

Reactions of the *closo*-Dodecaborate Anion $B_{12}H_{12}^{2-}$ with Hydrogen Halides in Dichloroethane

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Abstract—The reaction of the *closo*-dodecaborate anion with hydrogen halides in dichloroethane is studied. Regardless of the hydrogen halide used (HCl, HBr, HI), the chlorination process with the formation of mono- and disubstituted products is the main in all cases. The substitution has a weakly pronounced stepwise character. The synthesized compounds are identified by IR spectroscopy, ^{11}B NMR, and ESI mass spectrometry. The structure of a single crystal of the complex $Ni(Bipy)_3(B_{12}H_{10.668}Cl_{1.332}) \cdot 3CH_3CN \cdot 0.464H_2O$ is determined by X-ray diffraction analysis.

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The *closo*-dodecaborate anion is aromatic and, hence, easily enters into the reactions of exopolyhedral substitution, in particular, chlorination. The monosubstituted anion $B_{12}H_{11}Cl^{2-}$ can be obtained by the reaction of tetrabutylammonium dodecaborate with dichloromethane in the presence of trifluoroacetic acid, the reaction of *closo*-dodecaborate acid with anhydrous hydrogen chloride at 85°C or by the treatment of an aqueous solution of sodium dodecaborate with hydrogen tetrachloroaurate(III) $H[AuCl_4]$ [1, 2]. The chlorination of the $B_{12}H_{12}^{2-}$ anion with chlorine in water gives a mixture of 1-, 1,2-, 1,7-, 1,2,3-, and 1,7,9-chlorosubstituted derivatives [3, 4], which can be separated chromatographically on DEAE cellulose [5]. The reaction of *closo*-dodecaboric acid with chlorine at 0°C affords $B_{12}H_6Cl_6^{2-}$ [2]. The perchlorinated $B_{12}Cl_{12}^{2-}$ anion can be obtained by the treatment of $B_{12}H_{12}^{2-}$ with chlorine at 85°C in an aqueous acid solution [6, 7] or in water at 150°C [2, 8].

Presently, the most urgent is the search for new methods of regioselective introduction of exopolyhedral substituents into the *closo*-borane cage. This is related to the necessity of targeted syntheses of derivatives of specified structure for boron neutron capture therapy for malignant tumors [9]. Previously [10], we reported the regioselective reaction of the *closo*-dodecaborate anion with carboxylic acids yielding carboxylate-substituted products with the equatorial substituents. The present work continues these studies and is devoted to the reaction of the *closo*-dodecaborate anion with hydrogen halides.

EXPERIMENTAL

The dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ was prepared using a known procedure [11], and tetrabutylammonium *closo*-dodecaborate was synthesized by the exchange reaction of alkali-metal dodecaborates with Bu_4NBr .

Hydrogen halides used in the reactions were prepared as described in [12]: hydrogen chloride was prepared by the reaction of sodium chloride with sulfuric acid, hydrogen bromide was obtained by the interaction of an aqueous solution of the corresponding acid with phosphorus pentoxide or by the reaction of bromine with tetralin; and hydrogen iodide was prepared by the interaction of an aqueous solution of the corresponding acid with phosphorus pentoxide or by the reaction of boiling tetralin with a solution of iodine in tetralin.

Before feeding to the reaction flask, the prepared gas was passed through two absorbing tubes filled with phosphorus pentoxide for complete drying.

Halogenation of the *closo*-dodecaborate anion. A solution of tetrabutylammonium dodecaborate (1 g) in $C_2H_4Cl_2$ (30 mL) was heated to 60°C, and thoroughly dried hydrogen halide was continuously bubbled for 5–6 h through the solution. Then, the yellow reaction mixture was concentrated on a rotary evaporator at 45°C (100 mbar) until the formation of a precipitate, which was dried in an oil-pump vacuum (10^{-2} mmHg). The reaction conditions, starting substances, and reaction products are presented in Table 1.

Compounds with the $[Ni(Bipy)_3]^{2+}$ complex cation were synthesized from all the mixtures (Table 1) of halogen-substituted products formed by the reactions. The syntheses were carried out as follows. The result-

ing mixture of the products (0.8 g) was dissolved in CH_3CN (25 mL). A solution of nickel(II) nitrate (5 g in 20 mL of H_2O) was added under stirring to the resulting solution, and its color changed from pale yellow to blue. Then, 2,2'-dipyridyl (0.5 g) dissolved in acetonitrile (50 mL) was poured to the mixture. After 30 min, a pink finely crystalline precipitate was formed, filtered off, and recrystallized from acetonitrile, yielding pink crystals. Visually the best crystals were grown from a mixture of halogen-substituted products prepared by prolong passing of HI. Of them, a crystal for X-ray diffraction analysis was selected.

Elemental analyses for carbon, hydrogen, and nitrogen were conducted on a CHNS-3 FA 1108 elemental analyzer (Carlo Erba). Boron was determined by atomic absorption spectroscopy using electrothermal atomization on HGA-700 (model 2100) and HGA-72 (model 403) spectrophotometers (Perkin-Elmer) [13]. Elemental analysis data are given in Table 2.

IR spectra of the compounds were recorded as Nujol mulls on an Infracum FT-02 FT-IR spectrophotometer (Lyumeks NPF AP) in the range $4000-400\text{ cm}^{-1}$. Assignment of the most informative absorption bands observed in the IR spectra of chlorosubstituted *closo*-dodecaborates is presented in Table 3.

The ^{11}B NMR spectra of solutions of the substances under study in acetonitrile were recorded on a Bruker AC-200 spectrometer at a frequency of 64.297 MHz with internal deuterium lock. Boron trifluoride etherate was used as the external reference. The ^{11}B NMR data of chlorosubstituted *closo*-dodecaborates are given in Table 4.

The electrospray ionization mass spectra (ESI/MS, microspray, 4500 V) of solutions of the compounds under consideration were measured on a Bruker Esquire 3000 plus mass spectrometer in a water-acetonitrile (50%) mixture with an additive of formic acid (0.2%). The average analytical concentration of samples for ESI/MS was $1.00 \pm 0.20\text{ mg/mL}$ of the solution. The molecular weights of the singly charged anions (CatAn) $^-$ obtained from the spectra by the analysis of the reaction mixtures are presented in Table 1.

X-ray diffraction. A set of reflections was obtained on a CAD4 automated diffractometer (λMoK_{α} radiation, graphite monochromator, ω scan mode, $1.61^\circ < \theta < 27.96^\circ$) from a crystal $0.36 \times 0.33 \times 0.33\text{ mm}$ in size covered with a layer of Fluorolube fluorinated oil. Absorption correction was applied using the azimuthal scan method. The crystals are trigonal: $a = 14.2168(6)\text{ \AA}$, $c = 37.954(3)\text{ \AA}$, $Z = 6$, $V = 6643.5(7)\text{ \AA}^3$, $\rho_{\text{calcd}} = 1.268\text{ g/cm}^3$, $\mu(Mo) = 0.559\text{ mm}^{-1}$, space group $R\bar{3}$.

The structure was solved by direct methods. All hydrogen atoms were located in difference Fourier syntheses. The site occupancies of the Cl(1), Cl(2), and O(1w) atoms were 0.366(3), 0.078(3), and 0.155(5), respectively. All non-hydrogen atoms, except Cl(2) and O(1w), were refined by the least-squares method in the

Table 1. Reaction conditions, yields of products, and data of mass spectrometry

| Hydrogen halide | Compounds present in reaction mixture | Content, % | Molecular weight of (CatAn) $^-$ |
|--------------------------------------|---------------------------------------|------------|----------------------------------|
| Temperature 60°C, synthesis time 1 h | | | |
| HCl, HBr, HI | $(Bu_4N)_2B_{12}H_{12}$ | 47 | 384.46 |
| | $(Bu_4N)_2B_{12}H_{11}Cl$ | 49 | 419.30 |
| Temperature 80°C, synthesis time 1 h | | | |
| HCl, HBr, HI | $(Bu_4N)_2B_{12}H_{12}$ | 28 | 384.50 |
| | $(Bu_4N)_2B_{12}H_{11}Cl$ | 45 | 419.32 |
| | $(Bu_4N)_2B_{12}H_{10}Cl_2$ | 24 | 452.30 |
| Temperature 80°C, synthesis time 5 h | | | |
| HCl | $(Bu_4N)_2B_{12}H_{11}Cl$ | 85 | 419.36 |
| | $(Bu_4N)_2B_{12}H_{10}Cl_2$ | 11 | 452.47 |
| HBr | $(Bu_4N)_2B_{12}H_{11}Cl$ | 24 | 419.35 |
| | $(Bu_4N)_2B_{12}H_{10}Cl_2$ | 58 | 452.91 |
| | $(Bu_4N)_2B_{12}H_{10}ClBr$ | 12 | 497.64 |
| HI | $(Bu_4N)_2B_{12}H_{11}Cl$ | 16 | 419.42 |
| | $(Bu_4N)_2B_{12}H_{10}Cl_2$ | 62 | 453.34 |
| | $(Bu_4N)_2B_{12}H_{10}ClI$ | 17 | 544.21 |

Table 2. Maxima of some absorption bands observed in the IR spectra of chlorosubstituted *closo*-dodecaborates, cm^{-1}

| Compound | $\nu(H-B)$ | $\nu(B-Cl)$ | $\nu(C\equiv N)$ |
|--|------------|-------------|------------------|
| $(Bu_4N)_2(B_{12}H_{11}Cl)$ | 2479 | 960 | – |
| $(Bu_4N)_2(B_{12}H_{10}Cl_2)$ | 2475 | 962 | – |
| $Ni(Bipy)_3(B_{12}H_{10.668}Cl_{1.332}) \cdot 3CH_3CN \cdot 0.464H_2O$ | 2474 | 962 | 2252 |

anisotropic approximation. The Cl(2), O(1w), and H(C) atoms of the bipyridyl molecule were refined independently in the isotropic approximation, and the other H atoms were refined imposing different constraints. The H atoms of an acetonitrile molecule were refined in idealized positions using the riding model with the thermal displacement parameters $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the C(12) atom. The H(3B) and H(4B) atoms of the polyhedral anion were also refined in the riding model in the idealized positions but their parameters U_{iso} were refined independently. The positions of the H(1B) and H(2B) atoms, whose site occupancies were 0.635 and 0.922, respectively, were fixed. The final refinement estimates were $R1 = 0.0418$, $wR2 = 0.0960$ for 1819 reflections with $I > 2\sigma(I)$; $R1 = 0.1316$, $wR2 = 0.1211$ for a full set of 4050 reflections; $S = 0.976$. The maximum and minimum residual electron densities were 0.320 and -0.235 e/\AA^3 , respectively.

Table 3. ^{11}B NMR spectra of chlorosubstituted *closo*-dodecaborates (simple salts were dissolved in CH_3CN , the complex was dissolved in DMF)

| Compound | ^{11}B { ^1H } NMR | | | |
|--|--------------------------------------|----------------------|---|------------------------|
| | chemical shift δ , ppm | integrated intensity | ^{11}B NMR signal multiplicity | signal assignment |
| $(\text{Bu}_4\text{N})_2\text{B}_{12}\text{H}_{11}\text{Cl}$ | -3.5 | 1 | s | B(1) |
| | -14.9 | 4 | d | B(2–5) |
| | -16.6 | 4 | d | B(6–11) |
| | -20.2 | 1 | d | B(12) |
| $(\text{Bu}_4\text{N})_2\text{B}_{12}\text{H}_{10}\text{Cl}_2$ | -5.1 | 1 | s | B_{Cl} |
| | -15.0 | 1 | d | B_{H} |
| | -16.7 | 2 | d | |
| | -18.6 | 1 | d | |
| | -20.3 | 1 | d | |
| $(\text{Bu}_4\text{N})_2\text{B}_{12}\text{H}_{10}\text{ClBr}$ | -3.5 | 1 | s | B_{Cl} |
| | -5.5 | 1 | s | B_{I} |
| | -15.2 | 10 | w | B_{H} |
| | -18.6 | | | |
| $(\text{Bu}_4\text{N})_2\text{B}_{12}\text{H}_{10}\text{ClI}$ | -3.5 | 1 | s | B_{Cl} |
| | -15.2 | 10 | w | B_{H} |
| | -18.6 | | | |
| | -20.4 | | | |
| $\text{Ni}(\text{Bipy})_3 \cdot [\text{B}_{12}\text{H}_{10.668}\text{Cl}_{1.332}] \cdot 3\text{CH}_3\text{CN} \cdot 0.464\text{H}_2\text{O}$ | -24.6 | 1 | s | B_{I} |
| | -3.1 | 1 | s | B(1) |
| | -14.8 | 4 | d | B(2–5) |
| | -14.9 | 4 | d | B(6–11) |
| | -20.2 | 1 | d | B(12) |

All calculations were performed using the SHELXS97 and SHELXL97 programs [14].

The atomic coordinates and thermal displacement parameters are presented in Table 5. The composition of the crystal determined by X-ray diffraction corresponds to the formula $\text{Ni}(\text{Bipy})_3(\text{B}_{12}\text{H}_{10.668}\text{Cl}_{1.332}) \cdot 3\text{CH}_3\text{CN} \cdot 0.464\text{H}_2\text{O}$ (**I**). The structures of the anions in the crystal are shown in Figs. 1a–1c.

RESULTS AND DISCUSSION

The reactions of the *closo*-dodecaborate anion with hydrogen halides in dichloroethane in the temperature range 40–80°C afford mono- and dichloro-substituted *closo*-dodecaborates. Chloro-substituted products are formed regardless of hydrogen halide used (HCl, HBr, HI). The process has a weakly pronounced stepwise character. The ^{11}B NMR spectra of solutions of the synthesized compounds and the ESI mass spectra were analyzed in all steps of the synthesis. The analysis showed the presence of the mono- and disubstituted products (the yields of the reaction products are given in Table 1).

The following trends were found. At a relatively low temperature of the synthesis (60°C), the reaction gave within 1 h the monosubstituted product but the unsubstituted initial $\text{B}_{12}\text{H}_{12}^{2-}$ anion remains in the reaction mixture.

At a higher temperature (80°C) and a short reaction time, the monosubstituted product is mainly formed along with some amount of the disubstituted product. The initial unreacted anion $\text{B}_{12}\text{H}_{12}^{2-}$ also remains in the reaction mixture. When the reaction time is increased, the conversion of the initial anion increases, and upon the reaction during 5 h, the spectrum of the reaction mixture contains no signal of the initial $\text{B}_{12}\text{H}_{12}^{2-}$ anion.

It should be mentioned that the reaction does not occur when the reactants interact at room temperature

Table 4. Elemental analysis data for chlorosubstituted *closo*-dodecaborates

| Compound | B, % | C, % | N, % | H, % |
|--|------------------|------------------|------------------|------------------|
| | found/calculated | found/calculated | found/calculated | found/calculated |
| $(\text{Bu}_4\text{N})_2(\text{B}_{12}\text{H}_{11}\text{Cl})$ | 19.61/19.62 | 58.10/58.13 | 4.20/4.24 | 12.62/12.65 |
| $(\text{Bu}_4\text{N})_2(\text{B}_{12}\text{H}_{10}\text{Cl}_2)$ | 18.62/18.65 | 55.23/55.25 | 4.01/4.03 | 11.83/11.88 |
| $(\text{Bu}_4\text{N})_2(\text{B}_{12}\text{H}_{10}\text{ClBr})$ | 17.49/17.53 | 51.87/51.93 | 3.75/3.79 | 11.14/11.17 |
| $(\text{Bu}_4\text{N})_2(\text{B}_{12}\text{H}_{10}\text{ClI})$ | 16.42/16.48 | 48.79/48.83 | 3.51/3.56 | 10.48/10.51 |
| $\text{Ni}(\text{Bipy})_3 \cdot [\text{B}_{12}\text{H}_{10.668}\text{Cl}_{1.332}] \cdot 3\text{CH}_3\text{CN} \cdot 0.464\text{H}_2\text{O}$ | 15.84/15.89 | 55.86/55.89 | 11.98/12.01 | 4.60/4.69 |

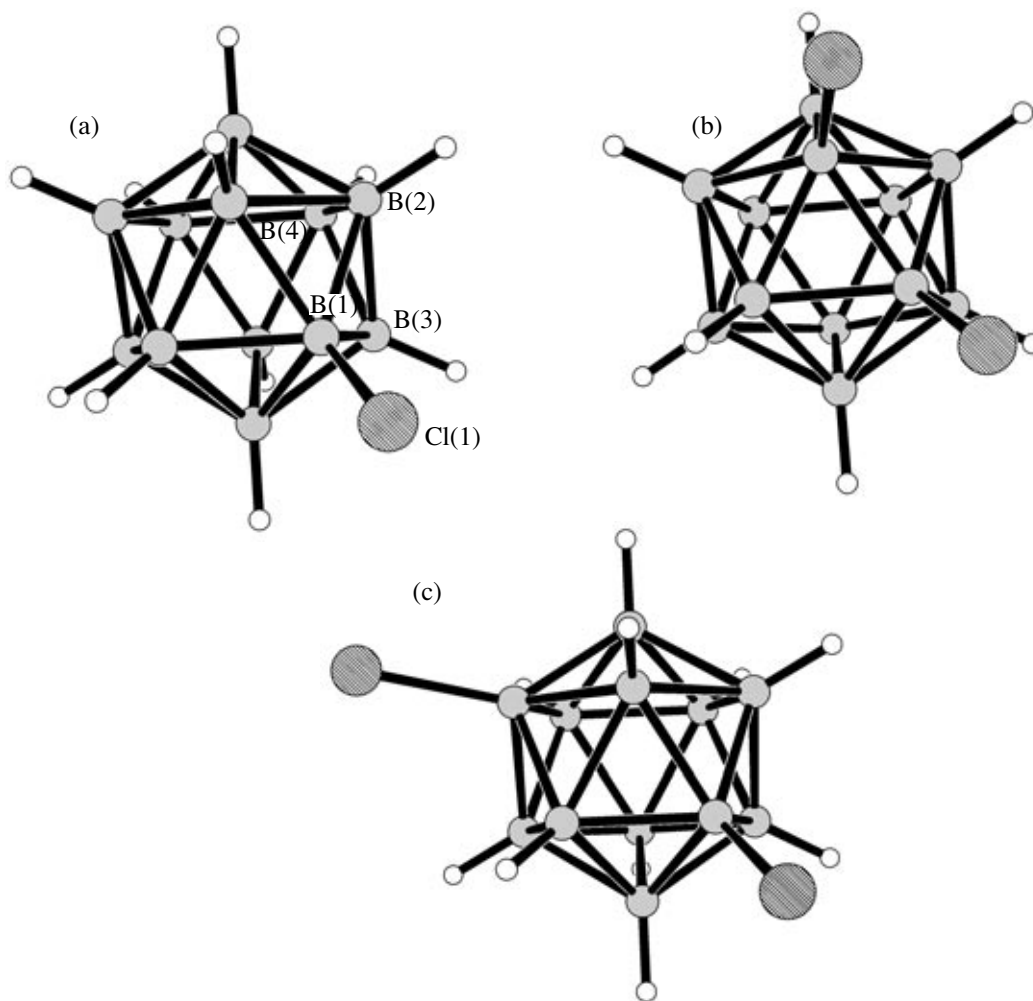


Fig. 1. Structures of the anions in the single crystal of $Ni(Bipy)_3(B_{12}H_{10,668}Cl_{1,332}) \cdot 3CH_3CN \cdot 0.464H_2O$: (a) monochlorosubstituted, (b) *ortho*-dichlorosubstituted, and (c) *meta*-dichlorosubstituted anions.

for 5 h. However, when the reaction time was increased to 40 h, a mixture of the initial $B_{12}H_{12}^{2-}$ anion and monochloro-substituted $B_{12}H_{11}Cl^{2-}$ anion was obtained.

Side processes accompanying the course of these reactions afford products with a mixed halide composition, $(Bu_4N)_2B_{12}H_{10}ClBr$ and $(Bu_4N)_2B_{12}H_{10}ClI$. However, their formation was observed only after prolong reflux of the reaction mixtures in a hydrogen bromide or hydrogen iodide flow, and the yield of these products does not exceed 17%.

The compositions and structures of the synthesized compounds were determined by different physicochemical methods. The molecular weight of the prepared singly charged anions was estimated from the ESI mass spectra for all syntheses (Table 1). Note that similar spectra of the *closo*-borate anions show, as a rule, signals from the singly charged species $CatAn^-$. In

all cases, the data obtained indicate the formation of the $[B_{12}H_{11}Cl]^-$ and $[B_{12}H_{10}Cl_2]^-$ anions.

The ^{11}B NMR spectrum of $(Bu_4N)_2B_{12}H_{11}Cl$ contains four signals: -3.5 (B(1)), -14.9 (B(2)–B(5)), -16.6 (B(6)–B(11)), and -20.2 (B(12)) ppm with the ratio of integrated intensities 1 : 4 : 4 : 1, which is characteristic of the spectra of “classical” monosubstituted anions. In the absence of broadband decoupling, the B–H signal at -3.5 ppm is not split because it corresponds to the boron atom bonded to the substituent, whereas other signals are split into symmetric doublets.

The ^{11}B NMR spectrum of $(Bu_4N)_2B_{12}H_{10}Cl_2$ exhibit five signals at -5.1 , -15.0 , -16.7 , -18.6 , and -20.3 ppm with the intensity ratio 1 : 1 : 2 : 1 : 1, which is characteristic of the disubstituted anions with substituents in the 1,2- or 1,7-positions. The first signal corresponds to the boron atoms bonded to chlorine atoms and, therefore, only this signal is not split in the absence of broad-

Table 5. Atomic coordinates and thermal parameters U_{eq} in the structure of compound **I**

| Atom | x | y | z | $U_{eq}/U_{iso}, \text{\AA}^2$ |
|--------|------------|-----------|-------------|--------------------------------|
| Ni(1) | 0 | 0 | 0.09883(1) | 0.0392(2) |
| Cl(1)* | 0.0681(2) | 0.1561(2) | 0.44271(5) | 0.0592(8) |
| Cl(2)* | -0.2138(9) | 0.0576(9) | 0.3830(3) | 0.072(4) |
| N(1) | -0.0266(2) | 0.1099(2) | 0.07010(5) | 0.0414(5) |
| N(2) | 0.0957(2) | 0.1436(2) | 0.12633(5) | 0.0458(5) |
| C(1) | 0.0310(2) | 0.2140(2) | 0.08095(6) | 0.0410(5) |
| C(2) | 0.0219(2) | 0.2956(2) | 0.06428(8) | 0.0508(7) |
| C(3) | -0.0484(2) | 0.2701(2) | 0.03650(8) | 0.0551(7) |
| C(4) | -0.1091(2) | 0.1641(2) | 0.02590(7) | 0.0538(7) |
| C(5) | -0.0952(2) | 0.0871(2) | 0.04317(7) | 0.0491(6) |
| C(6) | 0.1029(2) | 0.2333(2) | 0.11166(6) | 0.0455(6) |
| C(7) | 0.1733(3) | 0.3353(2) | 0.12463(8) | 0.0630(8) |
| C(8) | 0.2346(3) | 0.3456(3) | 0.15349(10) | 0.080(1) |
| C(9) | 0.2268(3) | 0.2561(3) | 0.16888(9) | 0.077(1) |
| C(10) | 0.1573(3) | 0.1561(3) | 0.15427(7) | 0.0608(8) |
| B(1) | 0.0281(3) | 0.0818(3) | 0.40092(7) | 0.0542(8) |
| B(2) | -0.0875(2) | 0.0455(3) | 0.37404(8) | 0.0499(7) |
| B(3) | 0.0450(2) | 0.1327(2) | 0.35755(8) | 0.0471(7) |
| B(4) | -0.0539(2) | 0.0279(2) | 0.33074(8) | 0.0436(6) |
| N(3) | 0.4061(5) | 0.2410(4) | 0.1093(1) | 0.158(2) |
| C(11) | 0.4410(4) | 0.3158(4) | 0.0928(1) | 0.097(1) |
| C(12) | 0.4814(5) | 0.4071(4) | 0.0714(1) | 0.149(2) |
| O(1w)* | 0.067(2) | 0.049(4) | 0.5002(8) | 0.109(8) |
| H(2) | 0.064(2) | 0.371(2) | 0.0733(7) | 0.059(8) |
| H(3) | -0.055(2) | 0.327(2) | 0.0244(7) | 0.058(8) |
| H(4) | -0.160(2) | 0.143(2) | 0.0061(7) | 0.064(8) |
| H(5) | -0.131(2) | 0.014(2) | 0.0365(7) | 0.068(9) |
| H(7) | 0.174(2) | 0.398(3) | 0.1147(8) | 0.074(9) |
| H(8) | 0.285(3) | 0.411(3) | 0.1622(9) | 0.10(1) |
| H(9) | 0.263(3) | 0.258(3) | 0.1893(9) | 0.09(1) |
| H(10) | 0.150(2) | 0.094(2) | 0.1642(7) | 0.054(8) |
| H(1B)* | 0.046 | 0.138 | 0.424 | 0.050 |
| H(2B)* | -0.145 | 0.075 | 0.380 | 0.050 |
| H(3B) | 0.074 | 0.219 | 0.352 | 0.048(7) |
| H(4B) | -0.089 | 0.046 | 0.308 | 0.062(8) |
| H(12A) | 0.556 | 0.432 | 0.066 | 0.178 |
| H(12B) | 0.475 | 0.463 | 0.083 | 0.178 |
| H(12C) | 0.441 | 0.389 | 0.050 | 0.178 |

* Site occupancies of the atoms are the following: Cl(1) 0.366(3), Cl(2) 0.078(3), O(1w) 0.155(5), H(1B) 0.634(3), and H(2B) 0.922(3).

band decoupling. The other signals in this spectrum are split into symmetric doublets.

The ^{11}B NMR spectra of two disubstituted products of mixed halogenation, $(\text{Bu}_4\text{N})_2\text{B}_{12}\text{H}_{10}\text{ClBr}$ and $(\text{Bu}_4\text{N})_2\text{B}_{12}\text{H}_{10}\text{ClI}$, contain the signal at -3.5 ppm corresponding to the boron atom bonded to the chlorine atom. The spectrum of the compound in which the bromine atom is the substituent also has a signal at -5.5 ppm from the boron atom bonded to this bromine atom. When the boron atom is bonded to the iodine atom, the spectrum exhibits a signal at -24.5 ppm. These boron atoms in the absence of broadband decoupling give rise to singlets, which confirms the presence of the substituents at these atoms. The spectra of both products with the mixed halide substituents have broadened signals at -15 , -16 , and -18 ppm (corresponding to the remaining 10 boron atoms), which are split into complicated multiplets in the absence of broadband decoupling.

The IR spectrum of $(\text{Bu}_4\text{N})_2\text{B}_{12}\text{H}_{12-n}\text{Cl}_n$ ($n = 1, 2$) contains absorption bands characteristic of the $(\text{Bu}_4\text{N})^+$ organic cation and, in addition, an intense band of stretching vibrations $\nu(\text{B}-\text{H})$ with a maximum at $2475\text{--}2479$ cm^{-1} and a band of $\text{B}-\text{Cl}$ stretching vibrations at $960\text{--}962$ cm^{-1} .

Analysis of the obtained spectral data made it possible to establish the formation of mono- and dichloro-substituted dodecaborates in all the reactions. For a more precise determination of the structures of the synthesized substituted anions by the procedure described in the Experimental section, we synthesized complex salt **I**.

The structure of **I** is composed of complex cations $[\text{Ni}(\text{Bipy})_3]^{2+}$, chloro-substituted polyhedral anions $(\text{B}_{12}\text{H}_{12-n}\text{Cl}_n)^{2-}$, and crystallization molecules of acetonitrile and water. The cations and anions are on three-fold inversion axes. The chlorine atoms are partially substituted for the positions of the H atoms at the B(1) and B(2) atoms. The total site occupancy of the Cl positions equals 0.444, which corresponds to the presence of the mono- (see Fig. 1a) and disubstituted anions in a 2 : 1 ratio in the crystal.

Isomerism is possible in the disubstituted anion. The Cl atoms can be attached to the adjacent (linked by the common edge) (Fig. 1b) or to remote (not connected by an edge) B atoms (Fig. 1c). The first of these isomers is certainly present in the crystal, at least in a small amount, because the site occupancy of the position of the Cl(1) atom slightly exceeds a value of 0.333 corresponding to the monosubstituted anion. It is impossible to determine the relative arrangement of the Cl(1) and Cl(2) atoms from the X-ray diffraction data. The B(1)–Cl(1) and B(2)–Cl(2) bond lengths are 1.831(3) and 1.917(11) \AA , respectively. The increased length of the latter bond suggests that not only the chlorine atom but also the iodine atom is involved in the substitution at the B(2) atom. Their positions cannot be separated

because of too low occupancy. The peak appeared in the averaged position is attributed to the Cl(2) atom.

The *closo*-borane cage undergoes no changes. The B–B bond lengths are within the range 1.765–1.782 Å.

The IR spectrum of compound **I** exhibits an intense absorption band of stretching vibrations of the B–H bond of the substituted *closo*-dodecaborate anion at 2474 cm^{-1} , and the band of stretching vibrations $\nu(B-Cl)$ at 962 cm^{-1} is retained. The IR spectrum also contains a set of narrow discrete bands in the range 1600–700 cm^{-1} of the 2,2'-dipyridyl molecule vibrations. The frequencies of stretching–bending vibrations $\nu(C-N)$ at 1597 cm^{-1} point to the coordination of the 2,2'-dipyridyl molecules to the central nickel atom. In addition, the IR spectrum shows a narrow $\nu(C\equiv N)$ band at 2252 cm^{-1} .

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