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## Thermal Conversions of Chitosanium Dodecahydro-*closo*-Dodecaborate

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**Abstract**—The thermal behavior of chitosanium dodecahydro-*closo*-dodecaborate,  $(C_6O_4H_9NH_3)_2B_{12}H_{12}$ , was studied by thermal analysis, X-ray diffraction, and IR and X-ray photoelectron spectroscopy. As this compound is heated at a rate above 10–20 K/min, it ignites at a temperature of about 300°C. As the compound is heated to 1000°C at a rate below 10 K/min in an inert atmosphere, it yields a mixture of carbon and amorphous boron and/or boron carbides. The presence of a small amount of boron oxide in the product is explained by the formation of a partially oxidized hydroborate anion at the early stages of  $(C_6O_4H_9NH_3)_2B_{12}H_{12}$  decomposition via the interaction between oxygen of the chitosanium cation and the  $B_{12}H_{12}^{2-}$  anion. Heating the initial compound in air at a rate below 10 K/min yields carbon and boron oxide as the main products. Molten boron oxide protects boron and/or boron carbides and boron nitride forming in small amounts in the particle bulk from oxidation.

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A fairly comprehensive review of thermal studies of salts of dodecahedral hydroborate anions was presented by Ivanov et al. [1]. Depending on the composition of the starting compound, on the pyrolysis atmosphere, and on the final temperature, hydroborate decomposition can yield various compounds, including polymers, amorphous and crystalline boron, boron carbides, hexagonal boron nitride, and metal borides [2–4]. The decomposition of alkylammonium salts with  $B_{12}H_{12}^{2-}$ ,  $B_{10}H_{10}^{2-}$ ,  $B_{20}H_{18}^{2-}$ , and  $B_{20}H_{19}^{3-}$  anions in an inert atmosphere initially yields a polymer based on  $B_{12}H_{12}^{2-}$ , the most stable and energetically favorable anion [1]. The pyrolysis of acrylonitrile– and cellulose–5-vinyl-2-methylpyridine copolymers in the presence of  $B_{10}H_{10}^{2-}$ ,  $B_{12}H_{12}^{2-}$ ,  $B_{20}H_{18}^{2-}$ , and  $B_{12}H_{11}NH_3^-$  anions at 1000–1900°C affords non-woven fibrous boron–carbon materials containing up to 45 wt % boron [5]. The thermal decomposition of graphite oxide intercalation compounds (GOICs) with dodecahydro-*closo*-dodecaboric acid,  $H_2B_{12}H_{12}$ , was investigated in detail [6, 7]. A reaction mechanism was suggested for this process, and it was elucidated how the character of decomposition of these compounds (smooth/explosion-like) and the outcomes of the process depend on the composition of the initial compounds and on the heat treatment conditions.

Here, we report the thermal conversions of chitosanium dodecahydro-*closo*-dodecaborate  $(C_6O_4H_9NH_3)_2B_{12}H_{12}$  (**I**) [8] as the starting compound for obtaining boron-containing materials.

### EXPERIMENTAL

The synthesis of  $(C_6O_4H_9NH_3)_2B_{12}H_{12}$ , which is carried out via the reaction between chitosan [9] and an aqueous solution of  $H_2B_{12}H_{12}$  or via the exchange reaction between a water-soluble chitosanium salt (acetate, fluoride, or nitrate) and dodecahydro-*closo*-dodecaboric acid or its soluble salt  $Na_2B_{12}H_{12}$  or  $K_2B_{12}H_{12}$  (2 : 1 mol/mol) in aqueous solution, was detailed in [8]. The starting compound in these syntheses was chitosan powder with a degree of deacetylation of 75.0% and an effective molecular weight of 171.7 amu, which is produced by OOO Biopolimery (Partizansk, Primorskii krai) according to the specifications TU 9283-174-200472012-03.

Boron in the filtrates that resulted from treatment of heat treatment products with water was quantified by flame photometry [10].

Thermoanalytical profiles for the starting chitosan and compound **I** were obtained in air or in an inert atmosphere (argon) between 18 and 1000°C on a Q-1500 D thermal analyzer at a heating rate of 5–20 K/min. Samples of these compounds, in nickel crucibles placed in quartz tubes, were heat-treated in

argon by raising the temperature to 1000°C at a rate of 5–10 K/min.

The X-ray diffraction patterns of the starting chitosan, compound **I**, and the solid residues obtained in thermal studies were taken from films or powdered samples on a D8 Advance diffractometer ( $\lambda\text{CuK}\alpha$  radiation).

IR spectra were recorded as mineral-oil or perfluorocarbon mulls or KBr pellets in the 400–4000  $\text{cm}^{-1}$  range on an IFS Equinox-55S Fourier-transform spectrometer. For some samples, spectra were taken from thin films.

The X-ray photoelectron spectra of the surfaces of **I** and heat treatment products were recorded on an ES-2401 spectrometer. The XPS conditions and procedure were reported in an earlier publication [8].

## RESULTS AND DISCUSSION

The thermoanalytical data for compound **I** (Fig. 1a) indicate an exotherm between 145 and 195°C accompanied by weight loss, which is likely due to the decomposition of this compound.

Heat treatment of **I** at 165°C in argon for 2 h changes its color and results in a slight weight loss. The heat treatment product is more brittle than **I**. Under the action of water, it softens to the consistency of treacle and evolves gaseous products. Universal indicator paper turns red when wetted with this mass. Upon drying, this mass sticks very tightly to the surface and can hardly be cleared away.

The IR spectrum of this heat treatment product (Fig. 2, curve 3) is identical to the spectrum of **I** (Fig. 2, curve 2), while its X-ray diffraction pattern (Fig. 3, curve 2) indicates changes in the structure of **I** (Fig. 3, curve 1).

The B1s line in the X-ray photoelectron spectrum of the heat treatment product, with its major component at  $E_b = 188.0$  eV, which is due to the  $\text{B}_{12}\text{H}_{12}^{2-}$  anion, is nonuniformly broadened because of the presence of a minor component at  $E_b = 189.4$  eV (Fig. 4b). A similar spectrum was observed in our earlier study of the thermal behavior of the GOIC with  $\text{H}_2\text{B}_{12}\text{H}_{12}$  [7]. It was hypothesized that, upon heating, the intramolecular redox reaction between graphite oxide (GO) and  $\text{H}_2\text{B}_{12}\text{H}_{12}$  replaces two terminal hydrogen atoms in the polyhedral hydroborate anion with an oxygen atom to yield the partially oxidized anion  $\text{B}_{12}\text{H}_{12}^{2-}$ . The heat-induced darkening of the GOIC, the presence of only the C1s signal from pure carbon in the spectrum of the heat treatment product, and the disappearance of the signal characteristic of the C–O bond (present in the spectrum of the initial GO) suggest that the source of oxygen is GO, which undergoes reduction to carbon. This is likely followed by the polymerization of the partially oxidized *closo*-hydroborate anions through oxygen atoms into a polymer with  $[-\text{B}_{12}\text{H}_{10}-$

$\text{O}-]^{2-}$  monomer units, and this process is likely complete once the GOIC is heated to 125°C. This assumption is based on the fact that, upon heating, the polyhedral hydroborate anions and their substituted derivatives tend to form polymers that are thermally and chemically stable and are inert toward water and many solvents [11–14]. The linking of hydroborate polyhedra into a polymer chain can take place through substituent heteroatoms in the  $\text{B}_{12}\text{H}_{12}^{2-}$  anion, such as oxygen, halogens, and sulfur, and through groups of atoms. In the case of **I**,  $\text{B}_{12}\text{H}_{10}\text{O}^{2-}$  formation may involve oxygen atoms of the chitosanium cation. We think that the higher onset temperature of the formation of partially oxidized *closo*-hydroborate in this case is due to the fact that, as compared to GO, which is fairly readily reduced to carbon under the action of hydrazine, hydroxylamine, alkali metals, and other reductants [15–17], chitosan is chemically and thermally stable [9]. Chitosan undergoes restructuring above 170°C and decomposes above 230°C [18]. As follows from thermoanalytical data (Fig. 1b), chitosan begins to lose weight, evolving heat, above 180°C. It can be assumed that it is in the 195–425°C range that  $\text{B}_{12}\text{H}_{12}^{2-}$  turns completely into  $\text{B}_{12}\text{H}_{10}\text{O}^{2-}$  (Fig. 1a) since, at these temperatures, chitosan decomposes actively to release oxygen or oxygen-containing groups (Fig. 1b), thus providing the necessary oxidizer. It is likely that the polymerization of the resulting anion also takes place in this temperature range.

Heat treatment of **I** at 260°C in argon verified this assumption. The heat treatment product obtained at this temperature is brown-black and is readily grindable into a bright brown fine powder. According to X-ray diffraction data, heating induces structural changes in **I** (Fig. 3, curve 3). The product is inert toward water. This confirms the formation of the partially oxidized polymer based on the  $\text{B}_{12}\text{H}_{12}^{2-}$  anion. As was demonstrated by studies of the thermal decomposition of  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12} \cdot 4\text{H}_2\text{O}$  [11–14], this compound polymerizes above 140°C. The IR spectrum of the resulting polymer shows a band at 1080  $\text{cm}^{-1}$ , which is believed to be evidence that polymerization does not break the icosahedral backbone  $\text{B}_{12}$  [11–14]. However, this absorption band is greatly shifted to shorter wavelengths (by 50  $\text{cm}^{-1}$ ) relative to the same band characterizing the initial compound. This likely indicates some distortion of the  $\text{B}_{12}$  polyhedron. At the same time, the position of the B–H stretching band ( $\sim 2500$   $\text{cm}^{-1}$ ) remains almost unchanged. In the IR spectrum of the heat treatment product of **I** (Fig. 2, curve 4), the  $\nu_{\text{B-H}}$  band (2484  $\text{cm}^{-1}$ ) also remains in its initial position. It is difficult to follow the changes in the  $\text{B}_{12}\text{H}_{12}^{2-}$  bending band because it is overlapped by strong absorption bands of chitosan.

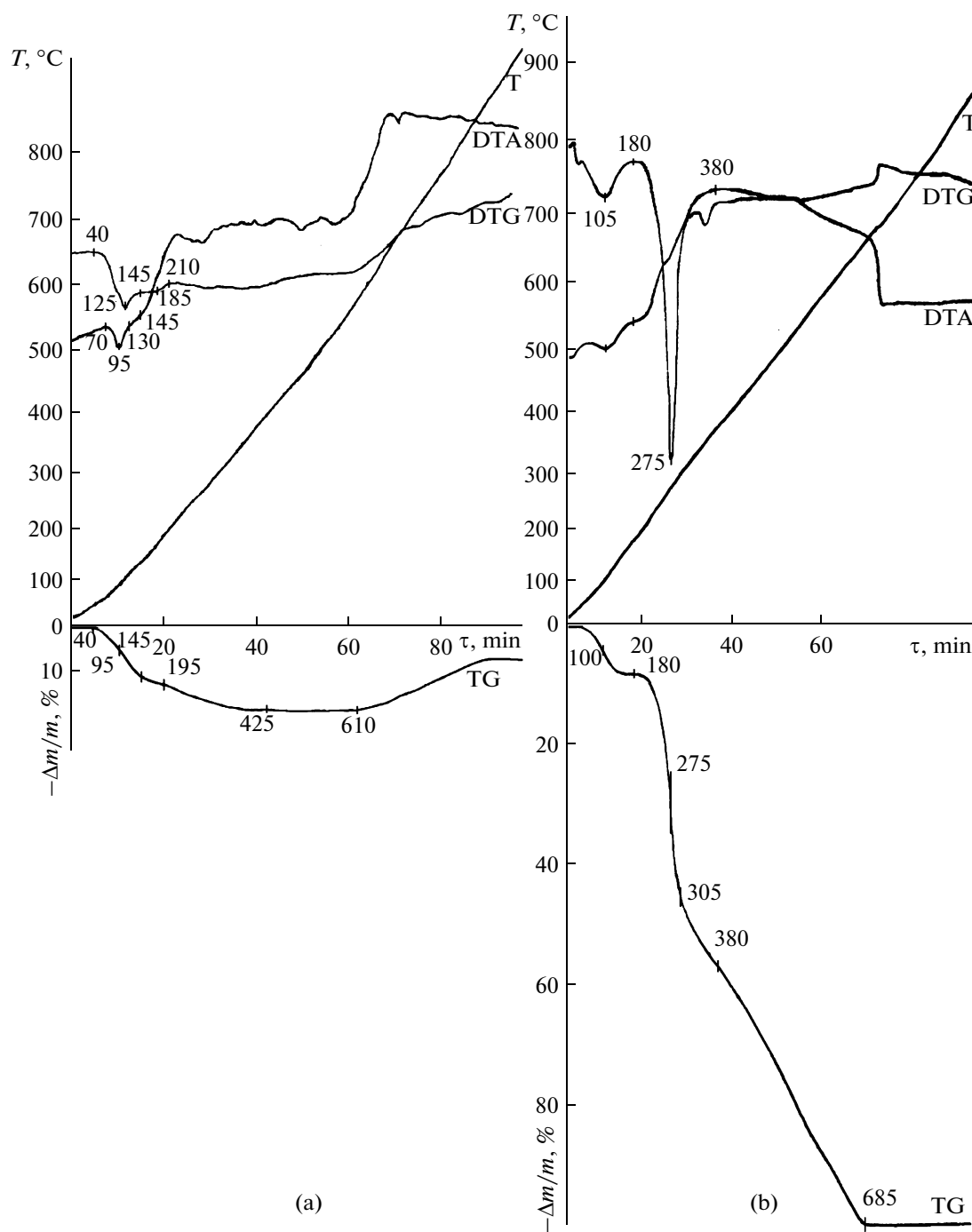
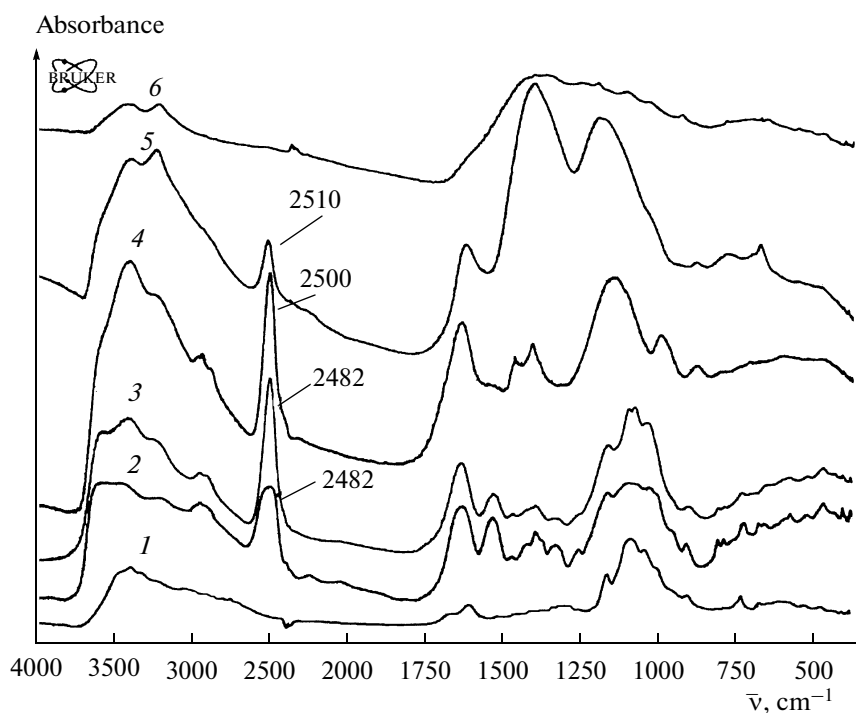


Fig. 1. Thermoanalytical curves for (a) compound I and (b) chitosan heated in air.

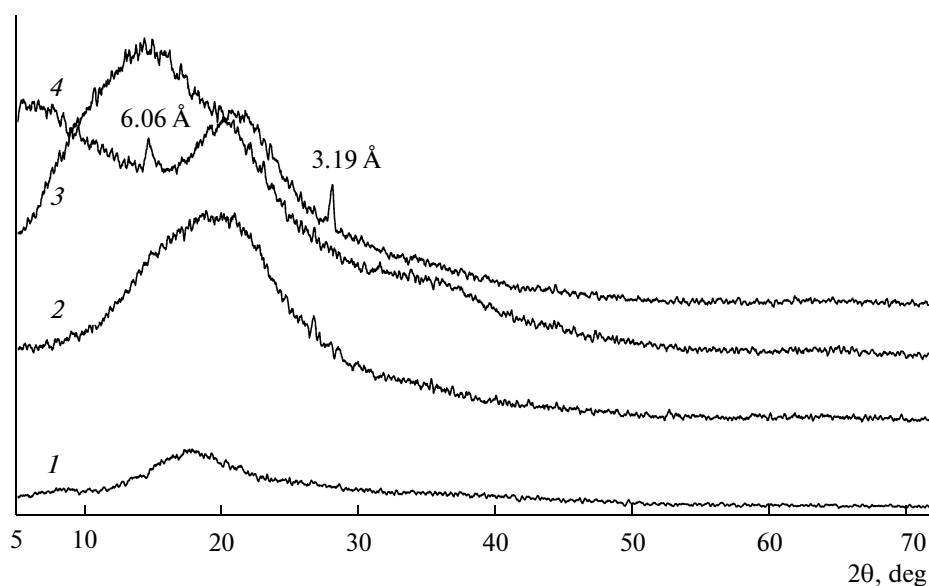
In the X-ray photoelectron spectrum of this heat treatment product of I, the nonuniform broadening of the boron line is still more pronounced, indicating an increase in the proportion of the partially oxidized anion. The integrated B1s line intensity for boron atoms not bonded with oxygen is  $\approx 5$  higher than is observed for boron atoms bonded with oxygen (Fig. 4c). The variation of the position of the strong component

of the nitrogen line indicates changes in the interaction of the chitosan moiety (or chitosan destruction products) with the hydroborate polyhedra.

The successive processes in compound I—chitosan decomposition, the formation of  $B_{12}H_{10}O^{2-}$ , and the polymerization of this anion—are accompanied by the evolution of a rather large amount of heat. At a heating rate above 10–20 K/min, particularly for large



**Fig. 2.** IR absorption spectra of (1) chitosan, (2) compound I, and (3–6) I heat-treated in argon at (3) 165, (4) 260, (5) 530, and (6) 940°C.



**Fig. 3.** X-ray diffraction patterns of (1) compound I and (2–5) I heat-treated in argon at (2) 165, (3) 260, and (4) 530°C.

sample sizes, when the evolved energy has no time to dissipate into the environment, the resulting combustible material ignites at  $\approx 300^\circ\text{C}$  both in air and in an inert atmosphere. The decomposition product is an expanded dark brown substance. According to X-ray diffraction data, it consists largely of carbon and boric

acid ( $d = 6.07$  and  $3.19 \text{ \AA}$ ). Residual amounts of the initial compound I were also detected in the decomposition product, particularly after ignition in an inert atmosphere.

As I is heated in air (Fig. 1a) between  $425$  and  $610^\circ\text{C}$ , its weight remains almost invariable. As is clear

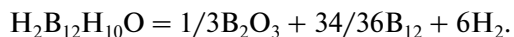
from the thermoanalytical data for chitosan (Fig. 1b), the chitosanium cation undergoes oxidation accompanied by weight loss at these temperatures. It can, therefore, be assumed that the hydroborate moiety oxidizes simultaneously to gain weight. The formation of a protective boric acid or boron oxide film, which hampers oxygen diffusion into the particle bulk, is another weight stabilization factor. The product is a black alloy, which confirms the formation of  $B_2O_3$  or  $B(OH)_3$ .

As **I** is heated in argon to  $530^\circ\text{C}$ , it decomposes, changing its structure and yielding  $B_2O_3$  or  $B(OH)_3$  (Fig. 3, curve 4). In the IR spectrum of the product (Fig. 2, curve 5), the  $\nu_{B-H}$  band has a markedly different intensity and is shifted to higher frequencies. This is likely due to the pronounced decomposition of the partially oxidized polymeric form of the  $B_{12}H_{12}^{2-}$  anion. The spectrum shows no bands due to the chitosanium cation.

The complete decomposition of **I** is observed upon heating of this compound in argon to  $940^\circ\text{C}$ . The heat treatment product in this case is a black, slightly agglomerated powder. It scratches the jasper mortar as it is ground; therefore, it contains a very hard material. According to X-ray diffraction data, there is  $B_2O_3$  in the product, which agglomerates the powder.

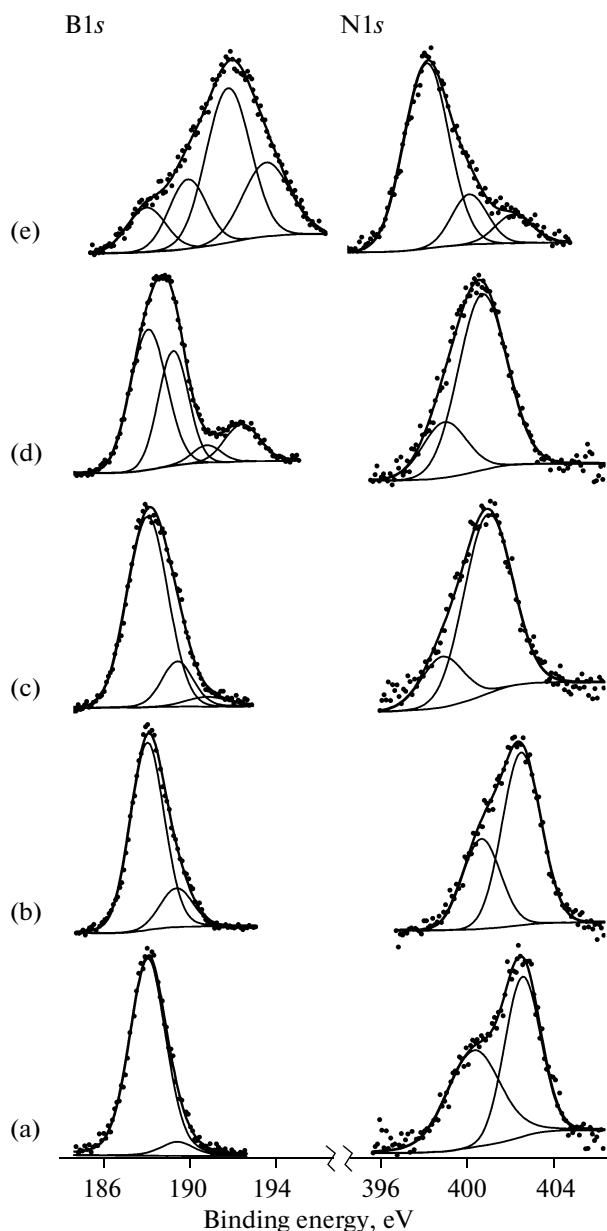
The IR spectrum of this product (Fig. 2, curve 6) confirms the complete decomposition of the hydroborate moiety. It does not show the band characteristic of the hydroborate anion. Instead, it exhibits a well-defined band in the  $800\text{--}1600\text{ cm}^{-1}$  range, indicating the presence of  $B_2O_3$  [19]. The IR spectrum of the heat treatment product washed with water (Fig. 5) is much simpler. Its analysis confirms the presence of boron or boron carbides ( $1091\text{ cm}^{-1}$ ) [1, 20] and BN ( $1370\text{ cm}^{-1}$ ) [1]. There are a number of bands in the  $300\text{--}800\text{ cm}^{-1}$  range, which are typical of  $B_{12}$  icosahedra linked into a disordered spatial structure by intericosahedral nitrogen, carbon, or boron atoms [1].

The appearance of  $B_2O_3$  in the heat treatment product obtained in argon is evidence that the decomposition of **I** proceeds via the formation of the partially oxidized hydroborate anion, which then polymerizes through oxygen atoms. The amount of the resulting boron oxide can be estimated using the following chemical equation describing the decomposition of the partially oxidized polymer:



As determined by atomic absorption spectrometry, the boron content of the filtrate obtained after washing of the heat treatment product with hot water checks well with the theoretical value. For example, after the heat treatment of  $0.53580\text{ g}$  of **I**,  $0.14\text{ g}$  of **B** passes into the filtrate, which is very close to  $1/12$  of the boron contained in the initial compound.

XPS data (Fig. 4e) confirm the presence of oxidized boron as  $B_2O_3$  and  $B(OH)_3$  in this product (peak



**Fig. 4.** X-ray photoelectron spectra (B1s and N1s lines) of (a) compound **I** and (b–e) **I** heat-treated at (b)  $165^\circ\text{C}$ , (c)  $260^\circ\text{C}$ , (d)  $530^\circ\text{C}$ , and (e)  $940^\circ\text{C}$ .

components at  $E_b = 193.6$  and  $191.8\text{ eV}$ , respectively). The N1s peak for the product indicates the complete decomposition of compound **I**. While the spectrum of the sample heated to  $165^\circ\text{C}$  (Fig. 4b) still shows a line due to the nitrogen of protonated amino groups oriented toward the  $B_{12}H_{12}^{2-}$  anion [8], the spectrum of the sample heated in argon to  $940^\circ\text{C}$  shows an intense peak component at  $E_b = 398.2\text{ eV}$  [21], which is characteristic of nitrogen in the form of boron nitride. The formation of amorphous BN takes place starting at  $500^\circ\text{C}$  [22]. The binding energy for the corresponding

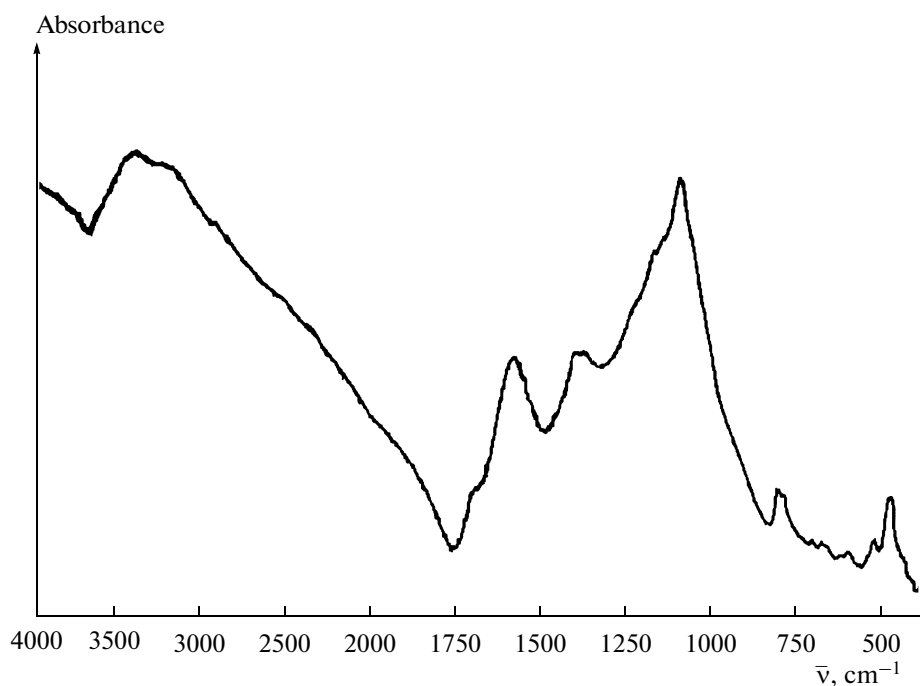


Fig. 5. IR absorption spectrum of compound **I** heat-treated in argon at 940°C and water-washed from boron oxide.

$E_b$  component is 190.0 eV (Fig. 4e). Nitrogen can also be involved in the linking of  $B_{12}$  icosahedra [1]. The weak components on the higher  $E_b$  side of the N1s peak are assignable to nitrogen bound to the carbon residue [23].

The final product resulting from the heating of **I** to 1000°C in air is a lustrous black alloy. It scratches the mortar as it is ground. According to X-ray diffraction data, it consists of  $B_2O_3$  and an X-ray-amorphous phase. After boric acid is washed away, the filtrate contains approximately 70% of the initial boron as compound **I**. A considerable proportion of the boron remains unoxidized as, appearing as elemental boron and/or boron carbides (which scratch the mortar) and boron nitride. These products form in the particle bulk owing to the protective film of the  $B_2O_3$  melt.

Thus, the pyrolysis of **I** in an inert atmosphere yields a complicated mixture consisting of carbon, amorphous boron and/or boron carbides, and hexagonal boron nitride. The product also contains nitrogen, which is likely bound to carbon and  $B_{12}$  icosahedra. It is agglomerated by boric anhydride, whose appearance can be explained by the formation of the  $B_{12}H_{10}O^{2-}$  anion via the intramolecular interaction between the chitosanium cation and  $B_{12}H_{12}^{2-}$  at the early stages of the decomposition of **I**.

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