Boron cluster anions $B_{10}H_{10}^{2-}$ and $B_{10}H_{11}^{-}$ in complexation reactions of copper(I). Positional isomers of the complex $[Cu_2(9Nphen)_4B_{10}H_{10}]$

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The complexation reactions of Cu^{I} with the $B_{10}H_{10}^{2-}$ anion and its protonated form, the $B_{10}H_{11}^{-}$ anion, were studied in the presence of phenanthridine (9Nphen). Depending on the reaction conditions, positional isomers of the monomeric copper(I) complex $[Cu_2(9Nphen)_4B_{10}H_{10}]$ were selectively isolated. The *closo*-decaborate anion in the complexes is coordinated to the Cu(I) atoms through the apical edges 1—2, 7(8)—10 or 1—2, 1—4 *via* the formation of multicenter CuHB bonds. The crystal structures and IR spectra of the complexes were studied. The compound $[Cu_2(9Nphen)_4B_{10}H_{10}]$ is the first monomeric complex isolated in the form of the 1—2, 7(8)—10 isomer. It extends the series of positional isomers, which we have described earlier.

Key words: coordination chemistry, positional isomers, *closo*-decaborate anion, undecahydrodecaborate anion, copper(I) complexes, IR spectroscopy, X-ray diffraction.

Studies of metal complexes with the *closo*-decaborate anion showed that, in most cases, the $B_{10}H_{10}^{2-}$ anion is coordinated to the central atom by two adjacent BH groups. This coordination mode for the monomeric complexes with the ratio $B_{10}H_{10}^{2-}$: M = 1 : 1 allows the formation of three isomers since there are three types of edges in the polyhedral boron cage: apical edges, equatorial edges, and edges in the basal plane of the pyramids (Fig. 1). In the monomeric complexes with the ratio $B_{10}H_{10}^{2-}$: M = 1 : 2, the number of theoretically possible positional isomers increases to 25, 17 of them being optically active.[1] Evidently, it is impossible to experimentally isolate all isomers. Up to now, positional isomers of the complex $[Ag_2(Ph_3P)_4B_{10}H_{10}]$ were obtained and structurally characterized. In these compounds, the 1—2, 6(9)—10 edges (enantiomers) of the opposite apical vertices of two tetragonal pyramids,[2] the opposite 1—2, 1—4 edges at one apical vertex,[2] or the 1—2, 3—7 (5—8) edges (enantiomers) at the apical vertex and between the basal planes of the tetragonal pyramids[3] are involved in the coordination to the Ag^+ atoms. The Cu^+ complex with a similar composition $[Cu_2(Ph_3P)_4B_{10}H_{10}]$ was isolated as the 1—2, 6(9)—10 isomers.[1] The complex $[Cu_2(NCCH_3)_4B_{10}H_{10}]$ with the coordination through the 1—2, 3—6 edges was also described.[4] The formation of different isomers was explained[1—4] by the difference in the procedures used for their preparation and attendant processes.

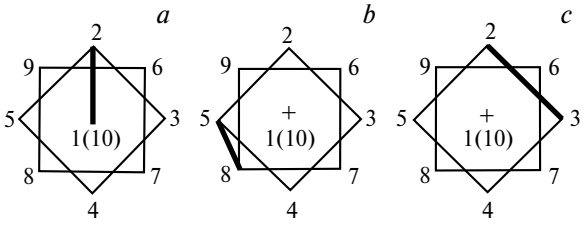

Fig. 1. Theoretically possible edge isomers in the monomeric complexes with the ratio $B_{10}H_{10}^{2-}$: M = 1 : 1: apical isomer (*a*), equatorial isomer (*b*), and pyramid-base edge isomer (*c*).

In continuation of investigations of the complexation reactions of copper(I) with the *closo*-decaborate anion in the presence of soft bases, we synthesized the positional isomers 1—2, 7(8)—10 and 1—2, 1—4 of the complex $[Cu_2(9Nphen)_4B_{10}H_{10}]$, where 9Nphen is the monodentate azaheterocyclic ligand phenanthridine.

Experimental

Elemental analysis was performed on a CHNS-3 FA 1108 Elemental Analyser (Carlo Erba). Boron was determined by atomic absorption spectroscopy as described earlier[5] on a Perkin-Elmer (USA), model 2100, spectrophotometer equipped with a HGA-700 electrothermal atomizer; copper was determined on a Perkin-Elmer atomic absorption spectrophotometer (USA), model 303, in an acetylene—air flame.

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IR spectra were recorded on an Infralyum FT–02 Fourier-transform infrared spectrophotometer (Lyumeks R&D Production Company) in the range of 4000—400 cm^{-1} at 1 cm^{-1} resolution as Nujol mulls.

Decahydro-*closo*-decaboratodicopper(I), $[Cu_2B_{10}H_{10}]$, was synthesized from $(Et_3NH)_2B_{10}H_{10}$ according to a procedure described earlier;[6] the compound $(Et_3NH)_2B_{10}H_{10}$ was prepared by the multistep synthesis from decaborane-14 through the formation of 1,6-bis(triethylamine)decaborane.[7]

μ^2-(1—2,8—10)-Decahydro-*closo*-decaboratodi[bis(phenanthridine)copper(I)], diacetonitrile solvate, $[Cu_2(9Nphen)_4B_{10}H_{10}]\cdot 2CH_3CN$ (1), and μ^2-(1—2,1—4)-decahydro-*closo*-decaboratodi[bis(phenanthridine)copper(I)], 0.85 acetonitrile solvate, $[Cu_2(9Nphen)_4B_{10}H_{10}]\cdot 0.85CH_3CN$ (2). Phenanthridine (1.4 g) and $Cu_2B_{10}H_{10}$ (0.5 g) were dissolved in acetonitrile (10 mL). The process was accompanied by a change in the color of the reaction solution from brown to dark-yellow. Yellow needle-like crystals of **1** that precipitated after one day were filtered off (yield 60%). The further isothermal evaporation of the reaction solution in air resulted in the isolation of the second fraction, *viz.*, olive-colored prismatic crystals (compound **2**). The total yield of complexes **1** and **2** was ~80% based on boron. Compounds **1** and **2** were dried in air.

Complex 1. Found (%): Cu, 13.21; C, 64.91; H, 4.82; N, 5.82; B, 11.24. $C_{52}H_{46}B_{10}N_4Cu_2$. Calculated (%): Cu, 13.41; C, 64.19; H, 4.91; N, 5.74; B, 11.44. IR (NaCl, Nujol): ν(BH) 2516, 2491, 2477, 2466, 2457 cm^{-1}; $\nu(BH)_{CuHB}$ 2300 cm^{-1}; ν(C≡N) 2362, 2247 cm^{-1}; ν(Het) 1614—700 cm^{-1} (Het is heterocycle).

Complex 2. Found (%): Cu, 13.21; C, 64.91; H, 4.82; N, 5.82; B, 11.24. $C_{52}H_{46}B_{10}N_4Cu_2$. Calculated (%): Cu, 13.38; C, 64.26; H, 4.90; N, 5.77; B, 11.39. IR (NaCl, Nujol): ν(BH) 2532, 2481, 2464 cm^{-1}; $\nu(BH)_{CuHB}$ 2255, 2175 cm^{-1}; ν(C≡N) 2310, 2271 cm^{-1}; ν(Het) 1613—700 cm^{-1}.

Synthesis of the complex 1—2-, 1—4-$[Cu_2(9Nphen)_4B_{10}H_{10}]\cdot 0.85CH_3CN$ (2). Solutions of $(Bu_4N)B_{10}H_{11}$ (0.4 g), CuCl (0.2 g), and phenanthridine (0.7 g) in acetonitrile were sequentially mixed. The isothermal evaporation of the resulting yellow solution in air for 1 day afforded olive-colored prismatic crystals. The unit cell parameters of these crystals are identical to those of **2** (Table 1). The yield was ~75%.

The same compound was obtained with the use of $((NaphCH_2)Ph_3P)B_{10}H_{11}$ and $(Ph_4P)B_{10}H_{11}$ as the starting salts.[8]

X-ray diffraction study. The intensities of X-ray reflections for crystals of **1** and **2** were measured on a Bruker SMART APEX2 automated diffractometer (λMo-Kα radiation, graphite monochromator) at 150 K. Main crystal data, parameters of the data collection, and structure refinement statistics for **1** and **2** are given in Table 1.

The structures of **1** and **2** were solved by direct methods. In the structure of **1**, one of the phenanthridine molecules is disordered over two orientations sharing a common N(2) atom with an occupancy ratio of 0.739(4) : 0.261(4). In both structures, acetonitrile solvent molecules were found. In the structure of **1**, one of two CH_3CN molecules is ordered, whereas another molecule is disordered over two closely spaced positions with an occupancy ratio of 0.692(11) : 0.308(11). In the structure of **2**, the acetonitrile molecule is disordered over two closely spaced positions with occupancies of 0.5 and 0.346(6). The C(14A)—C(26A) atoms of the minor component of the disordered phenanthridine molecule and the C and N atoms of the disordered acetonitrile molecules in the structure of **1** were refined isotropically. In the structure of **2**, the thermal parameters of the N(5), C(53), and C(54) atoms were refined isotropically, whereas the thermal parameters of the N(6), C(55), and C(56) atoms, whose occupancies are 0.346(6), were kept equal to 0.08 $Å^2$. The remaining nonhydrogen atoms in both structures were refined with anisotropic displacement parameters. The H atoms of the phenanthridine and acetonitrile molecules were positioned geometrically and refined using the riding model. The H atoms of the $B_{10}H_{10}^{2-}$ anions were located in difference electron density maps and refined isotropically in the structure of **1** and using a riding model in the structure of **2**. The X-ray diffraction data for the crystal of **2** were collected from a nonhomogeneous sample, as evidenced by the residual peak with a height of 2.08 e $Å^{-3}$ and the list of reflections that are the most disagreeable with the structural model (weak reflections with $F_H > F_B$).

The X-ray diffraction data (I_{hkl}) were collected and processed with the use of the APEX2, SAINT, and SADABS programs.[9] The calculations were carried out using the SHELX97 program package.[10]

The crystallographic data for compounds **1** and **2** were deposited with the Cambridge Crystallographic Data Centre (CCDC 818749 and 818750).

Table 1. Main crystal data, parameters of the data collection, and structure refinement statistics for compounds **1** and **2**

Parameter	**1**	**2**
Crystal description	Yellow needle	Olive-colored prism
Molecular formula	$C_{56}H_{52}B_{10}Cu_2N_6$	$C_{53.69}H_{48.54}B_{10}Cu_2N_{4.85}$
M	1044.22	996.80
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Z	2	4
a/Å	9.3333(11)	16.5478(8)
b/Å	16.0781(19)	16.3241(8)
c/Å	17.491(2)	18.8462(10)
α/deg	80.578(2)	90.0
β/deg	88.732(2)	104.8190(10)
γ/deg	83.353(2)	90.0
V/$Å^3$	2571.9(5)	4921.6(4)
D_x/g cm^{-3}	1.348	1.345
μ_{Mo}/mm^{-1}	0.873	0.908
T_{min}, T_{max}	0.6307, 0.7461	0.6323, 0.7455
F(000)	1076	2050
Crystal dimensions/mm	0.32×0.06×0.02	0.22×0.20×0.16
θ-Angle range/deg	1.89—25.00	1.92—27.01
Number of reflections:		
measured	21075	38392
unique (N)	9040	10730
[R_{int}]	[0.0451]	[0.0562]
with $I > 2\sigma(I)$ (N_o)	6346	6931
Number of refined parameters	758	635
R_1, wR_2 for N_o	0.0463, 0.0946	0.0499, 0.1197
R_1, wR_2 for N	0.0780, 0.1047	0.0904, 0.1371
S	0.983	1.022
$(\Delta\rho_{max}/\Delta\rho_{min})$/e $Å^{-3}$	0.335/–0.337	2.085/–0.442

Results and Discussion

In the present study, we investigated the complexation reactions of Cu^{I} with the $B_{10}H_{10}^{2-}$ anion and its protonated form, the $B_{10}H_{11}^{-}$ anion, in the presence of phenanthridine in acetonitrile at room temperature. The reactions produced the complexes $[Cu_2(9Nphen)_4B_{10}H_{10}]$ characterized by elemental analysis, IR spectroscopy, and X-ray diffraction. In the former reaction, two products, needle-like crystals of **1** and prismatic crystals of **2**, were isolated separately. The reaction with the involvement of the protonated anion $B_{10}H_{11}^{-}$ affords only isomer **2**.

The X-ray diffraction study showed that compounds **1** and **2** consist of the complexes $[Cu_2(9Nphen)_4B_{10}H_{10}]$ and acetonitrile solvent molecules. In both compounds, the coordination environment of the Cu^{+} atoms is composed of two BH groups that form three-center two-electron CuHB bonds and the N atoms of two phenanthridine molecules.

Complexes **1** and **2** are positional isomers, which differ in the types of the edges of the polyhedral anion involved in the coordination to the Cu^{+} ions. In complex **1** (Fig. 2), the anion is coordinated through the B(1)—B(2) and B(8)—B(10) edges that connect the apical and equatorial vertices of two tetragonal pyramids. In complex **2** (Fig. 3), the anion is coordinated through the B(1)—B(2) and B(1)—B(4) edges sharing the apical vertex. It can be seen from Table 2 that in compound **1**, the Cu—B(H) bonds with the apical boron atoms of both edges are slightly shorter than the bonds with the equatorial atoms (Cu(1)—B, 2.219(4) and 2.244(4) Å; Cu(2)—B, 2.253(4) and 2.280(4) Å). In compound **2**, the bonds of both Cu atoms with the shared apical B(1) atom (2.316(3) and 2.313(3) Å) are

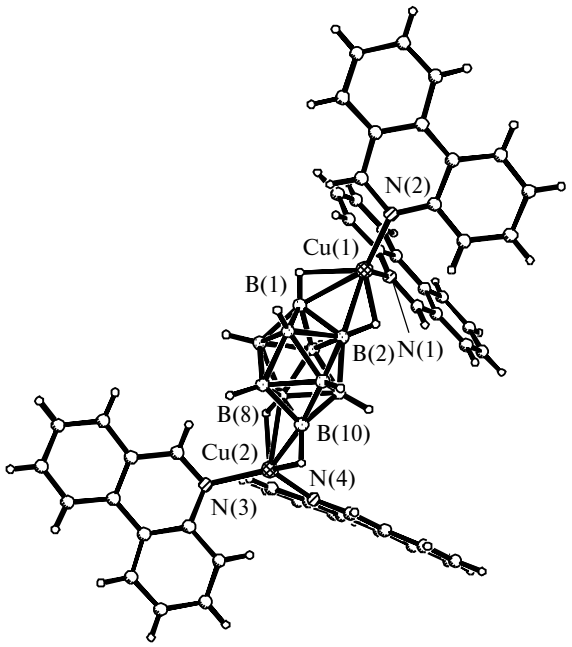

Fig. 2. Structure of complex **1**.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in structures **1** and **2**

Bond	*d*/Å
Cu(1)—N(2)	1.987(3)
Cu(1)—N(1)	2.089(2)
Cu(1)—B(1)	2.219(4)
Cu(1)—B(2)	2.244(4)
Cu(1)—H(1)	1.95(3)
Cu(1)—H(2)	1.85(3)
Cu(2)—N(4)	2.003(2)
Cu(2)—N(3)	2.008(2)
Cu(2)—B(10)	2.253(4)
Cu(2)—B(8)	2.280(4)
Cu(2)—H(8)	1.86(3)
Cu(2)—H(10)	1.93(3)
Cu(1)—N(2)	2.008(3)
Cu(1)—N(1)	2.022(3)
Cu(1)—H(1)	2.12
Cu(1)—B(2)	2.215(4)
Cu(1)—B(1)	2.316(3)
Cu(1)—H(2)	1.66
Cu(2)—N(4)	2.004(3)
Cu(2)—N(3)	2.030(2)
Cu(2)—B(4)	2.245(4)
Cu(2)—B(1)	2.313(3)
Cu(2)—H(1)	2.10
Cu(2)—H(4)	1.70

Angle	ω/deg
N(2)—Cu(1)—N(1)	104.04(10)
N(2)—Cu(1)—B(1)	136.61(12)
N(1)—Cu(1)—B(1)	111.74(12)
N(2)—Cu(1)—B(2)	139.13(11)
N(1)—Cu(1)—B(2)	110.13(11)
B(1)—Cu(1)—B(2)	44.53(13)
N(2)—Cu(1)—H(1)	116.0(9)
N(1)—Cu(1)—H(1)	109.7(9)
N(2)—Cu(1)—H(2)	118.5(9)
N(1)—Cu(1)—H(2)	106.2(9)
H(1)—Cu(1)—H(2)	101.9(13)
N(4)—Cu(2)—N(3)	126.24(10)
N(4)—Cu(2)—B(10)	112.57(11)
N(3)—Cu(2)—B(10)	119.65(12)
N(4)—Cu(2)—B(8)	114.67(11)
N(3)—Cu(2)—B(8)	111.42(12)
B(10)—Cu(2)—B(8)	43.58(13)
N(4)—Cu(2)—H(8)	106.0(9)
N(3)—Cu(2)—H(8)	100.3(9)
N(4)—Cu(2)—H(10)	102.9(10)
N(3)—Cu(2)—H(10)	115.1(10)
H(8)—Cu(2)—H(10)	104.0(14)

Angle	ω/deg
N(2)—Cu(1)—N(1)	122.43(11)
N(2)—Cu(1)—H(1)	100.2
N(1)—Cu(1)—H(1)	102.2
N(2)—Cu(1)—B(2)	120.14(11)
N(1)—Cu(1)—B(2)	117.03(11)
N(2)—Cu(1)—B(1)	113.20(11)
N(1)—Cu(1)—B(1)	111.72(11)
B(2)—Cu(1)—B(1)	43.90(13)
N(2)—Cu(1)—H(2)	113.1
N(1)—Cu(1)—H(2)	112.9
H(1)—Cu(1)—H(2)	102.0
N(4)—Cu(2)—N(3)	126.46(10)
N(4)—Cu(2)—B(4)	122.13(11)
N(3)—Cu(2)—B(4)	109.36(11)
N(4)—Cu(2)—B(1)	113.84(11)
N(3)—Cu(2)—B(1)	113.22(11)
B(4)—Cu(2)—B(1)	43.22(12)
N(4)—Cu(2)—H(1)	97.8
N(3)—Cu(2)—H(1)	111.7
N(4)—Cu(2)—H(4)	112.2
N(3)—Cu(2)—H(4)	105.4
H(1)—Cu(2)—H(4)	100.1

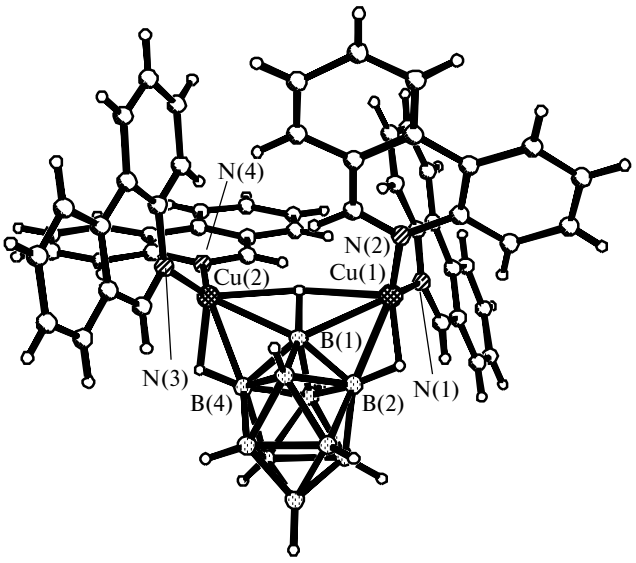

Fig. 3. Structure of complex **2**.

substantially longer than the bonds with the equatorial boron atoms (2.215(4) and 2.245(4) Å).

The difference in the structures of complexes **1** and **2** is reflected in the IR spectra of the resulting compounds. Thus, the spectrum of complex **1** shows an intense split band ν(BH) belonging to vibrations of the free BH groups with maxima at 2516, 2491, 2477, 2466, and 2457 cm^{-1} and a weak broad band at ~2300 cm^{-1} assigned to stretching vibrations $\nu(BH)_{CuHB}$ of the BH groups involved in three-center CuHB interactions. In addition, this spectral region has weak narrow bands at 2247 and 2362 cm^{-1} assigned to stretching vibrations ν(C≡N) of acetonitrile molecules that are included in compound **1**.

The IR spectrum of complex **2** shows an intense split stretching band ν(BH) of free BH groups with maxima at 2532, 2481, and 2464 cm^{-1} and two weak broad bands with maxima at 2255 and 2175 cm^{-1} belonging to stretching vibrations of BH groups involved in the three-center interactions with the Cu^I atom, $\nu(BH)_{CuHB}$. In the range of 1614—700 cm^{-1} of the spectra of both compounds, a complete set of vibrational bands of the phenyl rings of phenanthridine molecules is observed. The involvement of the phenanthridine molecules in the coordination of the Cu^+ ions manifests itself in the increased frequency of predominantly stretching vibrations ν(CN) of the heterocycle, ν(CN) 1614 cm^{-1}, as compared with the corresponding frequency in the spectrum of free phenanthridine ($\Delta\nu = 20$ cm^{-1}).

In the polymeric complexes $Cat[MB_{10}H_{10}]$ having a chain structure, the $B_{10}H_{10}^{2-}$ anion is bound to two metal atoms and, consequently, these complexes are characterized by the same positional isomerism as the monomeric complexes. Thus, the coordination through the apical edges 1—2 and 7(8)—10 similar to that observed in complex **1** was found in the compounds $(Me_2NH_2)[CuB_{10}H_{10}]$ (see Ref. 11) and $(Et_3NH)[AgB_{10}H_{10}]$,[12] and the coordination through the edges 1—2 and 1—4, like in complex **2**, was observed in the compound $Cs[AgB_{10}H_{10}]$.[11] In the chains of the compound $(Et_3NH)[CuB_{10}H_{10}]$, the edges 1—2 and 3—7 (5—8) are involved in the coordination to the Cu^I atom.[13]

Thus, the isomer with the coordination of the $B_{10}H_{10}^{2-}$ anion to the copper(I) atom through the 1—2 and 7(8)—10 edges, which was isolated in the present study for the complex $[Cu_2(9Nphen)_4B_{10}H_{10}]$, complements the series of isomers that were found for monomeric compounds.

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