



Interaction of polyhedral boron hydride anions $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ with cyclic copper and silver 3,5-bis(trifluoromethyl)pyrazolate complexes

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ABSTRACT

The interactions of cyclic trinuclear copper $\{[3,5-(CF_3)_2Pz]Cu\}_3$ and silver $\{[3,5-(CF_3)_2Pz]Ag\}_3$ complexes with polyhedral borate anions $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ in solvents of low-polarity were studied using IR spectroscopy (190–290 K). Two types of complexes were found in solution: $\{[(3,5-CF_3)_2PzM]_3[B_nH_n]\}^{2-}$ and $\{[(3,5-CF_3)_2PzM]_2[B_nH_n]\}^{2-}$ ($M = Ag, Cu; n = 10, 12$). The stability constants of these complexes were determined from IR-spectra.

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1. Introduction

Polyhedral boron hydrides are known to be weakly coordinating anions able to stabilize highly reactive and usually unstable coordination-unsaturated metallacomplexes [1,2], that stimulates growing interest in use of such anions for synthesis of catalytically active complexes [3]. Contrary to typical complex-forming *d*-metals, that are hard/borderline Lewis acids, soft Lewis acids (e.g. Group 11 metals) are able to form complexes with polyhedral boron hydride compounds. At present several examples of polyhedral boron hydride complexes with the Group 11 metal were described [4–9]. It should be noted that practically all these reports dealt with formation of silver(I) and copper(I) complexes in solid state, whereas solution chemistry of interaction of polyhedral boron hydrides with the Group 11 metal is practically unexplored.

Metallacrowns containing several Lewis acid centers are known to efficiently form complexes with neutral and anionic Lewis bases. The host/guest complexes of mercury-containing macrocycles are the best known up to date [10,11]. 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 complex of carborane-based mercury-containing macrocycle (*o*- $C_2B_{10}H_8Et_2Hg$)₄ with *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ was reported by Hawthorne et al. [12]. More recently it was shown that planar cyclic trimeric perfluoro-*o*-phenylenemercury (*o*- C_6F_4Hg)₃ is capable of binding different boron hydride anions $(Bu_4N)[BH_4]$, $(Bu_4N)[BH_3CN]$, $(Bu_4N)_2[B_{10}H_{10}]$, $(Bu_4N)_2[B_{12}H_{12}]$, $(Bu_4N)_2[B_{12}H_{11}SCN]$ [13] forming complexes of different composition and structure depending on the reagent ratio and the anion nature. The Hg atoms of the metallacycle are coordinated with boron hydrides through Hg··H–B bridges of different types, including the simultaneous coordination of a B–H group to all three Hg atoms of the macrocycle and coordination of B–H groups to particular Hg atoms.

Macrocyclic trinuclear complexes of the Group 11 metals are well-known [14–19] and represent an important class of coordination compounds having potential interest for study of such fundamental phenomena as acid–base chemistry, supramolecular assemblies, M–M-bonded excimers and exciplexes, and host/guest chemistry. It was demonstrated that trinuclear cyclic copper(I) and silver(I) complexes of fluorinated pyrazolates are able to form π -acid–base complexes with aromatics. In this contribution we present the first example of complex formation of trinuclear copper(I) and silver(I) metallacycles of 3,5-bis(trifluoromethyl)pyrazolate with polyhedral boron hydrides $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ in solution.

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2. Results and discussion

2.1. Interaction of $[B_{12}H_{12}]^{2-}$ with $\{(3,5-(CF_3)_2Pz)Ag\}_3$ and $\{(3,5-(CF_3)_2Pz)Cu\}_3$

Interaction of $\{(3,5-(CF_3)_2Pz)Ag\}_3$ (**1a**) and $\{(3,5-(CF_3)_2Pz)Cu\}_3$ (**1b**) with tetra(*n*-butyl)ammonium dodecahydro-*closo*-dodecaborate $(Bu_4N)_2[B_{12}H_{12}]$ in CH_2Cl_2 solution was studied by IR spec-

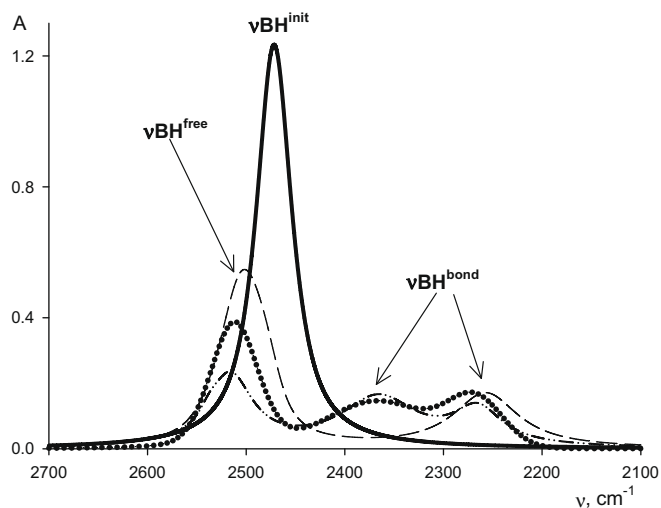


Fig. 1. IR spectra in the $\nu(BH)$ range of $(Bu_4N)_2[B_{12}H_{12}]$ (0.006 M, solid line) and in the presence of $\{(3,5-(CF_3)_2Pz)Ag\}_3$ in ratio: 1:3 (dashed line), 1:5 (dotted line), 1:10 (dash-dot line), CH_2Cl_2 , $d = 0.12$ cm.

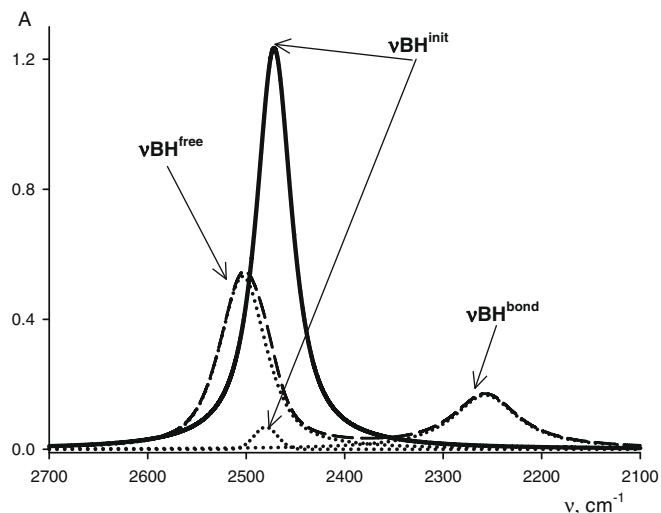


Fig. 2. IR spectra in the $\nu(BH)$ range of $(Bu_4N)_2[B_{12}H_{12}]$ (0.006 M, solid line); in the presence of $\{(3,5-(CF_3)_2Pz)Ag\}_3$ (0.012 M, dashed line) (ratio 1:2) with bands decomposition (dotted lines), CH_2Cl_2 , $d = 0.12$ cm.

Table 1

Spectral characteristics of complexes $(Bu_4N)_2[B_{12}H_{12}]$ with $\{(3,5-(CF_3)_2Pz)Ag\}_3$ ((LAG)₃, L = 3,5-(CF₃)₂Pz), $\{(3,5-(CF_3)_2Pz)Cu\}_3$ ((LCu)₃, L = 3,5-(CF₃)₂Pz).

	$\nu(BH)^{free}$ ($\Delta\nu$) (cm ⁻¹)	$\nu(BH)^{bond}$ ($\Delta\nu$) (cm ⁻¹)	K_f
$\{[(LAG)_3][B_{12}H_{12}]^{2-}\}^{2-}$ (2a)	2498 (26)	2251 (-221)	$1.3 \pm 0.1 \times 10^3$ L mol ⁻¹
$\{[(LCu)_3][B_{12}H_{12}]^{2-}\}^{2-}$ (2b)	2492 (20)	2216 (-256)	$1.7 \pm 0.1 \times 10^3$ L mol ⁻¹
$\{[(LAG)_3]_2[B_{12}H_{12}]^{2-}\}^{2-}$ (3a)	2532 (63)	2475(3); 2354 (-118)	$4.6 \pm 0.2 \times 10^4$ L ² mol ⁻²
$\{[(LCu)_3]_2[B_{12}H_{12}]^{2-}\}^{2-}$ (3b)	2515 (43)	2444 (-28); 2337 (-135)	$4.7 \pm 0.2 \times 10^4$ L ² mol ⁻²

Band shifts are calculated as $\Delta\nu(BH)^{free} = \nu(BH)^{free} - \nu(BH)^{init}$, $\Delta\nu(BH)^{bond} = \nu(BH)^{bond} - \nu(BH)^{init}$, where $\nu(BH)^{init} = 2472$ cm⁻¹.

troscopy. Titration of the boron hydride solution with solution of **1a** and **1b** results in decrease of the $\nu(BH)$ band intensity of free $[B_{12}H_{12}]^{2-}$ anion and appearance of new high- and low-frequency bands corresponding to two different types of complexes (Fig. 1).

The titration of solution of $(Bu_4N)_2[B_{12}H_{12}]$ in CH_2Cl_2 with macrocycle **1a** (molar ratio from 10:1 to 1:3) leads to decrease of intensity of the $\nu(BH)$ band intensity of initial $[B_{12}H_{12}]^{2-}$ anion ($\nu(BH)^{init} = 2472$ cm⁻¹) and appearance of new high-frequency $\nu(BH)$ band at 2510 cm⁻¹ and low-frequency $\nu(BH)$ band at 2251 cm⁻¹ corresponding to formation of complex **2a** (Figs. 1 and 2 and Table 1).

The band at 2251 cm⁻¹, shifted by 221 cm⁻¹ relative to the $\nu(BH)$ band of the free anion, can be assigned to stretching vibrations of the B–H bonds coordinated to the macrocycle **1a** through B–H...Ag bridges. The high-frequency band at 2510 cm⁻¹ assigned to the stretching vibrations of the terminal B–H bonds. The assignments are based on the similar changes upon the complexation of $[B_{12}H_{12}]^{2-}$ and cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-C₆F₄-Hg)₃ [13c].

Similar spectral changes were observed in the case of macrocycle $\{(3,5-(CF_3)_2Pz)Cu\}_3$ (**1b**) indicating formation of complex **2b** (Table 1). The main differences are in the shifts of $\nu(BH)^{free}$ and $\nu(BH)^{bond}$ stretches in the complex **2b** in comparison with the complex **2a**.

The compositions of the complexes were determined by the mole ratio and continuous variation (Job) methods (Fig. 3) [20].

Complexes **2a** and **2b** contain one polyhedral borane anion per molecule of **1a** and **1b**, and consequently they can be formulated as $\{[(3,5-(CF_3)_2Pz)Ag]_3[B_{12}H_{12}]^{2-}\}^{2-}$ (**2a**) and $\{[(3,5-(CF_3)_2Pz)Cu]_3[B_{12}H_{12}]^{2-}\}^{2-}$ (**2b**).

The increase of the $(Bu_4N)_2[B_{12}H_{12}]$: **1a** molar ratio from 1:3 to 1:10 resulted in decrease of the $\nu(BH)$ band intensities of complex **2a** ($\nu(BH)^{free} = 2510$ cm⁻¹ and $\nu(BH)^{bond} = 2251$ cm⁻¹) and appearance of new bands at 2532, 2475 and 2354 cm⁻¹ (Fig. 4 and Table 1).

The low- (2354 cm⁻¹) and high-frequency (2532 cm⁻¹) bands correspond to stretching vibrations of bonded ($\nu(BH)^{bond}$) and free ($\nu(BH)^{free}$) BH groups of new complex **3a**. The less intense band at 2475 cm⁻¹ also can be assigned to the $\nu(BH)^{bond}$ stretching vibration. The presence of two $\nu(BH)^{bond}$ bands in the spectrum of complex **3a** can be explained by two different coordination types of the *closo*-dodecaborate anion having different strength.

Similar changes in the IR spectra occur when excess of macrocycle **1b** was added to solution of complex **2b** in CH_2Cl_2 . The decrease in the intensities of the $\nu(BH)$ bands of complex **2b** ($\nu(BH)^{free} = 2492$ cm⁻¹ and $\nu(BH)^{bond} = 2216$ cm⁻¹) and appearance of one new high-frequency band (2515 cm⁻¹) and two new low-frequencies bands (2444 and 2337 cm⁻¹) correspond to formation of new complex **3b** (Table 1).

Complexes **3a** and **3b** contains two molecules of the macrocycle **1a** and **1b** per one anionic species – $\{[(3,5-(CF_3)_2Pz)Ag]_3[B_{12}H_{12}]^{2-}\}^{2-}$ (**3a**) and $\{[(3,5-(CF_3)_2Pz)Cu]_3[B_{12}H_{12}]^{2-}\}^{2-}$ (**3b**).

The stability constants of the complexes determined from the IR spectra are 1.3×10^3 L mol⁻¹ and 1.7×10^3 L mol⁻¹ for **2a** and **2b**, respectively. It means that the complexes **2a** and **2b** (Table 1) are considerably more stable than the similar complex of the

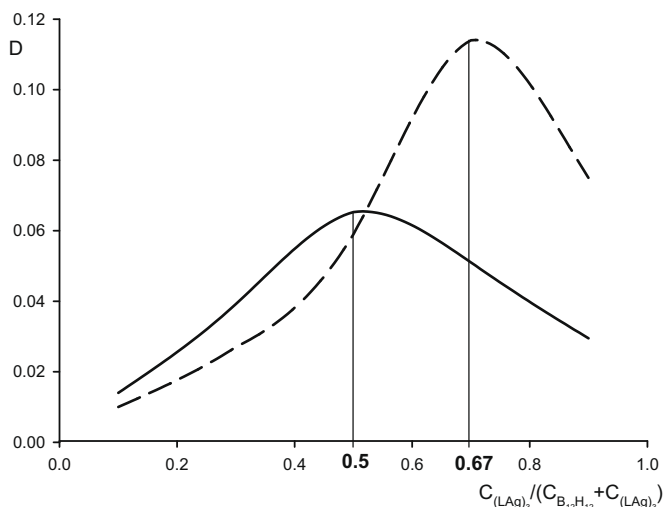


Fig. 3. The Job's plot: dependence of the complex **2a** band intensity (2251 cm^{-1}) (solid line) and of the complex **3a** (2354 cm^{-1}) (dashed line) from composition of isomolar solution.

$[B_{12}H_{12}]^{2-}$ anion with trimeric perfluoro-*o*-phenylenemercury ($o\text{-C}_6\text{F}_4\text{Hg}$)₃ ($0.7 \times 10^2\text{ L mol}^{-1}$). The stability constants of complexes **3a** and **3b** are $4.6 \times 10^4\text{ L}^2\text{ mol}^{-2}$ and $4.7 \times 10^4\text{ L}^2\text{ mol}^{-2}$, respectively. These complexes are also significantly more stable than the earlier described complex ($\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2[B_{12}H_{12}]\}^{2-}$, $K = 9.8 \times 10^2\text{ L}^2\text{ mol}^{-2}$) [13c]. All these facts indicate that interaction of boron hydrides with **1a** and **1b** are stronger than with ($o\text{-C}_6\text{F}_4\text{Hg}$)₃.

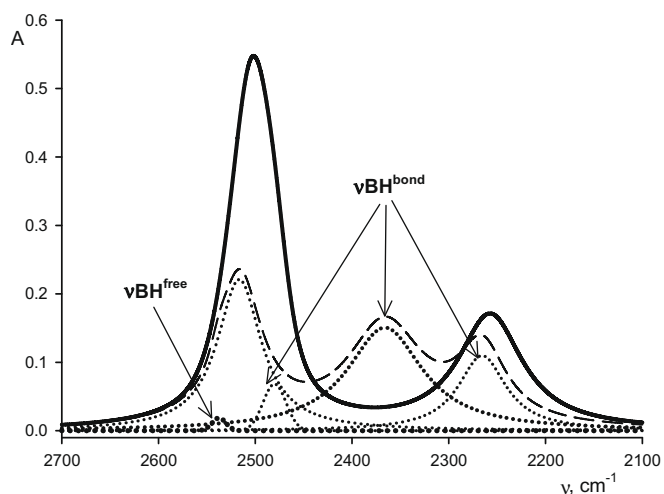


Fig. 4. IR spectra in the $\nu(\text{BH})$ range of $(\text{Bu}_4\text{N})_2[\text{B}_{12}\text{H}_{12}]$ (0.006 M) in the presence of 0.018 M $\{[3, 5\text{-(CF}_3)_2\text{Pz]Ag}\}_3$ (solid line); and in the presence of 0.06 M $\{[3,5\text{-(CF}_3)_2\text{Pz]Cu}\}_3$ (dashed line) with bands decomposition (dotted lines), CH_2Cl_2 , $d = 0.12\text{ cm}$.

2.2. Interaction of $[B_{10}H_{10}]^{2-}$ anion with $\{[3,5\text{-(CF}_3)_2\text{Pz]Ag}\}_3$ and $\{[3,5\text{-(CF}_3)_2\text{Pz]Cu}\}_3$

Titration of solution of $(\text{Bu}_4\text{N})_2[\text{B}_{10}\text{H}_{10}]$ in CH_2Cl_2 solution with **1a** or **1b** results in decrease of intensity of the $\nu(\text{BH})$ band of initial decahydro-*closo*-decaborate anion intensities ($\nu(\text{BH})_{\text{ax}}^{\text{init}} = 2494\text{ cm}^{-1}$ and $\nu(\text{BH})_{\text{eq}}^{\text{init}} = 2450\text{ cm}^{-1}$) and appearance of new bands at low- and high-frequency range (Table 2). It suggests formation of complexes $\{[(3,5\text{-(CF}_3)_2\text{PzAg})_3][\text{B}_{10}\text{H}_{10}]\}^{2-}$ (**4a**) and $\{[(3,5\text{-(CF}_3)_2\text{PzCu})_3][\text{B}_{10}\text{H}_{10}]\}^{2-}$ (**4b**) similar to the complexation of **1a** and **1b** with $[\text{B}_{12}\text{H}_{12}]^{2-}$.

The further addition of **1a** or **1b** results in decrease of the BH stretching intensities of complexes **4a** and **4b** and appearance of one high-frequency and two low-frequency bands (Table 2). The same trends as for $[\text{B}_{12}\text{H}_{12}]^{2-}$ allows to state the formation of 2:1 complexes $\{[(3,5\text{-(CF}_3)_2\text{PzAg})_3]_2[\text{B}_{10}\text{H}_{10}]\}^{2-}$ (**5a**) and $\{[(3,5\text{-(CF}_3)_2\text{PzCu})_3]_2[\text{B}_{10}\text{H}_{10}]\}^{2-}$ (**5b**) (Table 2).

The stability constants of complexes **4a** ($K = 2.3 \times 10^4\text{ L mol}^{-1}$) and **4b** ($K = 2.6 \times 10^4\text{ L mol}^{-1}$) are higher than stability constant of the similar complex of $[\text{B}_{10}\text{H}_{10}]^{2-}$ anion with trimeric perfluoro-*o*-phenylenemercury $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3][\text{B}_{10}\text{H}_{10}]\}^{2-}$ ($K = 1.0 \times 10^2\text{ L mol}^{-1}$) [13c]. The complexes **5a** and **5b** also are more stable than the related complex $\{[(o\text{-C}_6\text{F}_4\text{Hg})_3]_2[\text{B}_{10}\text{H}_{10}]\}^{2-}$ ($K = 2.6 \times 10^3\text{ L}^2\text{ mol}^{-2}$) [13c].

Notably, similar to complexes with trimeric perfluoro-*o*-phenylenemercury [13c], the complexes of **1a** and **1b** with the *closo*-decaborate anion are more stable than the corresponding complexes with the *closo*-dodecaborate anion (for example, $K = 8.6 \times 10^6\text{ L}^2\text{ mol}^{-2}$ for $\{[(3,5\text{-(CF}_3)_2\text{PzCu})_3]_2[\text{B}_{10}\text{H}_{10}]\}^{2-}$ and $K = 4.7 \times 10^4\text{ L}^2\text{ mol}^{-2}$ for $\{[(3,5\text{-(CF}_3)_2\text{PzCu})_3]_2[\text{B}_{12}\text{H}_{12}]\}^{2-}$ (Tables 1 and 2)).

Therefore, values of stability constants of the complexes formed by the metallocycles **1a** and **1b** with $[\text{B}_{10}\text{H}_{10}]^{2-}$, $[\text{B}_{12}\text{H}_{12}]^{2-}$ anions allow to conclude that effect of metal atoms in metallocycles **1a** and **1b** on the complex formation is not very significant. The complex stability increases with basicity of the polyhedral hydride $[\text{B}_{10}\text{H}_{10}]^{2-} > [\text{B}_{12}\text{H}_{12}]^{2-}$. This trend correlates well with our earlier conclusions concerning interactions of $[\text{B}_{10}\text{H}_{10}]^{2-}$, $[\text{B}_{12}\text{H}_{12}]^{2-}$ anions with Bronsted and Lewis acids [15,16].

3. Experimental

The starting macrocycles **1a** and **1b** were synthesized according to the published procedure [14]. The other starting reagents, $(\text{Bu}_4\text{N})_2[\text{B}_{10}\text{H}_{10}]$ and $(\text{Bu}_4\text{N})_2[\text{B}_{12}\text{H}_{12}]$, were obtained as described in Refs. [21,22]. The solvent CH_2Cl_2 was purified by distillation from CaH_2 before use. The anhydrous solvent was thoroughly degassed prior to use. The IR spectra of CH_2Cl_2 solutions were measured by Infracalum FT-801 (Lumex) FTIR spectrometer.

IR studies were carried out in the $\nu(\text{BH})$ region ($2700\text{--}2100\text{ cm}^{-1}$) at various concentrations ($10^{-3}\text{--}10^{-2}\text{ L mol}$) and ratios of the reagents in CaF_2 cell ($d = 0.12\text{ cm}$). The compositions of the complexes in solution were determined by the molar ratio and continuous variation (Job) methods [20].

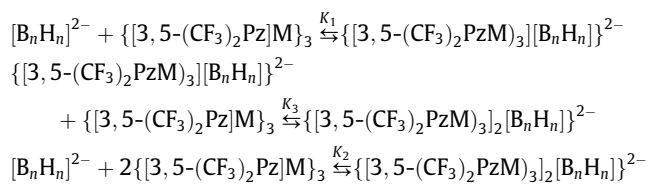
Table 2

Spectral characteristics of complexes $(\text{Bu}_4\text{N})_2[\text{B}_{10}\text{H}_{10}]$ with $\{[3,5\text{-(CF}_3)_2\text{Pz]Ag}\}_3$ ($(\text{LAG})_3$, $L = 3,5\text{-(CF}_3)_2\text{Pz}$), $\{[3,5\text{-(CF}_3)_2\text{Pz]Cu}\}_3$ ($(\text{LCu})_3$, $L = 3,5\text{-(CF}_3)_2\text{Pz}$).

	$\nu(\text{BH})^{\text{free}} (\Delta\nu) (\text{cm}^{-1})$	$\nu(\text{BH})^{\text{bond}} (\Delta\nu) (\text{cm}^{-1})$	K_f
$\{[(\text{LAG})_3][\text{B}_{10}\text{H}_{10}]\}^{2-}$ (4a)	2489 (39)	2291 (−159)	$2.3 \pm 0.1 \times 10^4\text{ L mol}^{-1}$
$\{[(\text{LCu})_3][\text{B}_{10}\text{H}_{10}]\}^{2-}$ (4b)	2477 (27)	2212 (−238)	$2.6 \pm 0.1 \times 10^4\text{ L mol}^{-1}$
$\{[(\text{LAG})_3]_2[\text{B}_{10}\text{H}_{10}]\}^{2-}$ (5a)	2538 (88)	2422 (−28); 2388 (−62)	$7.9 \pm 0.4 \times 10^6\text{ L}^2\text{ mol}^{-2}$
$\{[(\text{LCu})_3]_2[\text{B}_{10}\text{H}_{10}]\}^{2-}$ (5b)	2501 (51)	2417 (−33); 2349 (−101)	$8.6 \pm 0.4 \times 10^6\text{ L}^2\text{ mol}^{-2}$

Band shifts are calculated as $\Delta\nu(\text{BH})^{\text{free}} = \nu(\text{BH})^{\text{free}} - \nu(\text{BH})^{\text{init}}$, $\Delta\nu(\text{BH})^{\text{bond}} = \nu(\text{BH})^{\text{bond}} - \nu(\text{BH})^{\text{init}}$, where $\nu(\text{BH})^{\text{init}} = \nu(\text{BH})_{\text{eq}}^{\text{init}} = 2450\text{ cm}^{-1}$.

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



$$K_1 = [C_{B_nH_n} - D_{B_nH_n}/(\epsilon_{B_nH_n} \cdot d)] / \{ [D_{LM_3} / (\epsilon_{LM_3} \cdot d)] \cdot [C_{(LM)_3} - (C_{B_nH_n} - D_{B_nH_n}/(\epsilon_{B_nH_n} \cdot d))] \}$$

$$K_2 = K_1 \cdot K_3$$

$$K_3 = [C_{B_nH_n} - D_{B_nH_n}/(\epsilon_{B_nH_n} \cdot d) - D_I/(\epsilon_I \cdot d)] / \{ [D_I/(\epsilon_I \cdot d)] \cdot [C_{(LM)_3} (C_{B_nH_n} - D_{B_nH_n}/(\epsilon_{B_nH_n} \cdot d) - D_I/(\epsilon_I \cdot d))] \}$$

where $C_{B_nH_n}$ and $C_{(LM)_3}$ are the initial concentrations of $[B_nH_n]^{2-}$ anions and the macrocycles **1a** or **1b**, respectively; $D_{B_nH_n}$ is the optical density of the $\nu(BH)$ band of free $[B_nH_n]^{2-}$ anion; D_I is the optical density of complexes, containing one molecule of macrocycle **1a** or **1b** per one anionic species; $\epsilon_{B_nH_n}$ and ϵ_I are the $\nu(BH)$ bands extinctions of $[B_nH_n]^{2-}$ and complexes, containing one molecule of macrocycle **1a** or **1b** per one anionic species, in CH_2Cl_2 , respectively; d is the cell path length.

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