Electrochemical synthesis of halogen derivatives of bis(1,2-dicarbollyl)cobalt(III)

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A convenient electrochemical method for the synthesis of 8,8′-dihalogen derivatives of bis(1,2-dicarbollyl)cobalt(III) anion $[8,8'\text{-}X_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})]^-$ (X = Cl, Br, I) was developed. The method includes the electrolysis of a solution of alkaline metal halide and tetramethylammonium salt of bis(1,2-dicarbollyl)cobalt(III) in methanol at 50 °C in a one-compartment electrochemical cell with a nickel cathode and platinum anode.

Key words: bis(dicarbollyl)cobalt(III), halogenation, electrochemistry.

Bis(dicarbollyl)cobalt derivatives[1] found wide use for the liquid extraction of radionuclides.[2,3]. Many both radioactive and stable nuclides (Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+; Ca^{2+}, Ba^{2+}, Ra^{2+}, Pd^{2+}; lanthanides, *etc.*) can successfully be separated and isolated using bis(dicarbollyl)cobalt and its derivatives.[4—7] In addition, bis(dicarbollyl)cobalt derivatives turned out to be promising components of ion-selective electrodes and phase transfer catalysts.[1]

The introduction of a halogen into the $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ framework enhances its resistance to strong acids, oxidants, and intense radioactive radiation,[3,8,9] which extends possibilities of practical use of these compounds. Hence, the halogen derivatives of bis(dicarbollyl)cobalt can thus be challenging extracting agents for decontamination of radioactive waste.[7,10—14]

The syntheses of halogen derivatives of bis(1,2-dicarbollyl)cobalt by treatment with halogens,[9,15,16] iodine chloride,[17,18] hypochlorous acid,[9] and chloro- or bromosuccineimide are described in the literature.[9] It was shown that substitution occurs stepwise in these cases: first, hydrogen atoms were displaced from positions 8 and 8′ adjacent to the metal atom followed by substitutions of further halogens at positions 9, 9′, 12, and 12′ most remote from the carbon atoms.[15]

A drawback of all listed methods is a necessity to use expensive halogenating agents and the formation by-products (in particular, highly corrosive gaseous hydrogen halide).

In this work, we attempted to prepare $Me_4N[8,8'\text{-}X_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (X = Cl, Br, I) by the coupled electrolysis of $Me_4N[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$ (**1**) and alkaline metal halide in methanol.

Results and Discussion

Compound **1** was halogenated with a halogen species produced by the anodic oxidation of a halide ion. The reaction of **1** with halogen affords a halogen derivative of bis(1,2-dicarbollyl)cobalt and halide ion. The electrochemical halogenation of **1** is presented in Scheme 1.

The halide ions formed by the chemical reaction undergo anodic oxidation, which makes possible regeneration of the halogenating agent to form a target product in a preparative yield.

It is known[19] that the separation of mixtures of the mono- and dihalogen-substituted products and their isolation in the individual state are labor-consuming processes. The dihalogen derivatives are chemically, thermally, and radiationally more stable than the unsubstituted and monohalogenated bisdicarbollyl complexes of transition metals. Therefore, the purpose of our work was to find conditions for the preparation of precisely dihalogen derivatives of bis(dicarbollyl)cobalt(III). We found that an

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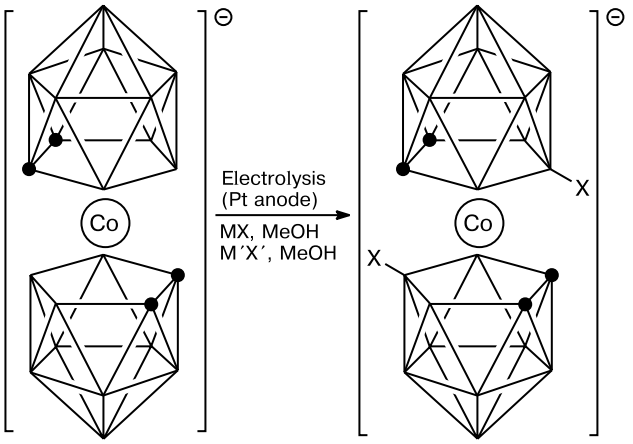
Scheme 1



MX = LiCl (42.7%); M´ = Na^+,
X´ = Br^- (72.1%), I^- (15.4%).

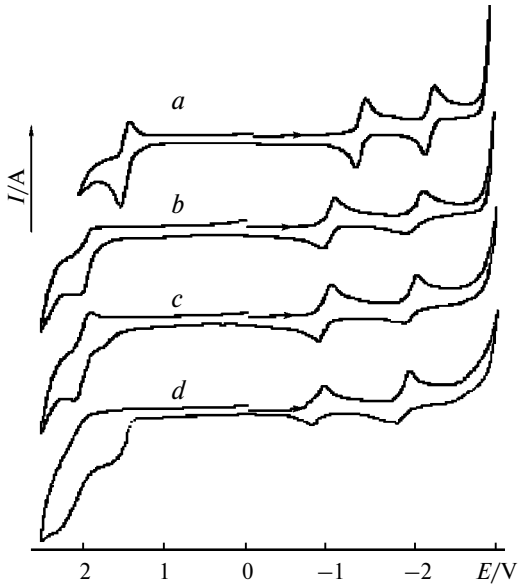


Fig. 1. Cyclic voltammograms of bis(dicarbollyl)cobalt(III) derivatives **1** (*a*), **2** (*b*), **3** (*c*), and **4** (*d*) in 0.1 *M* solutions of Bu_4NClO_4 at at glassy-carbon microelectrode in MeCN with a sweep rate of 200 mV s^{-1}. *C*/mol L^{-1} = $5.82 \cdot 10^{-3}$ (**1**), $4.15 \cdot 10^{-3}$ (**2**), $9.04 \cdot 10^{-3}$ (**3**), and $7.33 \cdot 10^{-3}$ (**4**).

increase in the electrolysis duration afforded disubstituted complexes. We used cyclic voltammetry (CV), IR and B^{11} NMR spectroscopy, and elemental analysis for analytical monitoring of the composition of the final products.

The study of the electrolysis products by CV showed that the halogenation is stepwise. In the first step, the monohalogen derivative Me_4N[8-X-3,3´-Co(1,2-$C_2B_9H_{10}$)(1,2-$C_2B_9H_{11}$)] is formed. In the second step, this complex undergoes halogenation to form Me_4N[8,8´-X_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$] (X = Cl (**2**), Br (**3**), I (**4**)).

The introduction of halogen into the carborane moiety results in a shift of the redox potentials to more positive values. The shift value depends on the halogen nature. All halogenated compounds are characterized by two reversible one-electron redox peaks in the cathodic region. These peaks correspond to the reduction of $Co^{3+/2+}$ and $Co^{2+/1+}$ (Table 1, Fig. 1).

The anodic region for complex **1** (see Fig. 1, *a*) contains a peak corresponding to the reversible oxidation $Co^{3+/4+}$ (see Table 1). The redox processes in the anodic region for compounds **2—4** can be considered irreversible (see Fig. 1, *b—d*).

The position of halogen in synthesized compounds **2—4** was established by ^{11}B NMR spectroscopy (Table 2). The upfield shift of singlet signals corresponding to the

Table 1. Redox potentials of dihalogen-substituted derivatives of bis(dicarbollyl)cobalt(III)

Compound	$E_{1/2}$/V		
[3,3´-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$	+1.61	−1.38	−2.25
[8,8´-Cl_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$	*	−0.99	−2.01
[8,8´-Br_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$	+1.94	−0.94	−1.97
[8,8´-I_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$	*	−0.85	−1.87

* Irreversible redox process.

substituted boron atom (13.70 ppm for **2**, 8.03 ppm for **3**, and −4.52 ppm for **4**) indicates an increase in the electron density on the B(8) and B(8´) atoms in the series of chloro-, bromo-, and iodosubstituted compounds **2—4**. The spectra of the synthesized compounds are close to those presented in the work.[15]

The presence of boron—halogen bonds in compounds **2—4** (Table 3) is confirmed by the appearance of intense

Table 2. ^{11}B NMR spectra of 8,8´-dihalogen derivatives of bis(dicarbollyl)cobalt(III)

Compound	δ
2	13.70 (s, 2 B, B(8), B(8´)); 1.18 (d, 2 B, B(10), B(10´)); −4.22 (d, 8 B, B(5), B(5´), B(9), B(9´), B(11), B(11´), B(12), B(12´)); −17.74 (d, 4 B, B(4), B(4´), B(7), B(7´)); −24.04 (d, 2 B, B(6), B(6´))
3	8.03 (s, 2 B, B(8), B(8´)); 2.20 (d, 2 B, B(10), B(10´)); −3.71 (d, 4 B, B(5), B(5´), B(9), B(9´), B(11), B(11´), B(12), B(12´)); −17.17 (d, 4 B, B(4), B(4´), B(7), B(7´)); −23.13 (d, 2 B, B(6), B(6´))
4	3.59 (d, 2 B, B(10), B(10´)); −2.60 (d, 4 B, B(5), B(5´), B(9), B(9´), B(11), B(11´), B(12), B(12´)); −4.52 (s, 2 B, B(8), B(8´)); −16.25 (d, 4 B, B(4), B(4´), B(7), B(7´)); −21.76 (d, 2 B, B(6), B(6´))

Table 3. Data of elemental analysis and IR spectra for 8,8′-dihalogen derivatives of bis(dicarbollyl)cobalt(III)

Compound	Found / Calculated (%)				Molecular formula	IR, ν/cm^{-1}
	C	H	Hal	N		
2	19.1 20.6	7.8 6.9	14.8 15.2	3.0 3.0	$C_8H_{32}B_{18}CoCl_2N$	3474 m, 3060 w, 3043 w, 2606 s, 2552 vs, 1627 w, 1578 w, 1481 vs, 1417 w, 1338 w, 1232 w, 1186 w, 1123 w, 1110 s, 1090 m, 1010 w, 988 s, 950 s, 914 w, 903 w, 883 w, 855 m, 840 s, 792 w, 754 w, 735 m, 700 w, 688 w, 658 w
3	17.0 17.3	6.5 5.8	28.3 28.8	2.5 2.5	$C_8H_{32}B_{18}CoBr_2N$	3440 m, 3054 w, 3038 w, 2604 s, 2565 vs, 2552 vs, 1627 w, 1481 vs, 1416 w, 1186 m, 1110 s, 1090 m, 1009 m, 984 s, 950 s, 901 w, 880 w, 832 m, 813 s, 787 m, 756 w, 734 m, 693 m, 656 m
4	14.8 14.8	5.3 4.9	39.3 39.1	2.2 2.2	$C_8H_{32}B_{18}CoI_2N$	3442 m, 3026 s, 2558 vs, 1638 w, 1478 vs, 1444 w, 1414 w, 1284 w, 1221 w, 1183 m, 1123 w, 1108 s, 1085 w, 1006 m, 982 s, 943 s, 923 w, 900 w, 879 w, 837 w, 815 w, 800 m, 774 s, 751 w, 730 w, 713 w, 690 w, 650 w, 607 w

absorption bands in the IR spectra: the B—Cl bands for **2** at 840 cm^{-1}, the B—Br bands for compound **3** at 813 cm^{-1}, and the B—I band in compound **4** at 774 cm^{-1}. The B—H vibrations appear as high-intensity bands at 2530 cm^{-1}. The numerical values of absorption frequencies for the tetramethylammonium salts of dichloro, dibromo, and diiodo derivatives of bis(dicarbollyl)cobalt(III) are almost identical to the data for these compounds (isolated as cesium salts) presented in Ref. 15.

Experimental

^{11}B NMR spectra of solutions of synthesized compounds dissolved in acetone-d_6 were recorded on a Bruker AMX-400 spectrometer at a working frequency of 128.38 MHz. The standard was $Et_2O \cdot BF_3$. IR spectra were obtained on a Protege-460 instrument in KBr pellets.

Halogenation was carried out in an electrochemical temperature-controlled one-compartment cell with a platinum anode, nickel cathode, and magnetic stirrer. The surface area of each electrode was 6 cm^2, and the distance between electrodes was 1 cm. The quantity of electricity that passed through the solution was measured using a copper coulometer. Tetramethylammonium salt of bis(dicarbollyl)cobalt(III) was prepared according to a known procedure.[20] A PI-50-1 potentiostat with a PR-8 programmer was used to record CV curves. Measurements were carried out in a three-electrode electrochemical cell with a glassy-carbon microelectrode in argon-deaerated 0.1 *M* solutions of Bu_4NClO_4 in MeCN at 25 °C. A saturated calomel electrode was used as a reference, and a platinum wire (1×2 cm) served as an auxiliary electrode. The sweep rate was 200 mV s^{-1}.

Electrochemical synthesis of tetramethylammonium 8,8′-dichloro-3,3′-cobalt[bis(1,2-dicarbollide)] (2). A solution of salt **1** (0.40 g, 1.0 mmol) and lithium chloride (0.30 g, 7.0 mmol) in anhydrous methanol (30 mL) was electrolyzed using a direct current with a density of 0.05 A cm^{-2} for 4 h at 50 °C. The quantity of electricity that passed through the solution was ~45 mF. After the end of electrolysis, the reaction mixture was evaporated almost to dryness and washed with water. The washed precipitate was recrystallized from a water—acetone mixture. The precipitate was separated, washed with a small amount of water and then with ether, and dried over $CaCl_2$ in a vacuum desiccator. The yield was 0.20 g (materials yield was 42.7% with respect to compound **1**).

Electrochemical synthesis of tetramethylammonium 8,8′-dibromo-3,3′-cobalt[bis(1,2-dicarbollide)] (3). A solution of salt **1** (0.40 g, 1.0 mmol) and sodium bromide (0.60 g, 5.8 mmol) in anhydrous methanol (30 mL) was electrolyzed using a direct current with a density of 0.05 A cm^{-2} for 5.5 h at 50 °C. The quantity of electricity that passed through the solution was ~61 mF. After the end of electrolysis, the reaction mixture was evaporated almost to dryness and washed with water. The washed precipitate was recrystallized from a water—acetone mixture. The precipitate was separated, washed with a small amount of water and then with ether, and dried over $CaCl_2$ in a vacuum desiccator. Product **3** was obtained in 72.1% (with respect to substance **1**) materials yield (0.40 g).

Electrochemical synthesis of tetramethylammonium 8,8′-diiodo-3,3′-cobalt[bis(1,2-dicarbollide)] (4). A solution of salt **1** (0.40 g, 1.0 mmol) and sodium iodide (0.45 g, 3.0 mmol) in anhydrous methanol (30 mL) was electrolyzed using a direct current with a density of 0.1 A cm^{-2} for 4 h at 50 °C. The quantity of electricity that passed through the solution was ~90 mF. After the end of electrolysis, the reaction mixture was treated as described for compounds **2** and **3**. A mixture of **4a** containing both mono- and diiodosubstituted products was obtained (0.18 g).

A solution of **4a** (0.18 g) and sodium iodide (0.45 g, 3.0 mmol) in anhydrous methanol (30 mL) was again electrolyzed using a direct current with a density of 0.1 A cm^{-2} for 3 h at 50 °C. The amount of passed electricity was ~67.5 mF. After the end of electrolysis, the reaction mixture was treated as described for compounds **2** and **3**. A mixture of **4b** containing mono- and diiodosubstituted products was obtained. This mixture (0.28 g) was electrolyzed for 1 h with a current density of 0.05 A cm^{-2}. The quantity of electricity that passed through the solution was ~8 mF. After the end of electrolysis, the reaction mixture was treated as described for compounds **2** and **3**. Diiodosubstituted product **4** was obtained (0.20 g). The yield based on compound **1** was 15.4%.

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