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Dedicated to the 90th birthday of Academician I.I. Moiseev

Boron Cluster Anions $[B_{10}X_{10}]^{2-}$ (X = H, Cl) in Manganese(II) Complexation with 2,2'-Bipyridyl

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Abstract—The complexation of manganese(II) with 2,2'-bipyridyl in the presence of the $[B_{10}H_{10}]^{2-}$ and $[B_{10}Cl_{10}]^{2-}$ boron cluster anions has been studied in acetonitrile. The effect of the ratio of reagents on the composition and structure of final complexes has been shown. Mono- and binuclear manganese(II) complexes $[(Mn(Bipy)_3]^{2+}$ and $[Mn_2(Bipy)_4Cl_2]^{2+}$ have been synthesized with the boron cluster anions as counterions. The X-ray diffraction studies have been performed for complexes $[Mn(Bipy)_3][B_{10}Cl\ (\mathbf{I})_{10}]$ (**I**), $[Mn(Bipy)_3][B_{10}Cl_{10}]_{0.5}[B_{10}Cl_9H]_{0.5} \cdot CH_3CN$ (**III**$\cdot CH_3CN$), and $[Mn_2(Bipy)_4(\mu\text{-}Cl)_2][B_{10}Cl_{10}] \cdot 2CH_3CN$ (**IV** $\cdot 2CH_3CN$) (CIF files CCDC nos. 1868278 (**I**), 1868279 (**III** $\cdot CH_3CN$), 1868280 (**IV** $\cdot 2CH_3CN$)). Thermal properties of complex **I** have been studied.

Keywords: decahydro-*closo*-decaborate anion, decachloro-*closo*-decaborate anion, complexes, manganese

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INTRODUCTION

Our systematic study of the coordination properties of the boron cluster anions $[B_nH_n]^{2-}$ (n = 10, 12) reveals that these systems containing electron-deficient bonds are capable of participating in complexion reactions. In this case, the decisive role in the formation of the coordination polyhedron is played by the nature of the complexing metal. It was established that in the complexation of soft acid metals according to Pearson's principle, the non-substituted boron cluster anions [1–3] are coordinated by the metal atom via three-center two-electron bonds, whereas the substituted derivatives of the boron cluster anions $[B_nH_{n-m}X_m]$ ($n = 10, 12$; $m = 1 - n$) [4–7] can be bound by a metal atom through a substituent (for example, $[Pb(Bipy)(DMF)(2\text{-}B_{10}H_9OH)] \cdot DMF$ [8], $\{Pb(Bipy)_2[2,6(9)\text{-}B_{10}H_8(OC(O)CH_3)(OH)]\}_2 \cdot 3H_2O$ [9]) or through the BH groups of the boron polyhedron, as it was found in $[Ag(CH_3CN)_3]_2(Ag_2(2\text{-}B_{10}H_9F)_2]$ [10] and $[Et_3NH][Cu[1\text{-}B_{10}H_9(N_2)]_2]$ [11].

An independent field of the coordination chemistry of boron cluster anions is the study of the complexation of metals having several stable oxidation states. The complexation reactions in their presence may be accompanied by redox processes, the occurrence of which results from the presence of the boron cluster anions exhibiting reducing properties. In [12–16], the reactions of copper(I)/copper(II) complex formation with azaheterocyclic ligands and $[B_nH_n]^{2-}$ anions (n = 10, 12) were studied in details. The behavior of the boron cluster anions in the reactions of iron(II/III), cobalt(II/III), and nickel(II) complexation is summarized in review [7].

The coordination chemistry of the perchlorinated *closo*-decaborate anion $[B_{10}Cl_{10}]^{2-}$ has been studied scarcely. A number of mononuclear complex compounds of silver(I) [17], copper(II) [18], iron(II) [19], cobalt(II) [20] with N-containing ligands (1,10-phenanthroline (Phen), 2,2'-Bipyridyl (Bipy), and NH_3) were reported. In these complexes, the $[B_{10}Cl_{10}]^{2-}$ anion was found to form the B–Cl···H–X (X = N, O) secondary bonds with molecules of organic ligands and solvents, which were revealed by analyzing the data obtained by the X-ray diffraction and ^{35}Cl NQR spectroscopy studies.

Another example of metals with several stable oxidation states is manganese. It belongs to biometals that are crucial for the vital activity of organisms [21] and is necessary for performing the functions of the reproductive, central nervous, and endocrine systems. Manganese, like other 3*d* metals, exhibits biological activity being a part of coordination compounds with organic ligands [22]. Manganese coordination compounds have catalytic activity. Manganese porphyrins which are molecular magnetics and complexes forming nanoporous structures [23] were discovered, which opens the possibility to manufacture new materials with desired properties.

The coordination chemistry of manganese(II) with boron cluster anions $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ remains practically unstudied. To date, tris-chelate complexes are known with other boron cluster anions $[Mn(Phen)_3][B_6H_7]_2$ [24] and $[Mn(Bipy)_3][B_{20}H_{18}] \cdot 2DMF$ [25], which were obtained by metathesis reactions when salts of the boron cluster anions were allowed to react with manganese(II) chloride in the presence of Phen and Bipy, respectively.

In this work, in the course of studying the complexation of metals with several stable oxidation states, we have studied the reaction of the manganese(II) complexation with the N-containing organic ligand Bipy in the presence of the $[B_{10}H_{10}]^{2-}$ and $[B_{10}Cl_{10}]^{2-}$ anions; the effect of the reaction conditions on the composition and structure of the compounds obtained has been determined.

EXPERIMENTAL

$(Et_3NH)_2[B_{10}H_{10}]$ was obtained in the course of multistage synthesis by the interaction between decaborane-14 and triethylamineborane through the formation of 1,6-bis(triethylamine)decaborane [26]. $(Et_3NH)_2[B_{10}Cl_{10}]$ was obtained by the chlorination of $(Et_3NH)_2[B_{10}H_{10}]$ with chlorine in an aqueous solution as reported [27].

Synthesis of $[Mn(Bipy)_3][B_{10}X_{10}]$ (X = H (I), Cl (II). A solution containing $MnCl_2$ (1 mmol) and Bipy (3 mmol) in acetonitrile (10 mL) was added to a solution of $(Et_3NH)_2[B_{10}X_{10}]$ (1 mmol) in the same solvent (5 mL). The yellow crystals of compound **I** or **II** precipitated after 24 h. Yield, ~90%.

For $C_{30}H_{34}N_6B_{10}Mn$ (**I**)

Anal. calcd., %	C, 56.15	H, 5.34	N, 13.10	B, 16.85	Mn, 8.56
Found, %	C, 56.09	H, 5.28	N, 13.07	B, 16.78	Mn, 8.44

For $C_{30}H_{24}N_6B_{10}Cl_{10}Mn$ (**II**)

Anal. calcd., %	C, 36.54	H, 2.45	N, 8.52	B, 10.96	Mn, 5.57
Found, %	C, 36.48	H, 2.40	N, 8.47	B, 10.90	Mn, 5.45

The single crystal of compound **I** suitable for X-ray diffraction was obtained directly from the reaction solution. In the synthesis of **II**, after separating the main fraction of crystals **II**, crystals $[Mn(Bipy)_3][B_{10}Cl_{10}]_{0.5}[B_{10}Cl_9H]_{0.5} \cdot CH_3CN$ (**III** · CH_3CN) precipitated from the diluted reaction solution in a small yield (less than 5%), which contained co-crystallized anions $[B_{10}Cl_{10}]^{2-}$ and $[B_{10}Cl_9H]^{2-}$. The presence of the $[B_{10}Cl_9H]^{2-}$ anion is explained by the incompleteness of the chlorination of the $[B_{10}H_{10}]^{2-}$ anion at the previous stage.

IR for **I** (NaCl; ν, cm^{-1}): ν(BH) 2488, 2446; ν(Bipy) 1590 s, 1471 s, 1441 s, 1378 s, 1314, 1246, 1159, 1016 s, 737, 652; π(CH) 776.

IR for **II** (NaCl; ν, cm^{-1}): ν(BCl) 1155, 1002, 843; ν(Bipy) 1599 s, 1468 s, 1440 s, 1378 s, 1316, 1244, 1014 s, 736, 652; π(CH) 766.

$[Mn_2(Bipy)_4(\mu\text{-}Cl)_2][B_{10}Cl_{10}]$ (IV) was synthesized according to the procedure described for **II** with the ratio of $MnCl_2$: Bipy = 1 : 2. Yellow crystals precipitated from the reaction solution after 24 h. A single crystal of **IV** · $2CH_3CN$ selected directly from the reaction solution was studied by X-ray diffraction.

For $C_{40}H_{32}N_8B_{10}Cl_{12}Mn_2$ (**IV**)

Anal. calcd., %	C, 40.13	H, 2.69	N, 9.36	B, 9.03	Mn, 9.18
Found, %	C, 39.97	H, 2.55	N, 9.22	B, 8.98	Mn, 9.10

IR (NaCl; ν, cm^{-1}): ν(BCl) 1156, 1004, 854; ν(Bipy) 1596 s, 1458 s, 1440 s, 1378 s, 1317, 1246, 1156, 1017 s, 737; π(CH) 762.

Elemental analysis for carbon, hydrogen, and nitrogen was carried out on a CHNS-3 FA 1108 Elemental Analyzer (Carlo Erba) automatic gas analyzer; boron and manganese were analyzed by the ICP MS method using an inductively coupled plasma iCAP 6300 Duo.

The IR spectra of the synthesized complexes were recorded on an INFRALUM FT-02 FTIR spectrometer (NPF AP Lumeks) in the region of 4000–600 cm^{-1} with a resolution of 1 cm^{-1}. Samples were prepared as Nujol mull (Aldrich) suspensions.

Thermogravimetric and differential thermal studies of compound **I** were performed on a Paulik–Paulik–Erdey Q 1500D derivatograph in air in the range of 20–1000°C in a platinum crucible. The heating rate of the sample is 10 K/min.

X-ray diffraction. A set of diffraction reflections for **I** was obtained by I.N. Polyakova (deceased) at the Shared Facility Center of the Kurnakov Institute on a Bruker SMART APEX2 automated diffractometer. X-ray diffraction studies for compounds **III** · CH_3CN and **IV** · $2CH_3CN$ were performed at the Centre for Molecular Studies of the Nesmeyanov Institute. The sets of diffraction reflections were collected on a Bruker APEX II diffractometer (two-coordinate CCD detector, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The data were corrected for absorption using the SADABS program [28]. Structures **III** and **IV** were solved by the SHELXT program [29]. All non-hydrogen atoms were localized on electron density difference syntheses and refined according to F^2_{hkl} (SHELXL-14 [30] and OLEX2 [31]). Non-hydrogen atoms were refined in the anisotropic approximation

Table 1. Crystallographic data, details of data collection, and characteristics of data refinement for the structures of **I**, **III** · CH_3CN, and **IV** · $2CH_3CN$

	I	**III** · CH_3CN	**IV** · $2CH_3CN$
FW	$C_{30}H_{34}N_6B_{10}Mn$	$C_{32}H_{27.9}N_7B_{10}Cl_{9.1}Mn$	$C_{44}H_{38}N_{10}B_{10}Cl_{12}Mn_2$
M	641.68	996.15	1350.22
T, K	120	120	120
Crystal system	Trigonal	Monoclinic	Orthorhombic
Space group	$R\bar{3}c$	$P2_1/c$	$Pna2_1$
Z	12	4	4
a, Å	14.1895(19)	17.5165(7)	25.6666(18)
b, Å	14.1895(19)	13.0253(5)	10.5239(7)
c, Å	57.520(8)	19.1401(7)	21.6195(15)
β, deg	90	95.794(1)	90
V, $Å^3$	10030(3)	4344.7(3)	5839.7(7)
ρ_{calc}, g cm^{-3}	1.275	1.523	1.536
μ, cm^{-1}	0.427	0.900	1.025
F(000)	3972	1994	2704
$2\theta_{max}$, deg	53	62	59
Number of reflections			
collected	23234	49639	57168
unique (*N*) [R_{int}]	2283	13807	15380
with $I > 2\sigma(I)$	1144	9397	12745
Number of parameters to be refined	173	542	705
R_1, wR_2 ($I > 2\sigma(I)$)	0.0667, 0.1240	0.0504, 0.1222	0.0478, 0.0957
R_1, wR_2 (*N*)	0.1383, 0.1555	0.0873, 0.1381	0.0741, 0.1065
GOOF	1.005	1.040	1.006
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	–0.434/0.456	–0.973/0.653	–0.537/0.935

except for the boron atoms of the *closo*-decaborate anion in structure **I**, which is disordered in two positions. Because of its disordering, this anion was refined in the isotropic approximation imposing restrictions on the B–B bond lengths. Hydrogen atoms were determined geometrically and refined in the isotropic approximation in the rigid body model; $U_{iso}(H)$ is $1.5U_{eq}(X_i)$ for methyl groups and $1.2U_{eq}(X_i)$ for other atoms, where $U_{eq}(X)$ is the equivalent thermal parameters of the atoms which the hydrogen atom is bound to.

Main crystal data, details of data collection, and characteristics of structure refinement are listed in Table 1. The crystallographic data have been deposited with the Cambridge Structural Database (CCDC nos. 1868278 (**I**), 1868279 (**III** · CH_3CN), and 1868280 (**IV** · $2CH_3CN$); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

In this work, the complexation of manganese(II) with Bipy in the presence of the *closo*-decaborate anions $[B_{10}H_{10}]^{2-}$ and $[B_{10}Cl_{10}]^{2-}$ has been studied. It has been found that the Bipy : Mn ratio affects the composition and structure of the resulting complexes.

With a tree-fold excess of Bipy, the cationic manganese(II) complex $[Mn(Bipy)_3]^{2+}$ forms in the reaction solution, which is removed from the reaction solution with the $[B_{10}H_{10}]^{2-}$ or $[B_{10}Cl_{10}]^{2-}$ counterions according to the scheme:

$$\mathrm{MnCl_2 + 3Bipy + (Et_3NH)_2[B_{10}X_{10}]}$$
$$\xrightarrow{\mathrm{CH_3CN}} \mathrm{[Mn(Bipy)_3][B_{10}X_{10}]},\ \mathrm{X = H\ (\mathbf{I}), Cl\ (\mathbf{II})}.$$

Compounds **I** and **II** precipitate from the reaction solution as bright yellow single crystals. In the IR spectra of **I** and **II**, there are bands of stretching vibrations of the B–Cl or B–H bonds and the full set of

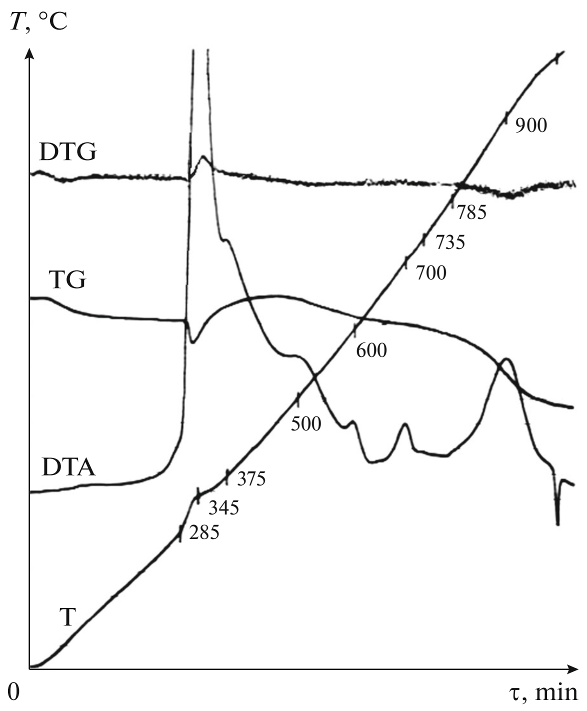

Fig. 1. Thermogramm for complex **I**.

vibrations of the coordinated heterocyclic ligand in the range of 1600–700 cm^{-1}.

According to the X-ray diffraction studies, compound **I** is built of the cationic $[Mn(Bipy)_3]^{2+}$ complexes and the $[B_{10}H_{10}]^{2-}$ anions disordered over two positions. The coordination polyhedron of MnN_6 is a distorted octahedron (Mn–N 2.221(1)–2.247(1) Å). The absence of strong intermolecular interactions leads to the disordering of the anion with the axial boron atoms rotation of ~90°.

Thermal properties of compound **I** were studied (Fig. 1). It was found that the complex has high thermal stability. It begins to decompose at 330°C which is accompanied by a strong exothermic reaction. The process of the thermal-oxidative degradation is stepwise. The thermal decomposition of compound **I** leads to the formation of volatile products, the decomposition of the boron cluster, and the formation of a complex mixture of oxidation products.

When carrying out the complexation reaction in the presence of the $[B_{10}Cl_{10}]^{2-}$ anion, after isolation of the main product (**II**) of this reaction from the mother liquor, crystals **III** · CH_3CN were obtained in a small yield, whose structure was determined by X-ray diffraction (Fig. 2). It was found that two compounds are crystallized in single crystal **III** · CH_3CN studied: complex **II** and the manganese complex with the $[B_{10}Cl_9H]^{2-}$ anion which is an intermediate product of chlorination of the *closo*-decaborate anion. Since the octahedral cation $[Mn(Bipy)_3]^{2+}$ is in general position, the Mn–N bonds fall in a wider range as compared to the analogous complex in structure **I** (Mn–N 2.221(2)–2.278(2) Å). In contrast to crystal **I**, compound **III** · CH_3CN contains a solvent molecule and the ordered boron cluster anion. The anion forms a multiple secondary B–Cl···H–C bonds with the participation of both Bipy and acetonitrile molecules.

When the complexation of manganese(II) with the decachloro-*closo*-decaborate anion was performed with a twofold excess of Bipy with respect to $MnCl_2$, binuclear complex of manganese(II) **IV** was isolated from the reaction solution according to the scheme:

$$MnCl_2 + 2Bipy + (Et_3NH)_2[B_{10}Cl_{10}]$$
$$\xrightarrow{CH_3CN} [Mn_2(Bipy)_4(\mu\text{-}Cl)_2][B_{10}Cl_{10}]\ (\mathbf{IV}).$$

Compound **IV** precipitated from the reaction solution as solvate **IV** · $2CH_3CN$. According to the data obtained, the compound is build of the binuclear manganese(II) cationic complex $[Mn_2(Bipy)_4(\mu\text{-}Cl)_2]^{2+}$ and anions $[B_{10}Cl_{10}]^{2-}$ (Fig. 3). The structure of the manganese(II) cationic complex is similar to the structure of the binuclear cobalt(II) complex reported $[Co_2(\mu\text{-}Cl)_2(Phen)_4][B_{10}Cl_{10}]$ [20]. In the MnN_4Cl_2 coordination polyhedra, the Mn–N bonds (2.210(4)–2.215(4) Å), which are opposite to two Mn–Cl bonds, are shortened as compared with the MnN_6 polyhedra in structures **I** and **III**. The values of the remaining Mn–N bonds fall in the range from 2.244(4) to 2.278(4) Å, and the lengths of the Mn–Cl bonds are 2.499(1)–2.536(1) Å. Numerous weak contacts including Cl···H–C are formed in the crystal between the chloride atoms of the cation and anion and hydrogen atoms of the solvent molecule or Bipy.

The IR of complex **IV** · $2CH_3CN$ have no pronounced differences from the IR spectrum of complex **II**, which indicates a similar state of bipyridyl and the boron cluster anion in both compounds.

It should be noted that for manganese(II), as well as for cobalt (II), the bulky binuclear cationic complex is isolated from the reaction solution only in the presence of the perchlorinated *closo*-decaborate anion, while from the reaction solution containing the $[B_{10}H_{10}]^{2-}$ anion, a twofold excess of ligand with respect to the metal affords complex **I** described above:

$$MnCl_2 + 2Bipy + (Et_3NH)_2[B_{10}H_{10}]$$
$$\xrightarrow{CH_3CN} [Mn(Bipy)_3][B_{10}H_{10}]\ (\mathbf{I}).$$

Thus, in the present work, the complexation of manganese(II) with the $[B_{10}H_{10}]^{2-}$ and $[B_{10}Cl_{10}]^{2-}$ boron cluster anions have been studied. It has been shown that using the $[B_{10}Cl_{10}]^{2-}$ anion mononuclear $[Mn(Bipy)_3][B_{10}Cl_{10}]$ and binuclear $[Mn_2(Bipy)_4(\mu\text{-}Cl)_2][B_{10}Cl_{10}]$ manganese complexes can be isolated, whereas the decahydro-*closo*-decaborate anion allows to obtain only tris-chelate complex

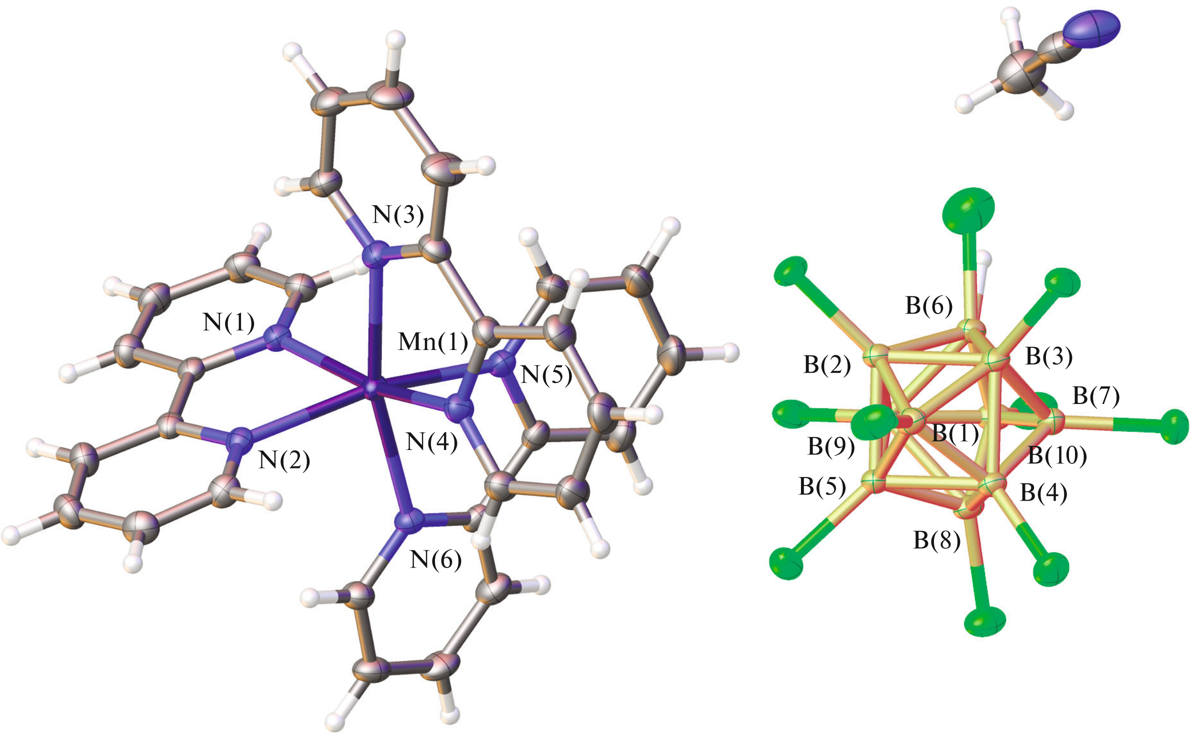

Fig. 2. View of structure **III** · CH_3CN in thermal ellipsoids (p = 50%).

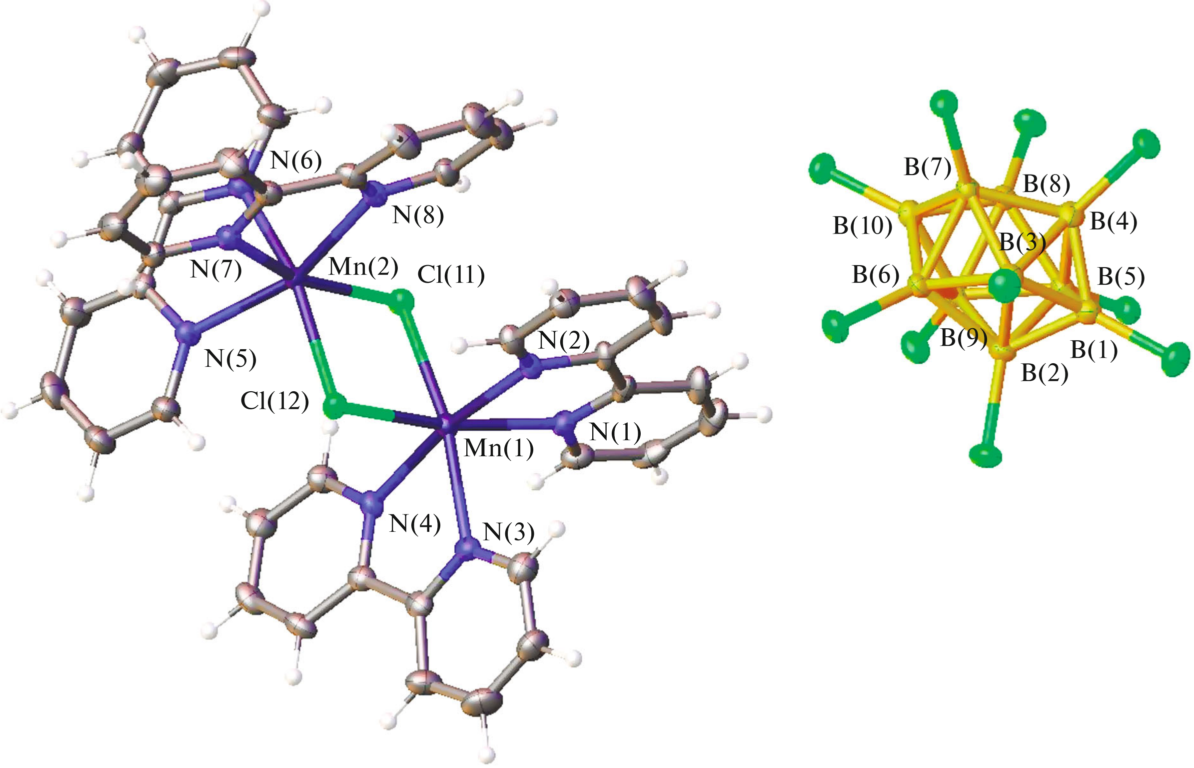

Fig. 3. View of structure **IV** · $2CH_3CN$. Solvent molecules are omitted.

$[Mn(Bipy)_3][B_{10}H_{10}]$. It has been found that complex $[Mn(Bipy)_3][B_{10}H_{10}]$ has high thermal stability.

The presence of two stable oxidation states in manganese allow one apply manganese compounds for the directed synthesis of Mn(II)/Mn(III) compounds similar to the previously studied Fe(II)/Fe(III), Co(II)/Co(III) complexes with boron cluster anions [7, 20]. The redox reactions proceeding allows the directed synthesis of new coordination compounds with desired properties. The study of manganese complexes is relevant for the development of theoretical and applied aspects of the coordination and bioinorganic chemistry.

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