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Complex Compounds of Iron(II) with 2,2'-Bipyridylamine and Boron Cluster Anions $[B_nH_n]^{2-}$ ($n = 10, 12$)

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Abstract—The complexation of iron(II) with 2,2'-bipyridylamine (BPA) in the presence of boron cluster anions $[B_nH_n]^{2-}$ ($n = 10$, 12) in aqueous solutions is studied. Mixed-ligand complexes $[Fe(BPA)_2(H_2O)_2][B_nH_n]$ ($n = 10$ (**I**), $n = 12$ (**II**)) with boron cluster anions in the outer sphere are synthesized. The reagent ratio does not affect the compositions and structures of the synthesized compounds. Compounds **I** and **II** are identified by elemental analysis and IR spectroscopy. The structure of the $[Fe(BPA)_2(H_2O)_2][B_{10}H_{10}] \cdot 3H_2O$ complex ($\mathbf{I} \cdot 3H_2O$) is determined by X-ray diffraction analysis (CIF file CCDC no. 1962445).

Keywords: mixed-ligand complexes, dodecahydro-*closo*-dodecaborate anion, X-ray diffraction analysis

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INTRODUCTION

Boron cluster anions can form inner-sphere complexes (in the presence of Cu(I), Ag(I), and Pb(II)) and stabilize cationic complexes of metals (Fe(II), Co(II), Ni(II)) to form an outer sphere [1–10]. Data on the reactivities of the *closo*-borohydride anions in the complexation reactions of transition metals in the presence of neutral organic ligands are systematized and the conditions of the reactions accompanying or prevailing over complexation are discussed in these works. It should be taken into account that solvent molecules can act as ligands and build up the coordination sphere of the metal atom in the absence of competitive organic ligands.

Iron forms compounds being in several stable oxidation states, which provokes interest in the complexation of iron. When studying the complexation, one should take into account the possibility of oxidation by air oxygen. In turn, the *closo*-decaborate anion can act as a reducing agent to decrease the oxidation state of the metals down to zero [1].

A restricted number of the iron(II) complexes with the boron cluster anions is described, and the boron cluster anions form an outer sphere in these compounds. The reactions of metal M(II) carbonates or hydroxides with $(H_3O)_2[B_{12}H_{12}]$ afford mixed-cationic *closo*-dodecaborates $[M(H_2O)_6](H_3O)_2[B_{12}H_{12}]_2 \cdot 6H_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd), whose structures were studied by X-ray diffraction analysis [11]. The formed compounds are isostructural and built of the cationic aqua complexes of the metals $[M(H_2O)_6]^{2+}$. Their structures are stabilized due to the formation of specific B–H···H–O interactions between the BH groups of the cluster anion and water molecules of the aqua cation. The iron(II) complexes with the cyclopentadienyl ligand (Cp) and boron cluster anions in the outer sphere, $(FeCp(Me_3NCH_2\text{-}Cp))_2[B_{10}H_{10}]$ [12], $(FeCp(Me_2CH\text{-}Cp))_2[B_{12}H_{12}]$ [12], and $(FeCp(Me_2NHCH_2\text{-}Cp))_2[B_{12}H_{12}]$ [13], were studied. The tris(chelate) iron(II) complexes with azaheterocyclic ligands L (L is bipyridyl (Bipy), phenanthroline (Phen)) [14] are formed by the reactions of the Fe(II) salts with ligands L in the presence of *closo*-borohydride anions $[B_nH_n]^{2-}$ ($n = 10$, 12). The reaction system containing the Fe(III) salt with ligands L and *closo*-decaborate anions gives the iron(II) complexes $[FeL_3][B_{10}H_{10}]$, and also the mixed-ligand iron(II) complex with the bridging CO_3 group $[Fe_2(\mu\text{-}CO_3)(Phen)_4][B_{10}H_{10}] \cdot 2.5DMF$ is formed on the solution surface [15]. This binuclear complex is formed during the redox reaction due to the participation of the *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ and is accompanied by a change in the coordination sphere of the metal. The coordination sphere of iron(II) is supplemented by carbonate ions, the source of which is CO_2 of air, and this is a reason for the formation of the crystals of the complex on the surface.

In this work, we continued the investigation of the reactions of transition metals M(II) with the boron cluster anions $[B_nH_n]^{2-}$ ($n = 10, 12$) in the presence of N-containing organic ligands, studied the complexation of iron(II) with 2,2'-bipyridylamine (BPA) in the presence of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions, and determined the influence of the reaction conditions on the compositions of the synthesized compounds.

EXPERIMENTAL

Triethylammonium decahydro-*closo*-decaborate $(Et_3NH)_2[B_{10}H_{10}]$ was synthesized from decaborane-14 via the step of 1,6-*bis*(trimethylamine)decaborane formation according to a known procedure [16]. Triethylammonium dodecahydro-*closo*-dodecaborate $(Et_3NH)_2[B_{12}H_{12}]$ was synthesized due to the pyrolysis of a solution of decaborane in triethylamineborane using a described procedure [17]. Cesium *closo*-dodecaborate was synthesized by reflux of $(Et_3NH)_2[B_{12}H_{12}]$ in an aqueous solution of cesium hydroxide until trimethylamine was removed completely. Tetrabutylammonium *closo*-dodecaborate $(Bu_4N)_2[B_{12}H_{12}]$ was synthesized by the exchange reaction between $Cs_2[B_{12}H_{12}]$ and the corresponding halides

Synthesis of $[Fe(BPA)_2(H_2O)_2][An]$ ([An] = $[B_{10}H_{10}]^{2-}$ (I), $[B_{12}H_{12}]^{2-}$ (II)). Solutions containing $(Et_3NH)_2[B_{10}H_{10}]$ (1.2 mmol) or $(Bu_4N)_2[B_{12}H_{12}]$ (1.2 mmol) and BPA (3.6 mmol) in H_2O (10 mL) were poured to a solution of $FeCl_2$ (1.2 mmol) in H_2O (15 mL). The reaction solution turned orange during the reaction. The colored crystals of compounds **I** · $3H_2O$ and **II** were formed within 24 h, filtered off, and dried in air. The yield was 70–75%.

For $C_{20}H_{32}B_{10}N_6O_2Fe$ (**I**)				
Anal. calcd., %	C, 43.48	H, 5.84	N, 15.21	B, 19.6
Found, %	C, 43.08	H, 5.37	N, 15.02	B, 19.2
For $C_{20}H_{34}B_{12}N_6O_2Fe$ (**II**)				
Anal. calcd., %	C, 41.70	H, 5.95	N, 14.59	B, 22.5
Found, %	C, 41.59	H, 5.85	N, 14.51	B, 22.3

IR for **I** (NaCl; ν, cm^{-1}): 2437, 2446 ν(BH); 1010 δ(BBH); 3250, 3166 ν(NH); 3571, 3472 ν(OH): 1600–700 ν(BPA).

IR for **II** (NaCl; ν, cm^{-1}): 2473 ν(BH); 1007 δ(BBH); 3247, 3168 ν(NH); 3573, 3475 ν(OH); 1600–700 ν(BPA).

Elemental analyses to carbon, hydrogen, and nitrogen were carried out on a CHNS-3 FA 1108 Elemental Analyser automated gas analyzer (CarloErba) (prior to analysis the samples were dried to a constant weight). Analysis to boron was conducted by the ICPMS method on an iCAP 6300 Duo atomic emission spectrometer with inductively coupled plasma.

The IR spectra of the initial compounds and reaction products were recorded on a INFRALYUM FT-02 FT-IR spectrometer (NPF AP Lyumeks) in a range of 4000–600 cm^{-1} with a resolution of 1 cm^{-1}. Suspensions of solid samples in Nujol (Aldrich) were studied. Plates of NaCl were used for spectra recording.

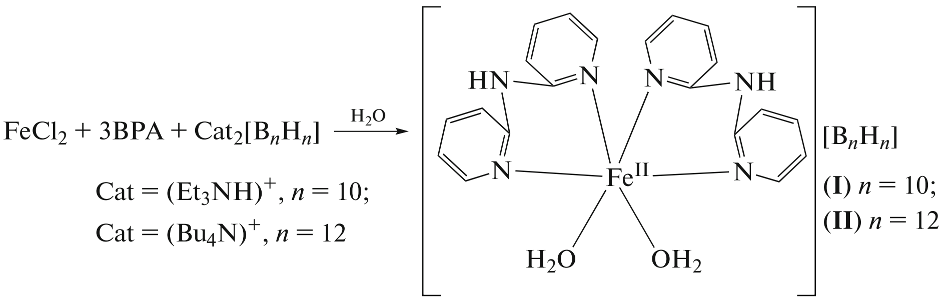
Diffraction reflection arrays for the crystals of compound **I** · $3H_2O$ were obtained at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) on a Bruker APEX 2 CCD automated diffractometer (λMoK_α, graphite monochromator, ω–φ scan mode). An absorption correction was applied by equivalent reflections using the semiempirical method. The nonhydrogen atoms in the structure of compound **I** · $3H_2O$ were refined in the anisotropic approximation. All hydrogen atoms were localized in the difference syntheses and refined in the isotropic approximation: the H(C) atoms were refined by the riding model with $U_{iso} = 1.2U_{equiv}(C)$, and other hydrogen atoms were refined independently.

The APEX2, SAINT, and SADABS programs were used for the collection and processing of the reflection arrays [18]. The structures were solved using the SHELXS-2008 programs [19]. Structure refinement was performed using the SHELXL programs (versions 2013 and 2014) [19]. The main crystallographic data, experimental parameters, and structure refinement characteristics are presented in Table 1.

The coordinates of atoms and other structural parameters for compound **I** · $3H_2O$ were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1962445); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac. uk/data_request/cif).

RESULTS AND DISCUSSION

The complexation reactions of iron(II) with 2,2'-bipyridylamine in the presence of the *closo*-borate anions $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ were studied. The $[Fe(BPA)_2(H_2O)_2][An]$ complexes ([An] = $[B_{10}H_{10}]^{2-}$ (**I**), $[B_{12}H_{12}]^{2-}$ (**II**)) are formed in a threefold BPA excess. The reactions occur via Scheme 1.



Scheme 1.

Remarkably, unlike the case of L = Bipy and Phen [13], the complexation in the presence of BPA gives no tris(chelate) complexes $[FeL_3][An]$ regardless of the metal to ligand ratio. This indicates that the cationic complex $[Fe(BPA)_2(H_2O)_2]^{2+}$ is more stable than the $[Fe(BPA)_3]^{2+}$ complex in an aqueous solution.

According to the IR spectroscopic data, the boron cluster anions exist in the outer sphere of the synthesized complexes. The IR spectra of complexes **I** and **II** exhibit bands corresponding to the stretching vibrations of the B–H bonds of the boron cluster anions and O–H bonds of the water molecules, as well as the full set of vibrations of the coordinated heterocyclic ligand in a range of 1600–700 cm^{-1}. The bands corresponding to the stretching vibrations of the N–H bond of coordinated 2,2'-bipyridylamine in complexes **I** and **II** are observed in a range of 3250–3166 cm^{-1}.

According to the X-ray diffraction data, the BPA ligand molecules in the structure of complex $\mathbf{I} \cdot 3H_2O$ (Fig. 1) close the six-membered chelate cycles to form an asymmetrical bath in such a way that the Fe atom and the N atom of the bridging NH group deviate from the plane of other atoms of the cycle to the same side by 0.969 and 0.196, 0.997, and 0.231 Å, respectively. The cationic complex $[Fe(BPA)_2(H_2O)_2]^{2+}$ has the *cis* structure. The pyridine cycles of one BPA molecule form a dihedral angle of 29.3°, and those of another BPA molecule form an angle of 19.9° between each other.

All the five water molecules form a chain of hydrogen bonds producing single associates O(1) → O(4) → O(3) → O(5) and O(2) → O(4) → O(3) → O(5) (Table 2). Owing to the formation of the hydrogen bond network, the complex cations $[Fe(BPA)_2(H_2O)_2]^{2+}$ are linked by two water molecules into 1D polymeric filaments in the direction of the *b* axis: Fe → O(1) → O(4) → O(3) → N'(6) and Fe → O(2) → O(4) → O(3) → N'(6). All hydrogen atoms of the water molecules and the H(3N) atom of the BPA molecule that are not involved in hydrogen bonds participate in the interaction with the hydrogen atoms of the borohydride anion (H···H 2.09(4)–2.41(5) Å). The complex is isostructural to the earlier described compound $[Ni(BPA)_2(H_2O)_2][B_{10}H_{10}] \cdot 3H_2O$ [20].

It should be mentioned that the binuclear Fe(II) complexes with the bridging carbonate group can be formed in the case of the Bipy and Phen ligands by the reactions with the Fe(III) salts [14]. It is found that the complexation in the presence of BPA and boron cluster anions using the Fe(III) salts results in the reduction of Fe(III) to Fe(II) to form described above complexes **I** and **II**, while no formation of similar binuclear iron(II) complexes is observed.

Thus, the reactions of iron(II) with the boron cluster anions $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ in the presence of the azaheterocyclic BPA ligand were studied in this work. The nature of the azaheterocyclic ligand is

Table 1. Crystallographic data and experimental and structure refinement parameters for compound $\mathbf{I} \cdot 3H_2O$

Parameter	Value
Empirical formula	$C_{20}H_{38}B_{10}N_6O_5Fe$
FW	606.51
T, K	120
Space group; *Z*	$P2_1/n$; 4
a, Å	10.7795(3)
b, Å	21.2357(6)
c, Å	12.9615(4)
β, deg	95.7480(10)
V, $Å^3$	2952.10(15)
ρ_{calc}, g/cm^3	1.365
μ_{Mo}, mm^{-1}	0.554
F(000)	1264.0
Crystal size, mm	0.34 × 0.3 × 0.2
Range 2θ angles, deg	4.254–64.3
Number of reflections measured/independent (*N*)	30479/9576
R_{int}	0.0364
R_1, wR_2 for N_o	0.0410, 0.1033
R_1, wR_2 for *N*	0.0594, 0.1120
GOOF	1.025
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	0.51/–0.47

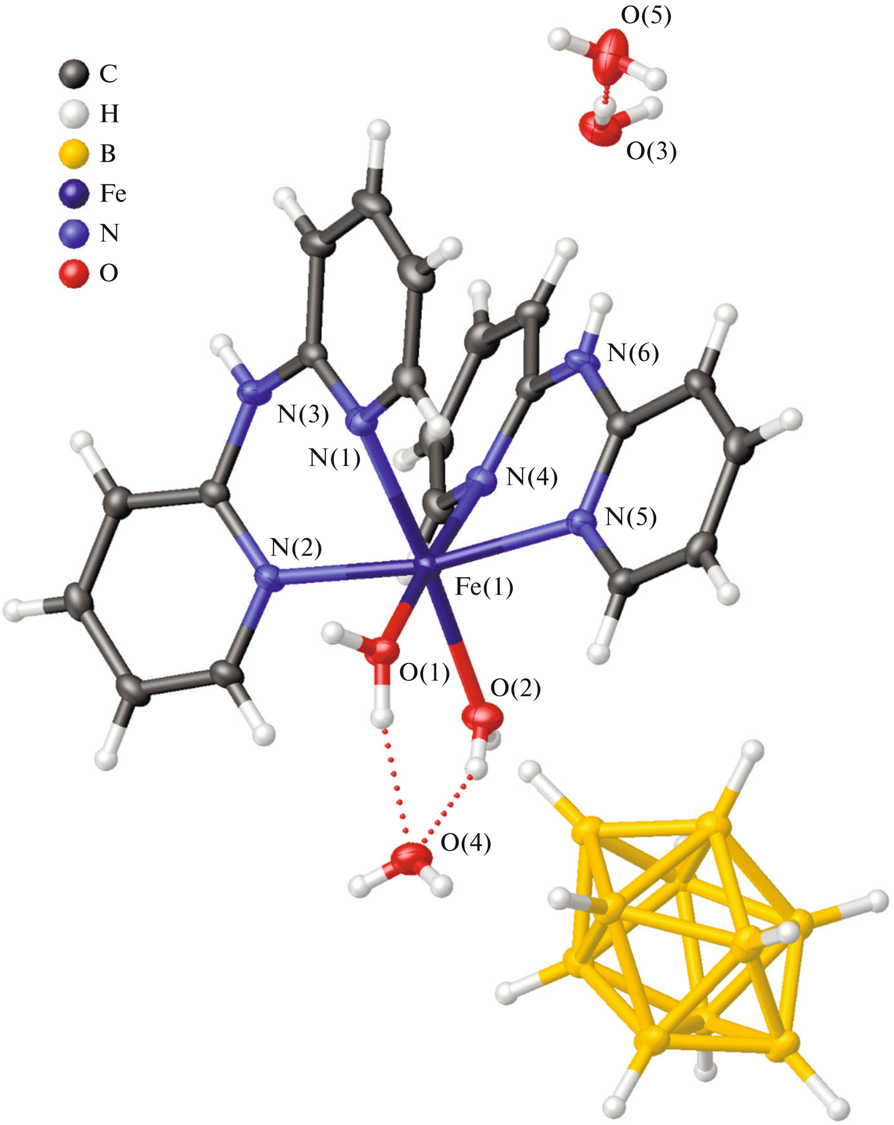


Fig. 1. Fragment of the structure of compound **I** · $3H_2O$. The O–H···O and N–H···O hydrogen bonds are shown by dotted lines.

shown to exert a substantial effect on the formation of complexes when the complexation occurs in an aqueous solution. The $[Fe(BPA)_2(H_2O)_2][An]$ complexes ($[An] = [B_{10}H_{10}]^{2-}$ (**I**), $[B_{12}H_{12}]^{2-}$ (**II**)) are formed regardless of the reagent nature. The complexation reaction using the Fe(III) salts results in the reduction

Table 2. Geometric parameters of hydrogen bonds in the structure of compound **I** · $3H_2O$*

D–H···A	Distance, Å		Angle DHA, deg
	H···A	D···A	
O(1)–H(1*A*)···O(4)	1.92(2)	2.721(2)	160(2)
O(2)–H(2*A*)···O(4)	2.02(3)	2.749(2)	155(3)
O(3)–H(3*C*)···O(5)	1.73(2)	2.698(2)	175(2)
O(4)–H(4*B*)···O(3)	2.10(3)	2.849(2)	169(3)
N(6)–H(6)···O(3)$^{\#1}$	2.23(2)	2.969(2)	160.4(2)

* Symmetry codes: $^{\#1}$ $1/2 - x, -1/2 + y, 1/2 - z$.

of Fe(III) to Fe(II) and formation of the above described complexes.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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