

Synthesis of cluster anion $[B_{12}H_{12}]^{2-}$ derivatives with B-OH reaction site for the subsequent modification in developing BNCT preparations

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The first stage of the development of BNCT preparations based on polyhedral $[B_{12}H_{12}]^{2-}$ boron anion consists in the introduction of primary substituent (reaction site) in the *closo*-dodecaborate system, which subsequently can be modified. In the present study, efficient methods for the synthesis of *closo*-dodecaborate anion derivatives in using hydroxyl group as the primary substituent are suggested.

An original method for the synthesis of water-soluble $1,2-[B_{12}H_{10}(OH)_2]^{2-}$ cluster boron anion derivative via the alkaline hydrolysis of product of the reaction between the bis(tetrabutylammonium) dodecahydro-*closo*-dodecaborate (2-) and benzene-1,2-dicarboxylic acid melt at temperatures of 190-195 °C in a dry argon atmosphere. In the reaction under consideration, the benzene-1,2-dicarboxylic acid is both reagent and solvent. The synthesis was performed using the tetrabutylammonium salt, which is sufficiently soluble in the benzene-1,2-dicarboxylic acid. The nucleophilic attack of benzene-1,2-dicarboxylic acid molecule to boron skeleton was found to be realized almost simultaneously on two sites with the formation of only a dihydroxy derivative. The attack of substrate with more than one benzene-1,2-dicarboxylic acid molecule is limited by the temperature of melting (accompanied by decomposition) of benzene-1,2-dicarboxylic acid oneself. It was shown that the regioselectivity under considered synthesis conditions is determined by the geometry of used reagent, namely, the benzene-1,2-dicarboxylic acid.

The single-stage method of introduction of hydroxyl group into monosubstituted $[B_{12}H_{11}X]^{2-}$ ($X = SCN, I, OC(O)CH_3$) cluster boron anion derivatives was developed. It was found that the reaction between monosubstituted $[B_{12}H_{11}X]^{2-}$ derivatives and acetic acid in the presence of oxygen and atmospheric moisture leads to the single-stage formation of $[B_{12}H_{10}X(OH)]^{2-}$ hydroxy derivatives without the formation of acetoxy derivatives. The experimental data allow us to suggest the mechanism of the process. The reaction between $[B_{12}H_{11}X]^{2-}$ anion and acetic acid in the presence of oxygen and atmospheric moisture is shown to have the regioselective character; $-SCN$, $-I$ and $-OC(O)CH_3$ substituents are *meta*-orientants with respect to introduced OH group.

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