Russian Journal of General Chemistry, Vol. 71, No. 7, 2001, pp. 1017–1018. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 7, 2001, pp. 1082–1083.
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Synthesis of 2-I-*closo*-$B_{10}H_9^{2-}$ by Iodination of *closo*-$B_{10}H_{10}^{2-}$

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Received January 10, 2000

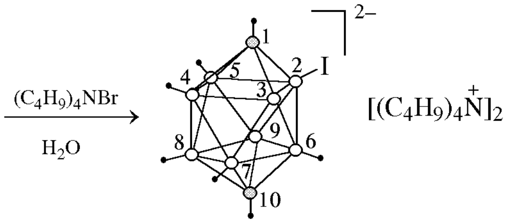
Abstract—A pure salt 2-I-$B_{10}H_9^{2-}[N^+(C_4H_9)_4]_2$ was obtained by treatment of ethanolic $Na_2^+B_{10}H_{10}^{2-}$ with ethanolic iodine at –75°C, followed by addition of tetrabutylammonium bromide.

The anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have first been halogenated by Muetterties and co-workers [1]; their kinetic studies showed that on iodination of $B_{10}H_{10}^{2-}$ the first three iodine atoms enter with the same rate even at –40°C, whereas $B_{12}H_{12}^{2-}$ at 25°C is iodinated 70 times faster than $B_{12}H_{11}I^{2-}$. These results led the referees to conclude that $B_{10}H_9I^{2-}$ is impossible to prepare by simple iodination with 1 mol of iodine, and the corresponding salt can only be isolated by repeated fractional crystallization.

To prepare $B_{10}H_9I^{2-}$, we performed iodination of the salt $(NH_4^+)_2B_{10}H_9^{2-}$ at 0–5°C in the presence of KI, $(CH_3)_4N^+Cl$, and CsF in aqueous methanol. A fairly pure salt containing the anion $B_{10}H_9I^{2-}$ was isolated by fractional crystallization; therewith, 17 fractions were obtained, and the seventh and eighth fractions were recrystallized several times more to obtain, in a low yield, two compounds whose elemental analyses corresponded to the formula $Cs^+(CH_3)_4N^+B_{10}H_9I^{2-}$. The ^{11}B NMR spectrum showed that the two compounds have iodine in different positions of the polyhedra.

Since we needed in our work much individual salt with the anion $B_{10}H_9I^{2-}$, we performed detailed studies of monoiodination of the anion $B_{10}H_{10}^{2-}$ and found reaction conditions for formation of a single isomer of $B_{10}H_9I^{2-}$. On treatment of ethanolic $Na_2^+B_{10}H_{10}^{2-} \cdot 2H_2O$ at –65 to –75°C with equimolar amount of ethanolic I_2 we observed fast iodination, and the solution got colorless within 30 min. The ethanol was removed in a vacuum, the residue was dissolved in water, and the resulting solution was treated with aqueous $(C_4H_9)_4NBr$. The colorless precipitate that formed was recrystallized from aqueous methanol to obtain individual $[(C_4H_9)_4N^+]_2B_{10}H_9I^{2-}$ (**I**).

$$Na_2^+B_{10}H_{10}^{2-} \cdot 2H_2O + I_2 \xrightarrow[-75°C]{C_2H_5OH} Na^+B_{10}H_9I^{2-} + H^+ + NaI$$



The ^{11}B NMR spectrum was assigned using the ^{11}B–^1H decoupled spectrum and the ^{11}B–^{11}B COSY spectrum (see figure). As seen from the figure, the apical B^{10} atom (–1.17 ppm) gives cross peak only with the most upfield signal that belongs to B^6, B^7, B^8, and B^9 (–29.16 ppm), whereas the other apical atom B^1 (–0.82 ppm) gives cross peaks with the signals at –25.82 and –26.93 ppm (B^4 and B^3, B^5, respectively). From these data it follows that the iodine atom is in the 2 position of the polyhedron.

In connection with our results we would like to mention the work of Dou *et al.* [2], who showed, contraty to Miller *et al.* [3], that the electrophilic attack on the anion $B_{10}H_{10}^{2-}$ is directed in the 2 position of the polyhedron to give 2-R-$B_{10}H_9^{2-}$ rather than 1-R-$B_{10}H_9^{2-}$.

EXPERIMENTAL

The NMR spectra were obtained on a Bruker AMX-400 spectrometer at 128.3 MHz, reference $BF_3 \cdot OEt_2$.

Bis(tetrabutylammonium) 2-iodo-*closo*-decahydrodecaborate (I). To 5 g of $Na_2B_{10}H_{10}$ in 35 ml of ethanol at –65 to –75°C we added over the course of 30 min 6.35 g of I_2 dissolved in 80 ml of ethanol. The solution decolorized within 30 min. It was allowed to warm to room temperature, and the ethanol was removed in a water-jet-pump vacuum. The dry residue was dissolved in a minimum of water, and the

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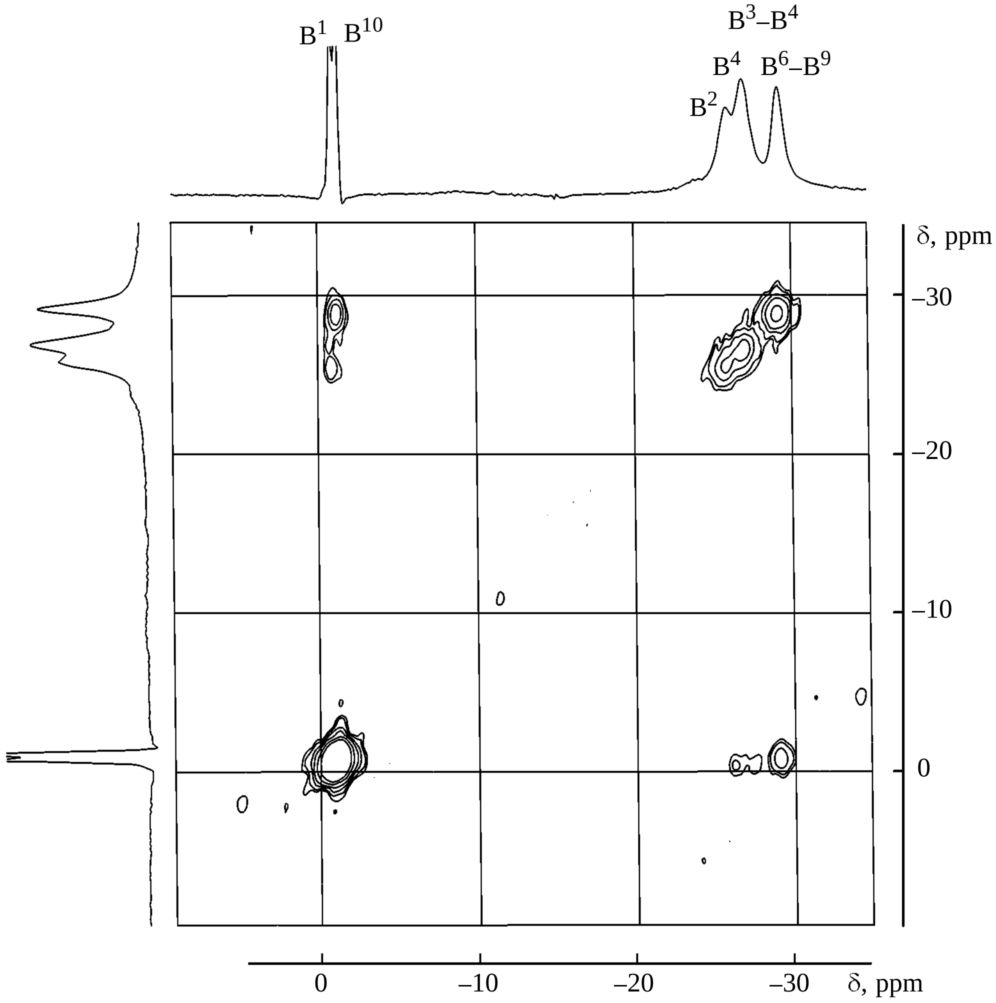

^{11}B–^{11}B COSY NMR spectrum of $[(C_4H_9)\overset{+}{N}]_2[2\text{-I-}B_{10}H_9]^{2-}$.

solution was treated with 29.5 g of $(C_4H_9)_4NBr$ in 70 ml of water. The precipitate that formed was filtered off, washed with two portions of distilled water, dried in a water-jet-pump vacuum at 50°C, and recrystallized, mp 202–203°C (methanol–water). ^{11}B NMR spectrum (CH_2Cl_2), δ_B, ppm ($J_{^{11}B-^{1}H}$, Hz): –0.82 s (1B, B^1, J 145), –1.17 s (1B, B^{10}, J 146), –23.89 br.s (1B, B^2), –25.82 br.s (1B, B^4, J 131), –26.93 br.s (2B, $B^{3,5}$, J 135), –29.16 br.s (4B, $B^{6,7,8,9}$, J 128) [cf. ^{11}B NMR spectrum of $Na_2B_{10}H_{10} \cdot 2H_2O$ (CH_3OH), δ_B, ppm (J, Hz): –2.20 s (2B, $B^{1,10}$, J 139), –30.7 s (8B, $B^{2,3,4,5,6,7,8,9}$, J 122)]. Found, %: C 52.81; H 10.98; B 14.32; I 18.12; N 3.60. $C_{32}H_{81}B_{10}IN$. Calculated, %: C 52.74; H 11.12; B 14.84; I 17.44; N 3.84.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 97-03-33020).

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