMR spectrum of a $[D_8]$THF solution of *n*-Bu_4NBH_4 shows multiplets of the alkyl groups ($\delta = 3.52$, 1.78, 1.55 and 1.10 ppm) and a typical well-resolved resonance of the BH_4^- protons ($\delta = -0.05$ ppm) with the $^1J(^1H-^{11}B)$ value of 81 Hz. The $^{11}B\{^1H\}$-NMR spectrum of this solution displays a singlet at -38.4 ppm. The room-temperature ^{199}Hg-NMR spectrum of macrocycle **1** in THF contains well-resolved triplet of triplets of triplets at -323.9 ppm with $^3J(^{199}Hg-^{19}F) = 437$ Hz, $^4J(^{199}Hg-^{19}F) = 124$ Hz and $^5J(^{199}Hg-^{19}F) = 27$ Hz.

2.2.1. *Complex 2*

According to the IR data, the addition of a three-fold excess of *n*-Bu_4NBH_4 to a THF solution of **1** leads to the formation of complex **2**. In good agreement with the IR spectra, the solution of **2** in $[D_8]$THF shows the strongly changed NMR parameters of **1** and the BH_4 groups. These groups exhibit now broadened resonances at 1.6 and -34.8 ppm in the room-temperature ^1H- and $^{11}B\{1H\}$-NMR spectra, respectively. At 200 K, the ^{11}B line is transformed into a sharp singlet at -38.4 ppm (free BH_4^-) and a broadened resonance at -30.4 ppm assigned to the coordinated BH_4^- ions in **2**. The transformation is reversible and thus **2** dissociates on the NMR time scale to give free BH_4^- anions and **1**. Unfortunately the BH_4 resonances were not detected in the low-temperature ^1H-NMR spectrum, probably, because of strong broadening effects.

The ^{199}Hg-NMR spectrum of the solution of **2**, recorded at 200 K, shows a poorly resolved triplet at -13.4 ppm with $J(^{199}Hg-^{19}F) = 440$ Hz. Thus, the interaction between **1** and *n*-Bu_4NBH_4 leads to the low-field displacement of the ^{199}Hg signal more than 300 ppm. Such a down-field position could be reasonable for **2** because similar shifts have been previously reported for the complexes of *o*-carboranylmercury macrocycles with *closo*–$B_{10}H_{10}^{2-}$ dianions [4c,f]. The ^{199}Hg spectra of **2** demonstrate a reversible temperature evolution to show finally a single resonance with δ -50 ppm at 295 K. Taking into account the temperature-dependent $^{11}B\{^1H\}$-NMR spectra, this behavior is well rationalised in terms of the dissociation of **2**.

2.2.2. *Complex 3*

As it follows from the IR spectra, the addition of a three-fold excess of **1** to a THF solution of *n*-Bu_4NBH_4 yields complex **3**. The ^{199}Hg-NMR spectrum of the solution of this complex in $[D_8]$THF at 190 K exhibits two broadened triplets at -153.9 and -340.7 ppm with $J(^{199}Hg-^{19}F) = 440$ Hz. It is well known that the ^{199}Hg chemical shifts in organomercury compounds dissolved in donor solvents are temperature-dependent [16]. Therefore, the resonance with δ -340.7 ppm can be well assigned to free **1**. Then, the triplet at −153.9 ppm could be attributed to complex **3**, showing an 187 ppm low-field change of δ (^{199}Hg) as a result of coordination of the BH_4^- anion with the mercury atoms. The BH_4 group exhibits now a broadened line at 4.8 ppm with Δν of 240 Hz in the 190 K ^{1}H-NMR spectrum. It is remarkable that the ^{1}H chemical shifts of the *n*-Bu groups remain practically unchanged excluding an upfield displacement of 0.14 ppm observed for the NCH_2 resonance.

As is known, the boron hydrides, bonded to transition metal centres [17] (as well as the hydride ligands in transition metal hydride systems) exhibit the signals in high-field region of the ^{1}H-NMR spectra. For the BH_4 resonance in **3**, we observe the low-field position (4.8 ppm). However, this result is not surprising because the terminal Hg–H hydrides give signals in unusually down fields (between 11 and 17 ppm) [18]. Hence, the chemical shift of 4.8 ppm (versus −0.05 ppm in free *n*-Bu_4NBH_4) could be a good NMR evidence for the presence of the Hg–H–B bridges in complex **3**.

Upon increasing the temperature, the above resonances in the 190 K ^{199}Hg-NMR spectrum broaden, coalesce (225 K) and give finally a single line with δ −242.6 ppm at room temperature. This spectral picture is completely reversible and thus complex **3** dissociates on the NMR time scale with the rate constant and ΔG* value of 1.5×10^4 s^{-1} and 8.7 kcal·mol^{-1}, respectively. These values were calculated at the coalescence temperature [19] on the basis of the low-temperature ^{199}Hg shifts.

2.2.3. Complex *4*

The room- and low-temperature IR spectra have shown that the interaction of *n*-Bu_4NBH_4 with **1** in THF at the equimolar ratio of the reagents results in a solution containing a mixture of complexes **2** and **3**. In contrast to this, the ^{199}Hg-NMR spectrum of this solution cooled to 180 K shows three broadened triplets with δ −14, −73 and −150 ppm. It becomes clear that two side resonances correspond to complexes **2** and **3**. Significantly, the position of the central line is well predicted by the averaging of the chemical shifts of two side lines. Linear additivity of δ ^{199}Hg values is well known [16] and therefore the resonance at −73 ppm can be assigned to complex **4**, $\{[(o\text{-}C_6F_4Hg)_3](BH_4)\}^-$, in which one BH_4^- ion is coordinated with one macrocycle molecule. Note that in agreement with the assignment, the ^{199}Hg resonance at δ −73 ppm has the greatest integral intensity.

Upon raising the temperature, all the ^{199}Hg resonances broaden and coalesce (220–230 K) to produce finally a broadened triplet with δ −102.8 ppm at room temperature. This reversible temperature behavior demonstrates an exchange by the BH_4^- groups between complexes **3**, **2** and **4** operating on the NMR time scale. Under conditions of the fast exchange, the room-temperature ^{11}B{1H}-NMR spectrum shows a sharp singlet at −24 ppm which is transformed to a broadened quintet with $^1J(^{11}B–^1H) = 78$ Hz in the proton-coupled spectrum. The ^{1}H-NMR spectrum exhibits a very broadened resonance with δ of 3.8 ppm. This line narrows with the {^{11}B} irradiation.

2.3. Quantum-chemical calculations

A characteristic feature of the presently known complexes of polymercury-containing macrocycles with anions is the simultaneous coordination of anionic species with all mercury atoms of the cycle which leads to realisation of unusual bipyramidal, sandwich and half-sandwich structures or fragments [3b–e,3k,4j]. One may suggest that the above-described complexes of **1** with borohydride anions have similar non-classic structures wherein BH_4^- ions are bonded to all mercury atoms. In order to check up this assumption, we modelled the fragments of the potential energy surface (PES) of the half-sandwich $[\mathbf{1}–BH_4]^-$, bipyramidal $[BH_4–\mathbf{1}–BH_4]^{2-}$ and sandwich $[\mathbf{1}–BH_4–\mathbf{1}]^-$ complexes corresponding by their composition to the really observed complexes 4, **2** and **3**, respectively. The calculations were performed by the AM1 method [20]. The results are given in Tables 1 and 2 and in Fig. 3.

2.3.1. Half-sandwich complexes

The full optimisation of the complex geometry was carried out. Together with the symmetric initial arrangement of the borohydride anion relatively to the macrocycle, the initial arrangements with coordination of one hydrogen atom of the BH_4^- ion to one Hg atom and with coordination of two hydrogen atoms of the BH_4^- ion to two Hg atoms have been tested.

The calculations revealed a high affinity of borohydride ion to macrocycle **1**, which contains three *sp*-hybridized Hg atoms having two unoccupied *p*-orbitals each. Two minima corresponding to the symmetric (C_{3v}) coordination of the BH_4^- anion with one (**4a**) or three (**4b**) hydrogen atoms directed towards the macrocycle were detected on the PES (Fig. 3). Complex **4a** is considerably more stable (by 26.1 kcal mol^{-1}) than complex **4b** (Table 1). It can be explained by the noticeable bonding of the Hg atoms in **4a** not only with the hydrogen atom lying on the symmetry axis of the complex and directed down from the boron atom to the macrocycle but also with three other hydrogen atoms which are directed upwards. It is noteworthy that the contribution of the boron atom in the bonding of the borohydride anion to the macrocycle is of the same order of magnitude as the contribution of the hydrogen atoms. Thus, the BH_4^- anion in the half-sandwich complex is bonded virtually as a whole to the macrocycle. The high-symmetric borohydride anion with its

Table 1

Heats of formation (ΔH_f), energies of **1**–BH_4^- bond cleavage (Δ), E_{homo} and E_{lumo} energy levels and effective charges (q) of the complexes of macrocycle **1** with BH_4^- (A) calculated by the AM1 method

Compound	ΔH_f (kcal mol^{-1})	Δ (kcal mol^{-1})	E_{homo} (eV)	E_{lumo} (eV)	q (a.u.)					
					Hg	C^1	B	H [a]	H	A
1	−248.2		−9.77	−1.38	0.63	−0.27				
BH_4^-	−2.9		−3.96	10.86			−0.16		−0.21	−1.00
[**1**–HBH_3]$^-$ (**4a**)	−394.1	143.0	−6.78	2.01	0.62	−0.28	0.02	−0.14	−0.07	−0.33
[**1**–H_3BH]$^-$ (**4b**)	−368.0	116.9	−6.83	1.95	0.63	−0.28	0.01	−0.12	−0.06	−0.41
[H_3BH–**1**–HBH_3]$^{2-}$ (**2a**)	−400.3	3.3	−4.07	5.09	0.66	−0.26	−0.06	−0.20	−0.10	−0.56
[HBH_3–**1**–H_3BH]$^{2-}$ (**2b**)	−390.3	19.4	−4.04	5.15	0.65	−0.27	−0.07	−0.11	−0.09	−0.49
[H_3BH–**1**–H_3BH]$^{2-}$ (**2c**) [b]	−408.4	37.5	−4.01	5.17	0.65	−0.27	−0.02	−0.18	−0.08	−0.44
		11.7					−0.02	−0.14	−0.11	−0.55
[**1**–$HBH_3\cdots$**1**]$^-$ (**3a**) [c]	−644.7		−6.93	−0.09	0.62	−0.28	0.01	−0.14	−0.07	−0.34
		2.4			0.64	−0.26				
[**1**–HBH_3–**1**]$^-$ (**3b**) [d]	−656.5	40.3	−7.59	0.49	0.59	−0.28	0.10	−0.09		−0.20
		14.2			0.61	−0.28		−0.07		
[**1**–HBH_2H–**1**]$^-$ (**3c**) [e]	−664.6	22.3	−7.60	8.44	0.59	−0.29	0.10	−0.09		−0.20
					0.60					
									−0.06	

[a] Hydrogen atoms of BH_4^- anion directed to macrocycle.

[b] The lower line corresponds to tridentate coordination of the anion.

[c] The lower line corresponds to 'solvating' macrocycle.

[d] The lower line corresponds to the macrocycle with tridentate coordination of the anion.

[e] The first line corresponds to four Hg atoms to which the anion is shifted; the second line corresponds to two other Hg atoms; the third line corresponds to hydrogen atoms lying in the horizontal plane.

filled a_1 and triply degenerate t_2 orbitals is well simulated by the model of united atom with lone pairs on the *s*- and three *p*-orbitals, respectively, and the electronic structure of complex **4a** is very close to that of the half-sandwich complexes of macrocycle **1** with the halide anions [3f, h]. It is likely that complex **4** detected by the NMR method has the structure of **4a**.

2.3.2. Bipyramidal complexes

The full optimisation of the complex geometry was carried out and three minima were detected on the PES. Two of them correspond to symmetric (D_{3h}) bipyramidal complexes with the coordination of one (**2a**) or three (**2b**) hydrogen atoms of each BH_4^- anion with the macrocycle (Fig. 3). The third, major minimum corresponds to complex **2**c (C_{3v} symmetry) wherein one of the BH_4^- ions is bonded to the macrocycle through a single hydrogen atom while the other BH_4^- ion is bonded to **1** via three hydrogen atoms[2].

One of the two vacant *p*-orbitals of each Hg atoms in the macrocycle is directed towards the upper BH_4^- anion whereas the other *p*-orbital is directed towards the lower BH_4^- anion. Therefore, the relatively independent bonding of the macrocycle to the upper and the lower anions is possible and so some additivity of this bonding could be expected. However in fact, the deviations from the additivity in the bipyramidal complexes are considerable. Thus, the total Wiberg indices [21] for the bonding of the macrocycle to the upper and the lower anions in complexes **2a**–**2c** are substantially smaller than the corresponding additive values[3]. Furthermore, in contrast to the expectations based on the additivity, the most stable complex is not complex **2a** but unsymmetric complex **2c** (Table 1). Presumably, complex **2a** is destabilized by too close contact (2.36 Å) between the hydrogen atoms lying on the symmetry axis (C_3) of the macrocycle. Both complexes (**2a** and **2c**) contain the half-sandwich fragment(s) **4a** but in these fragments the bonding of the Hg atoms to the hydrogen atoms directed out of the macrocycle is strongly weakened as compared to that in **4a** itself (Table 2).

As for the general picture of the bonding of the BH_4^- ions to the macrocycle in the bipyramidal complexes, it resembles that in the half-sandwich complexes. In the

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[2] Full optimization of this complex does not change the results.

[3] In accordance with Table 3, the total Wiberg indices are equal to $0.642+0.642=1.284$ for **2a**, $0.783+0.783=1.566$ for **2b** and $0.843+0.702=1.545$ for **2c**. The corresponding additive values, which are calculated as the sum of Wiberg indices for half-sandwiches are equal to $1.050+1.050=2.100$, $0.918+0.918=1.836$ and $1.050+0.918=1.968$.

Table 2
Distances (*d*), Wiberg indices (*W*), C–Hg–C bond angles and the angles (θ) between (*xy*) and $Hg_2C_6F_4$ planes for the complexes of macrocycle **1** with BH_4^- (A) calculated by the AM1 method

Compound	Hg–H [a]		Hg–H		Hg–B		B–H [a]		B–H		B–**1**	A–**1**	C–Hg–C (°)	θ (°)
	d (Å)	*W* (a.u.)	*d* (Å)	*W* (a.u.)	*d* (Å)	*W* (a.u.)	*d* (Å)	*W* (a.u.)	*d* (Å)	*W* (a.u.)	*d* (Å)	*W* (a.u.)		
1													177.0	0.0
BH_4^-									1.216	0.914				
[**1**–HBH_3]$^-$ (**4a**)	1.897	0.111	2.045	0.101	2.442	0.138	1.311	0.572	1.227	0.834	1.559	1.050	156.9	12.3
[**1**–H_3BH]$^-$ (**4b**)	1.819	0.177			2.754	0.116	1.236	0.733	1.201	0.943	2.035	0.918	148.6	17.2
[H_3BH–**1**–HBH_3]$^{2-}$ (**2a**)	1.943	0.105	2.508	0.036	2.766	0.073	1.271	0.577	1.212	0.898	2.447	0.642	163.6	0.0
[HBH_3–**1**–H_3BH]$^{2-}$ (**2b**)	1.860	0.148			2.746	0.104	1.230	0.766	1.204	0.942	2.095	0.783	166.0	0.0
[H_3BH–**1**–H_3BH]$^{2-}$ (**2c**) [b]	1.867	0.119	2.226	0.062	2.563	0.102	1.304	0.543	1.218	0.872	1.835	0.843	165.6	2.4
	1.898	0.142			2.805	0.090	1.234	0.772	1.204	0.939	2.159	0.702		
[**1**–HBH_3···1]$^-$ (**3a**) [c]	1.899	0.109	2.055	0.098	2.449	0.135	1.307	0.580	1.227	0.837	1.567	1.026	157.2	12.6
	7.703	0.000			6.458	0.000					6.095	0.000	175.2	2.7
[**1**–HBH_3–**1**]$^-$ (**3b**) [d]	1.971	0.093	2.277	0.055	2.641	0.092	1.275	0.641			1.849	0.720	158.6	14.0
	2.003	0.100			2.914	0.071	1.238	0.772			1.813	0.528	156.5	15.5
[**1**–HBH_2H–**1**]$^-$ (**3c**) [e]	2.16	0.072			2.57	0.111	1.263	0.705				0.641	151	22
	2.13	0.074			3.35	0.036							170	10
			2.07	0.083					1.245	0.763				

[a] Hydrogen atoms of BH_4^- anion directed to macrocycle.

[b] The lower line corresponds to tridentate coordination of the anion.

[c] The lower line corresponds to 'solvating' macrocycle.

[d] The lower line corresponds to the macrocycle with tridentate coordination of the anion.

[e] The first line corresponds to four Hg atoms to which the anion is shifted; the second line corresponds to two other Hg atoms; the third line corresponds to hydrogen atoms lying in the horizontal plane.

principal outline, the electronic structure of these bipyramidal complexes is identical to the electronic structure of the bipyramidal complexes of the halide anions with macrocycle **1** [3f,h].

2.3.3. *Sandwich complexes*

The calculations of sandwich complexes also revealed three minima on the PES. One minimum corresponds to unsymmetrical sandwich [**1**–HBH$_3$···**1**]$^-$ (**3a**) representing in fact half-sandwich **4a** as if solvated by the second molecule of macrocycle **1**. Two other, deeper minima correspond to the true sandwich complexes, **3b** and **3c**, with equidistantly arranged macrocycles (Fig. 3, Table 2). The major minimum belongs to complex **3c** (C_{2v} symmetry) which was calculated with the full geometry optimisation. In this complex, two hydrogen atoms of the BH$_4^-$ anion lie in the horizontal plane and each of them is bonded with two mercury atoms. One of these Hg atoms belongs to the upper macrocycle, while the other Hg atom belongs to the lower one[4]. Two other hydrogen atoms are located in the vertical plane and each of them is coordinated to the mercury atoms of the nearest molecule of **1**. This coordination is practically symmetric: the distance between the hydrogen atom and one of the Hg atoms is 2.13Å while the distances between the hydrogen atom and two other Hg atoms are 2.16Å. The BH$_4^-$ anion is shifted towards the edge of the rings and the distance from the boron atom to the former Hg atom is considerably larger than that between the boron atom and the two other Hg atoms. Thus, in accordance with the IR data for complex **3**, all four B–H bonds of the borohydride anion in the calculated structure **3c** are coordinated to the mercury atoms. As mentioned above, the stability constant of complex **3** is much larger than that of complex **2**. This is also in accord with the results of the quantum-chemical calculations. The energetic gain from the complexation of macrocycle **1** with BH$_4^-$ anions is 143.0 kcal mol^{-1} for half-sandwich complex **4a**, 154.4 kcal mol^{-1} for bipyramidal complex **2c** and 165.3 kcal mol^{-1} for sandwich complex **3c**. One may believe that the above-described complex **3** identified by the IR and NMR spectra has the sandwich structure **3c**.

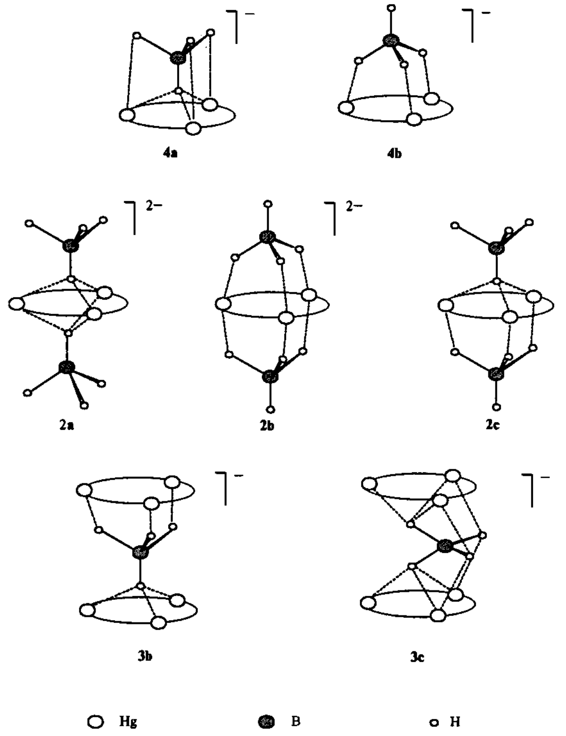

Fig. 3. The calculated structures of complexes **2**–**4**.

3. Conclusions

The results obtained demonstrate the fruitfulness of using the IR and multinuclear NMR spectroscopy methods for studying the complexation of BH$_4^-$ anions with mercuramacrocycle **1** in solutions. By means of these methods, three complexes of **1** with BH$_4^-$ ions have been detected in THF medium and for two of them (**2** and **3**), the composition and stability constants have been reliably determined. The possible structures of the detected complexes have been investigated by the quantum-chemical calculations. A comparative study of complexation of BH$_4^-$ with $(C_6F_5)_2Hg$, that can be considered as monomeric acyclic analogue of **1**, revealed a strong cooperative effect of the Hg atoms in **1** on the binding of BH$_4^-$ anions. According to this study, $(C_6F_5)_2Hg$, in contrast to **1**, is capable of forming only one complex (**5**) with BH$_4^-$ ions and the stability of this complex is much lower than that of **2** and **3**. The conclusion of the cooperative binding of BH$_4^-$ anion(s) by the Hg atoms in **1** is also supported by the results of the quantum-chemical calculations which indicate that the structures with simultaneous coordination of the anionic species to all Lewis acidic centres of the macrocycle must be the most favourable for complexes **2**–**4**.

4. Experimental procedure

The starting macrocycle **1** was prepared according to the published procedure [5a]. Tetrabutylammonium borohydride *n*-Bu$_4$NBH$_4$ (Fluka) and NaBD$_4$ (Aldrich) were dried in vacuum at 20°C until traces of moisture disappeared. The absence of moisture was controlled by the IR spectra. Solvents were purified by usual methods and were distilled from sodium benzophenone-ketyl (THF) and calcium hydride (DCE) under Ar before

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[4] The planes in which the mercury atoms of the upper and lower macrocycles are located deviate from the parallelism (by the angle 10°) towards the hydrogen atoms lying in the horizontal plane.

use. Solutions for IR and NMR studies were prepared in an Ar atmosphere as well. For dissolving $NaBD_4$ in THF, 18-crown-6 was used. The reactions were carried out at room temperature under Ar.

The IR spectra were measured on Specord M-80 and Specord M-82 instruments (Carl Zeiss Jena) with the resolution of 2 cm^{-1}. The IR spectra of the reaction solutions were recorded in the ν(BH) region (1500–2500 cm^{-1}) at different concentrations (8×10^{-2}–10^{-3} M) and ratios of the reagents in CaF_2 cells ($d = 0.0125$–0.0612 cm). The IR spectra of the solid samples were taken both in Nujol and as films deposited on CaF_2 and KBr matrix. The solid-state IR spectra were obtained in the region of 2500–400 cm^{-1}. The spectra of the solid films of complexes **2** and **3** in the ν(BH) region were essentially identical to those of **2** and **3** in solutions but the equilibrium between the complexes was shifted to more stable complex **3** during precipitation. The low-temperature IR measurements were carried out at 200 K in the ν(BH) region using Carl Zeiss Jena cryostat. The obtained data on the IR frequencies for **2** and **3** as well as for free BH_4^- anion are summarised in Table 3.

The composition of the complexes was determined by the mole ratio and continuous variation (Job) methods [13]. In the case of the mole ratio method, a series of solutions was prepared in which the initial BH_4^- concentration was constant (10^{-2} M) while the concentration of macrocycle **1** varied from 2×10^{-3} to 8×10^{-2} M. Optical densities (D) of the ν(BH) band of the BH_4^- ion at 2201 cm^{-1} were measured. The stoichiometry of the complex was determined by the inflection point of the optical density vs. concentration ratio ($[\mathbf{1}]_o/[BH_4^-]_o$) curve. On using the Job method, a series of solutions was prepared with varied initial BH_4^- and macrocycle **1** concentrations provided their constant total concentration in the mixture. The concentrations of BH_4^- and **1** varied in the ranges of 3×10^{-2}–3×10^{-3} and 3×10^{-3}–3×10^{-2} M, respectively. Optical densities were measured at 2201 cm^{-1} (ν(BH) of free BH_4^- ion) and 2015 cm^{-1} ($\nu(BH)^b$ of complex **2**). The composition of the complexes was determined from the positions of the maximum of the optical density vs. concentration ratio ($[BH_4^-]_o/([\mathbf{1}]_o + [BH_4^-]_o)$ curve (for complex **2**) and of the optical density vs. concentration ratio ($[\mathbf{2}]_o/([\mathbf{1}]_o + [\mathbf{2}]_o)$ curve (for complex **3**).

Stability constants of the complexes (K_1, K_2, K_3) were determined for the following equilibria:

$$(o\text{-}C_6F_4Hg)_3 + 2BH_4^- \overset{K_1}{\leftrightarrows} \{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-}$$

$$\{[(o\text{-}C_6F_4Hg)_3](BH_4)_2\}^{2-} + 3(o\text{-}C_6F_4Hg)_3 \overset{K_2}{\leftrightarrows} 2\{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$$

$$2(o\text{-}C_6F_4Hg)_3 + BH_4^- \overset{K_3}{\leftrightarrows} \{[(o\text{-}C_6F_4Hg)_3]_2(BH_4)\}^-$$

according to the equations:

$$K_1 = 1/2[C_{BH_4} - D/(\varepsilon_{BH_4}d)]/[(D/(\varepsilon_{BH_4}d))^2(C_1 - 1/2C_{BH_4} + 1/2D/(\varepsilon_{BH_4}d))]$$

$$K_2 = 2[C_2 - D/(\varepsilon_2 d)]/[(D/(\varepsilon_2 d))^2(C_1 - 2C_2 + 2D/(\varepsilon_2 d))]$$

$$K_3 = K_1K_2$$

where C_{BH_4}, C_1 and C_2 are the initial concentrations of BH_4^-, macrocycle **1** and complex **2**, respectively; D is the optical density of the ν(BH) band of free BH_4^- ion (for K_1) or $\nu(BH)^b$ band of complex **2** (for K_2); ε_{BH_4} and ε_2 are the ν(BH) and $\nu(BH)^b$ bands extinctions of $n\text{-}Bu_4NBH_4$ and complex **2** in THF, respectively; d is the cell path length.

The composition and the stability constant (K_4) of complex **5** were determined in a similar way.

$$Hg(C_6F_5)_2 + BH_4^- \overset{K_4}{\leftrightarrows} \{[Hg(C_6F_5)_2](BH_4)\}^-$$

$$K_4 = [C_{BH_4} - D/(\varepsilon_{BH_4}d)] /[(D/(\varepsilon_{BH_4}d))(C_{Hg(C_6F_5)_2} - C_{BH_4} + D/(\varepsilon_{BH_4}d))]$$

where C_{BH_4} and $C_{Hg(C_6F_5)_2}$ are the initial concentrations of BH_4^- and $Hg(C_6F_5)_2$; D is optical density of the ν(BH) band for BH_4^- ion; ε_{BH_4} is the ν(BH) band extinction of $n\text{-}Bu_4NBH_4$ in THF; d is the cell path length.

Table 3
The IR frequencies (cm^{-1}) for free BH_4^- anion and complexes **2** and **3**

BH_4^-			**2**			**3**			Assignment of the mode
Solid state	THF	DCE	Solid state	THF	DCE	Solid state	THF	DCE	
2197 s	2201 s	2201 s	2290 s	2300 s	2300 s				$\nu_{as}(BH)^t$
2265 w	2269 w	2269 w				2221	2230 w	2230 w	$\delta_s(BH) + \delta_{as}(BH)$
2129 w	2129 w	2129 w	2075 w	2080 w	2080 w				$2\delta_{as}(BH)$
			2015 s	2015 s	2015 s	2120 s	2129 s	2129 s	$\nu_{as}(BH)^b$
						2050 m	2057 m	2057 m	$\nu_{as}(BH)^b$
			1304 m			1300 m			ν(HgHB)
1072 s			1054 s			1037 s			$\delta_{as}(BH)$

The variable-temperature NMR data were collected with Bruker AMX–400 and WP–200 spectrometers. The ^{1}H chemical shifts were calculated from the resonances of [D_8]THF as internal standard. The ^{11}B and ^{199}Hg chemical shifts were determined using BF_3Et_2O and Ph_2Hg as external standards, respectively. All the NMR spectra were recorded starting at low temperatures (190 K). The studied solutions were prepared in 5 mm NMR tubes in a cold Pr^iOH bath and transferred into cold NMR probes. The initial concentration of macrocycle **1** was 8×10^{-2} M, and n-Bu_4NBH_4 concentration varied in the range of 3×10^{-2}–2×10^{-1} M.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (the Project codes 98-03-33037 and 96-03-33472).

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