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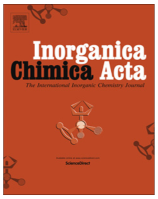

Reactivity of boron cluster anions $[B_{10}H_{10}]^{2-}$, $[B_{10}Cl_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ in cobalt(II)/cobalt(III) complexation with 1,10-phenanthroline

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ABSTRACT

Reactivity of three boron cluster anions $[B_{10}H_{10}]^{2-}$, $[B_{10}Cl_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ with cobalt(II) chloride and 1,10-phenanthroline was studied in acetonitrile and DMF, in the presence of an oxidizing agent Ce^{IV} and without it. It was found that the nature of the boron cluster, solvent used, reagents ratio and cobalt complexation chemistry affect reaction path. Cobalt(II) complexes $[Co(phen)_3][An]$ ($An = [B_{10}H_{10}]^{2-}$, $[B_{10}Cl_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$), $[Co(phen)_2(\mu\text{-}Cl)_2Co(phen)_2][B_{10}Cl_{10}]$ as well as the first cobalt(III) complex with boron cluster $[Co(phen)_3][B_{12}H_{12}]NO_3$ were formed and characterized by IR and UV–Vis spectroscopy as well as X-ray diffraction. Selective preparation of known substituted derivative 1,2-$[B_{10}H_8(phen)]$ was carried out. In addition, cobalt(II) and cobalt(III) complexes $[Co(phen)_3]Cl_2{\cdot}7.5H_2O$ and $[Co(phen)_2Cl_2]NO_3{\cdot}H_2O$ were structurally characterized.

1. Introduction

Boron cluster anions $[B_nH_n]^{2-}$ ($n = 6$–12) [1] represent an especial class of ligands in coordination chemistry. They tend to participate in numerous reactions of substitution of exo-polyhedral hydrogens to a wide set of functional groups without decomposition of the boron cage [2]. Besides, the boron cluster anions form numerous polymeric or mononuclear complexes with such metals as Pb, Cu, Ag, Au, Zn, Cd, Hg, *etc* [3]. Although these are compounds with electron-deficient bonds [4], they can form in addition to coordination bonds a wide set of specific B–H…H(X) (X = N, O, C) interactions [5]. To date, compounds based on boron clusters are applied in a variety of fields including boron neutron capture therapy, radionuclide diagnostics and therapy, preparation of safety coatings, extraction of radionuclides, design of thermal stable polymers, catalysis, *etc.* [6]. From this point of view, investigation of reactivity of boron cluster anions in complexation reactions is an actual task.

Up to now, there are limited data about reactivity of boron cluster anions in cobalt(II) complexation reactions. Complexes with proposed composition $[CoL_3][An]{\cdot}xH_2O$ (where $[An] = [B_{10}H_{10}]^{2-}$ or $[B_{12}H_{12}]^{2-}$; L = 1,10-phenanthroline (phen), 2,2′-bipyridyl, ethylenediamine, benzoylhydrazine (Bh)) and $[Co(m\text{-}NBh)_4(H_2O)_2][An]{\cdot}xH_2O$ (*m*-NBh = *m*-nitrobenzoylhydrazine) with *closo*-borates $[B_nH_n]^{2-}$ ($n = 10, 12$) have been described in our papers almost 25 years ago [7]. All the compounds were synthesized from water or water–ethanol solutions by interaction of cobalt(II) aqua-complexes of the corresponding boron cluster anions $[Co(H_2O)_6][B_nH_n]$ with threefold excess of ligand L. Indirect physical and chemical methods allowed to propose that bidentate ligands L in the synthesized complexes form *tris*-chelating environment around metal atom, and boron cluster anions act as counterions forming $[CoL_3][B_nH_n]$ ($n = 10, 12$). Among abovementioned complexes, only $[Co(Bh)_3][B_{12}H_{12}]{\cdot}3C_2H_5OH$ was characterized by X-ray diffraction analysis [7b]. Besides, Zimmermann and co-workers recently reported the structure of cobalt(II) aqua-complex $[Co(H_2O)_6][B_{10}H_{10}]{\cdot}3H_2O$ [8].

It is known that cobalt(II) can be easily oxidized to cobalt(III) at the presence of an appropriate ligand by an oxidizing reagent or even in air. Particularly, regarding to classical bidentate ligand phen, a number of phenanthroline-containing cobalt(II), cobalt(III) and even heterovalent cobalt(II,III) complexes $[Co(phen)_3]^{2+}$ [9], $[Co(phen)_3]^{3+}$ [9], $[Co(phen)_2Cl_2]$ [10], $[Co(phen)_2Cl_2]^{+}$ [11], $[Co(phen)_3][CoCl_4]^{-}$ [12] is known. The presence of chloride-anions and solvent molecules can effect complexation reactions: they are able to replace other ligands in metal coordination sphere, and the resulting metal/ligands ratio in the obtained products does not correspond to the initial molar ratio of reagents. Complexes $[Co(phen)_2Cl(H_2O)]Cl$ [13] and abovementioned $[Co(m\text{-}NBh)_4(H_2O)_2][An]{\cdot}xH_2O$ [7c] can be used as examples.

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Taking into account the nature and reactivity of boron cluster anions, their ability to interact as reducing agents in complexation reactions with metals possessing at least two stable oxidation states (namely, Cu^{2+} [14], Fe^{3+} [15]) allow us to suggest the possibility to obtain compounds of composition different from proposed $[Co(phen)_3][B_nH_n]$ ($n = 10, 12$). There is no data about effect of solvent, reagents ratio, temperature of the synthesis on reaction path, structure and composition of final products of these reactions. Besides, it was interesting to find out whether phen cobalt(III) complexes can be obtained with *closo*-borate anions. Moreover, there are limited data about complexation ability of perchlorinated *closo*-decaborate anion: up to now, neither metal complexes, no salts of the $[B_{10}Cl_{10}]^{2-}$ anion were structurally characterized.

Here, we report the reaction ability of three boron cluster anions $[An] = [B_{10}H_{10}]^{2-}$, $[B_{10}Cl_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ with $CoCl_2$ and phen in CH_3CN or DMF at [An]: Co: phen ratio equal to 1:1:1, 1:1:2 and 1:1:3. Structure of previously reported compounds $[Co(phen)_3][B_nH_n]$ ($n = 10, 12$) was proved by X-ray diffraction; first cobalt(II) compounds with perchlorinated *closo*-decaborate anion and cobalt(III) complex with the *closo*-dodecaborate anion were synthesized and structurally characterized.

2. Materials and methods

Elemental analysis was carried out on an EA1108 automatic CHN analyzer (Carlo Erba Instruments). All the samples were dried under vacuum at room temperature to constant weight to obtain solvent-free compounds. Determination of boron was performed by electrothermal atomic absorption on a Perkin-Elmer 2100 spectrophotometer with an HGA-700 furnace [16]. Cobalt was determined on a Perkin-Elmer 303 atomic absorption spectrophotometer in an acetylene-air flame on 248.3 nm analytical wave length; lamp current 25 mA, hollow cathode lamp (Carl Zeiss). Infrared spectra of compounds **1–10** were recorded on an InfraLum FT-02 FT-IR spectrometer (Lumex, St.-Petersburg, Russia) in the range 600–4000 cm^{-1} (Vaseline mull, NaCl pellets). Strong (s) and weak (w) bands are indicated while middle are the rest (without indication). UV–Vis spectra of cobalt complexes suspended in glycerol were measured in 13 000–50 000 cm^{-1} region using spectrophotometer SF 103. Small amounts of **9** did not allow to obtain UV–Vis spectrum. ^{11}B NMR spectra of compound **7** in $[D_7]$DMF were recorded with a Bruker AC 200 spectrometer at a frequency of 64.297 MHz using $BF_3{\cdot}Et_2O$ as an external standard.

Single crystals of $[Co(phen)_3][B_{10}H_{10}]$, $[Co_2(phen)_3][B_{12}H_{12}]{\cdot}1.5$ DMF, $[Co(phen)_3][B_{10}Cl_{10}]{\cdot}2$ CH_3CN, $[Co_2(phen)_3]Cl_2{\cdot}7.5$ H_2O, $[Co_2(phen)_4Cl_2][B_{10}Cl_{10}]{\cdot}CH_3CN$, $[Co(phen)_2Cl_2]NO_3{\cdot}H_2O$ and $[Co(phen)_3][B_{12}H_{12}](NO_3){\cdot}2$ DMF$\cdot 4H_2O$ compounds were isolated from reaction mixtures. X-ray diffraction data were obtained with Bruker APEX DUO CCD diffractometer using Mo Kα (**1**, **3**·2 CH_3CN, **4**·7.5 H_2O, **5**·CH_3CN, **9**·H_2O, **10**·2 DMF·4 H_2O) and Cu Kα (**2**·1.5 DMF) radiation. The structures were solved by the direct method and refined by full-matrix least squares method against F^2 of all data, using SHELXTL PLUS [17] and OLEX2 [18] software. Non-hydrogen atoms were found on difference Fourier maps and refined with anisotropic displacement parameters. Asymmetric units of **5**·CH_3CN and **10**·2DMF·4H_2O contain highly disordered solvate molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON [19]. The best available crystal of **10**·2DMF·4H_2O was twinned. The twin components were separated using PLATON. The structure was refined using additional BASF parameter and HKLF 5 command. Positions of H(C) and H(B) atoms were calculated, the H(O) were located from difference Fourier maps and H–O distances were normalized to 0.85 Å. All hydrogen atoms were included in refinement in isotropic approximation by the riding model with the $U_{iso}(H) = 1.5U_{eq}(O_i)$, $1.2U_{eq}(C_i)$ and $1.2U_{eq}(B_i)$, where $U_{eq}(X)$ are

Table 1
Crystallographic data and refinement parameters for the $[Co^{II}(phen)_3][B_{10}H_{10}]$, $[Co^{II}_2(phen)_3][B_{12}H_{12}]{\cdot}1.5$ DMF, $[Co^{II}(phen)_3][B_{10}Cl_{10}]{\cdot}2$ CH_3CN, $[Co^{II}(phen)_3]Cl_2{\cdot}7.5$ H_2O, $[Co^{II}_2(phen)_4Cl_2][B_{10}Cl_{10}]{\cdot}CH_3CN$, $[Co^{III}(phen)_2Cl_2]NO_3{\cdot}H_2O$ and $[Co^{III}(phen)_3][B_{12}H_{12}](NO_3){\cdot}2$ DMF·4 H_2O compounds.

	1	**2**·1.5DMF	**3**·2CH_3CN	**4**·7.5H_2O	**5**·CH_3CN	**9**·H_2O	**10**·2DMF 4H_2O
Empirical formula	$C_{36}H_{34}B_{10}CoN_6$	$C_{40.5}H_{46.5}B_{12}CoN_{7.5}O_{1.5}$	$C_{38}H_{27}B_{10}Cl_{10}CoN_7$	$C_{36}H_{39}Cl_2CoN_6O_{7.5}$	$C_{48}H_{32}B_{10}Cl_{12}Co_2N_8$	$C_{24}H_{18}Cl_2CoN_5O_4$	$C_{42}H_{58}B_{12}CoN_9O_9$
Formula weight	717.72	851.00	1103.20	805.56	1372.18	570.26	1021.62
T, K	120.0(2)	120.0(2)	120.0(2)	100.0(2)	120.0(2)	120.0(2)	220.0(2)
Color, habit	brown, prism	yellow, plate	yellow, cube	orange, prism	pink, plate	brown, needle	brown, plate
Radiation (λ)	Mo Kα (0.71073)	Cu Kα (1.54184)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
a (Å)	17.850(3)	13.8697(4)	16.830(11)	12.1736(7)	14.3267(15)	15.497(2)	11.417(4)
b (Å)	11.950(3)	32.9932(11)	15.346(9)	27.7238(16)	15.7407(19)	12.9382(17)	13.361(5)
c (Å)	31.153(5)	24.2060(9)	19.738(12)	13.3671(7)	29.253(3)	12.7396(17)	17.408(6)
α (°)	90	90	90	90	90	90	91.507(9)
β (°)	148.128(3)	127.266(3)	39.540(18)	117.022(1)	90	100.251(3)	100.646(8)
γ (°)	90	90	90	90	90	90	102.697(9)
V ($Å^3$)	3508.7(11)	8815.3(5)	5088(5)	4018.9(4)	6597.0(13)	2513.6(6)	2536.9(17)
Z	4	4	4	4	4	4	2
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C\,2\,2\,2_1$	$C2/c$	$P\bar{1}$
D_{calc} (g cm^{-3})	1.359	1.282	1.440	1.331	1.382	1.507	1.337
μ (mm^{-1})	0.528	3.387	0.900	0.614	1.028	0.936	0.400
Independent reflections (R_{int})	6879 (0.107)	15 090 (0.168)	14 087 (0.052)	7878 (0.027)	6431 (0.087)	3290 (0.096)	14 783 (0.133)
Observed reflections/ restraints/ parameters	4020/0/478	8682/1/1115	10 405/0/594	6987/6/488	5419/18/279	2116/27/171	8454/0/598
R,[a]% [$I > 2\sigma(I)$]	0.055	0.085	0.043	0.083	0.105	0.055	0.095
R_w,[b]%	0.098	0.210	0.092	0.182	0.253	0.178	0.233
Goodness-of-fit (GOF)[c]	1.01	1.02	0.99	1.02	1.08	0.99	1.01
F(000)	1476	3528	2204	1672	2736	1160	1064

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma(w(F_o{}^2 - F_c^2)^2)/\Sigma(w(F_o^2))]^{1/2}$.

[c] $GOF = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(N_{obs} - N_{param})]^{1/2}$.