

# Synthesis, Spectroscopic and Thermal Characterization of Non-Metal Cation (NMC) Pentaborates Salts Containing Cations Derived From Histidine and Arginine

## Katyonik Histidine ve Arjinin Türevleri İçeren Metal Katyonsuz (NMC) Pentaborat Tuzlarının Sentezi, Spektroskopik ve Termal Karakterizasyonu

Research Article

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### ABSTRACT

The new non-metal cation (NMC) pentaborate structures of cationic histidine and arginine aminoacids were synthesized and characterized using spectroscopic (<sup>11</sup>B NMR and IR) methods. Their thermal properties have been investigated by TG/DrTG-DTA. The histidine NMC pentaborate, [C<sub>6</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>].4H<sub>2</sub>O and the arginine pentaborate, [C<sub>6</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub>.3H<sub>2</sub>O are formulated with 4 and 3 waters of crystallization, respectively. The histidine pentaborate is more stable than the arginine pentaborate to thermal decomposition, but both decompose thermally via initial dehydration followed by loss of amino acid fragments to afford glassy B<sub>2</sub>O<sub>3</sub>.

### Key Words

Non-metal cation borate structure, Pentaborate, Thermal investigation, <sup>11</sup>B NMR

### ÖZET

Katyonik histidin ve arjinin aminoasitlerinin metal katyonu içermeyen (NMC) yeni pentaborat yapıları sentezlendi ve spektroskopik yöntemler (<sup>11</sup>B NMR and IR) kullanılarak karakterize edildi. Termal özellikleri TG/DrTG-DTA ile araştırıldı. Histidine NMC pentaborat, [C<sub>6</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>].4H<sub>2</sub>O ve arjinin pentaborat, [C<sub>6</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub>.3H<sub>2</sub>O yapılarının sırasıyla 4 ve 3 molekül Kristal suları içerdikleri tespit edilmiştir. Termal olarak histidine pentaborat arjinin pentaborat yapısına göre daha kararlıdır, fakat her iki NMC pentaborat yapısının bozunması dehidrasyonu izleyen aminoasit bölümlerinin uzaklaşması ve bozunma ürünü olarak camı yapıda B<sub>2</sub>O<sub>3</sub> kalmasıyla gerçekleşir.

### Anahtar Kelimeler

Metal katyonu içermeyen borat yapısı, Pentaborat, Termal inceleme, <sup>11</sup>B NMR

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## INTRODUCTION

Borate materials have attracted a great deal of attention in the past decades because of their rich structural chemistry and potential applications in mineralogy and industry [1-3]. From the structural point of view, boron atoms may coordinate with oxygen atoms not only in three-fold coordination (triangular,  $\text{BO}_3$ ), but also in four-fold coordination (tetrahedral,  $\text{BO}_4$ ). The  $\text{BO}_3$  and  $\text{BO}_4$  groups may be further linked via common oxygen atoms to form polynuclear anions, including isolated rings (or cages), infinite chains, sheets and frameworks [4-10], and salts containing polyanions such as  $[\text{B}_4\text{O}_5(\text{OH})_4]_2^-$  [11],  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$  [12] and  $[\text{B}_9\text{O}_{12}(\text{OH})_6]_3^-$  [13] have been reported. Compared to metal borates, the synthesis of borates containing non-metal cations are still a much less explored area, though a few cases have been reported in recent years [3,15-17]. However, no NLO property has been mentioned except for  $[\text{C}_2\text{H}_{10}\text{N}_2][\text{B}_5\text{O}_8(\text{OH})]$  [18] and a few tetrafluoro borates showing NLO properties [19,20]. Therefore, it is significant to explore the NLO properties of nonmetal borates for understanding the NLO effect and searching for new NLO materials.

Non-metal cations differ from metal cations in their potential for interactions with borate anions: metal cations are spherical and primarily accept electron density from oxygen donors, whilst non-metal cations may be non-spherical and may have H-bond donor sites [21]. Steric and electronic factors associated with non-metal cations may be fine-tuned and these properties will affect structure. In this respect, the only borate minerals that do not contain metal counterions (they contain the  $[\text{NH}_4]^+$  cation [22]) are ammonioborite,  $[\text{NH}_4]_3[\text{B}_{15}\text{O}_{20}(\text{OH})_8] \cdot 4\text{H}_2\text{O}$  and

larderellite  $[\text{NH}_4][\text{B}_5\text{O}_7(\text{OH})_2] \cdot \text{H}_2\text{O}$  and these polyborate minerals have anionic structures which are exclusively paired with the ammonium cation. Furthermore, the guanidinium and imidazolium polyborate systems both display the isolated nonaborate anion,  $[\text{B}_9\text{O}_{12}(\text{OH})_6]_3^-$ , and this anion is only observed with these non-metal cations [4]. In contrast, pentaborate(1-) salts are particularly stable and have been readily obtained for both metal and non-metal cations [23-25]. Quaternary ammonium and related non-metal pentaborate systems have also been studied but relatively few have been structurally characterized [15,26]. More recently some template complexed metal cation/pentaborate anion salts have been characterized [25]. In this study, we reported non-metal cation (NMC) pentaborate structures derived from the amino acids histidine and arginine and characterized by spectroscopic and thermal and methods.

## EXPERIMENTAL

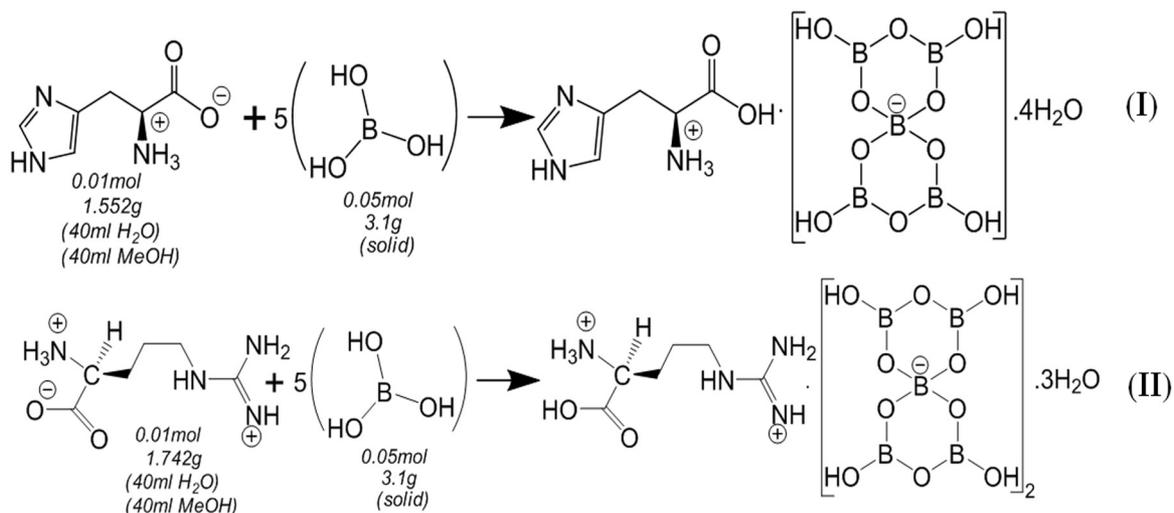
0.01 mol histidine or arginine amino acids (Sigma-Aldrich) were solved in a mixture of distilled water (40 mL) and methanol (Sigma-Aldrich) (40 mL). Then 0.05 mol  $\text{H}_3\text{BO}_3$  (Sigma-Aldrich) was added to each solution as solid (scheme 1). The solutions were stirred for 1 hour. The solutions were evaporated until dryness. The white solid products were collected and dried at 50 °C in a vacuum.

The synthesis reactions of histidine and arginine pentaborate were described in below and obtained in a 75% and 65% overall yield respectively. Analytical data are shown in Table 1.

$^{11}\text{B}$  NMR spectra (160 MHz,  $\text{D}_2\text{O}$ ) of histidine and arginine derived pentaborates were given Figure 1 and 2, respectively. The histidine pentaborate

**Table 1.** Analytical results of histidine and arginine derived pentaborates:

| Molecular Formula   | Molecular Weight | Yield (%) | Melting Point | C (%)<br>Exp.-Calc. | H (%)<br>Exp.-Calc. | N (%)<br>Exp.-Calc. |
|---|------------------|-----------|---------------|---------------------|---------------------|---------------------|
| $\text{C}_6\text{H}_{22}\text{B}_5\text{N}_3\text{O}_{16}$    | 446.32 g/mol     | 86%       | 98 °C         | 16.24-16.11         | 4.98-4.70           | 9.41-9.40           |
| $\text{C}_6\text{H}_{30}\text{B}_{10}\text{N}_4\text{O}_{25}$ | 666.44 g/mol     | 75%       | 73°C          | 10.70-10.77         | 4.87-4.35           | 8.31-8.38           |

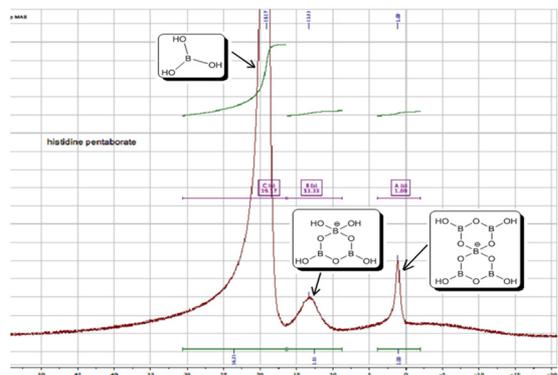


**Scheme 1.** Showig of reaction of histidine (1) and arginine (2) with boric acid.

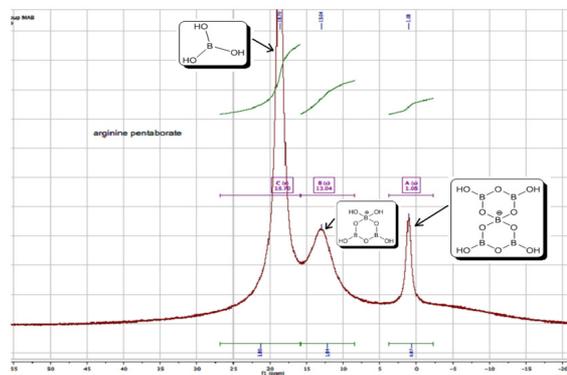
spectrum has three peaks that are at 19.17 ppm attributed to trigonal free boric acid, at 13.33 ppm attributed to triborate structure and at 1.09 ppm tetrahedral centre of pentaborate structure. The peaks of arginine pentaborate are similar to the histidine pentaborate spectrum with peaks at 18.70 ppm, 13.04 ppm and 1.05 ppm. These peaks belong to free boric acid, triborate structure and pentaborate structure, respectively. These results agree with previous literature [26-28]. The  $^{11}\text{B}$  NMR spectra of the histidine and arginine pentaborate salts are complex but explainable in terms of a complex series of equilibra existing in aqueous solution which link monomeric and oligomeric borate species [27].

The surface area of histidine pentaborate is 3.5  $\text{m}^2$  and the arginine pentaborate is 0.9  $\text{m}^2$  according to single point BET analysis.

The TGA/DTA curves of histidine and arginine pentaborate salts are shown Figure 3. TG data were recorded in the temperature range of 25-1000  $^{\circ}\text{C}$  in nitrogen media for both of them. The decomposition of histidine pentaborate has three stage processes. Firstly, four molecules hydrated waters remove in 95-195  $^{\circ}\text{C}$  range (exp. 14.18%; calc. 16.14%). The dehydration of compound occurs at 98  $^{\circ}\text{C}$  and 128  $^{\circ}\text{C}$  in two endothermic steps. The second stage belongs to removing of two water molecules from the pentaborate structure in 202-240  $^{\circ}\text{C}$  range with endothermic DTA peak at 215  $^{\circ}\text{C}$  (exp. 7.25%; calc. 8.07%). The organic cation histidine is decomposed at last stage process in 251-448  $^{\circ}\text{C}$  range with endothermic DTA peaks at 293  $^{\circ}\text{C}$  and 322  $^{\circ}\text{C}$ . Finally, a glassy  $\text{B}_2\text{O}_3$  oxide was obtained as decomposition product of histidine pentaborate salt (exp. 41.53%; calc. 39.23%). The decomposition peaks of arginine pentaborate are



**Figure 1.**  $^{11}\text{B}$  NMR curve of histidine pentaborate structure.



**Figure 2.**  $^{11}\text{B}$  NMR curve of arginine pentaborate structure.

**Table 2.** Decomposition data (TGA/DTA) of histidine and arginine pentaborate structure.

| Sample                     | Temperature Range (°C) | DTGmax (°C) | Removed Group      | Mass loss (%)<br>Exp.- Calc. | Total mass (%)<br>Exp.- Calc. | Decomposition Product             |
|----------------------------|------------------------|-------------|--------------------|------------------------------|-------------------------------|-----------------------------------|
| $C_6H_{22}B_5N_3O_{16}$    | 95-195                 | 98,128      | 4 H <sub>2</sub> O | 14.18-16.14                  |                               | $C_6H_{14}B_5N_3O_{12}$           |
|                            | 202-240                | 215         | 2 H <sub>2</sub> O | 7.25-8.07                    |                               | $C_6H_{10}B_5N_3O_{10}$           |
|                            | 251-448                | 293, 322    | $C_6H_{14}N_3O_2$  | 33.15-33.79                  | 41.53-39.23                   | 5/2 B <sub>2</sub> O <sub>3</sub> |
| $C_6H_{30}B_{10}N_4O_{25}$ | 90-140                 | 132         | 3 H <sub>2</sub> O | 9.08-8.14                    |                               | $C_6H_{24}B_{10}N_4O_{22}$        |
|                            | 200-226                | 208         | 4 H <sub>2</sub> O | 11.04-10.80                  |                               | $C_6H_{16}B_{10}N_4O_{18}$        |
|                            | 238-511                | 346         | $C_6H_{16}N_4O_2$  | 27.52-26.15                  | 54.53-52.56                   | 5 B <sub>2</sub> O <sub>3</sub>   |

similar to histidine pentaborate. According to TGA curves, it has three decomposition stage. Their first, removing of three molecules hydrated waters that occurs in 90-140 °C range with the endothermic DTA peak at 132 °C (exp. 9.08%; calc. 8.14%). The second stage consists removing of four molecules water from two pentaborate structure in 200-226 °C range with the endothermic DTA peak at 208 °C (exp. 11.04%; calc. 10.80%). At the third stage, the organic cation arginine removes from the structure in 238-511 °C range with endothermic DTA peak at 346 °C (exp. 27.52%; calc. 26.15%). Lastly, a glassy B<sub>2</sub>O<sub>3</sub> residue remains in the analysis capsule as decomposition product (exp. 54.53%; calc. 52.56%).

The FT-IR spectrum curves of histidine and arginine derived pentaborates are presented in Figure 4. The very strong bands at 1419 and 1310 cm<sup>-1</sup> for histidine pentaborate and 1427 and 1303 cm<sup>-1</sup> for arginine pentaborate are symmetric and symmetric vibrations of B-O in BO<sub>3</sub>, whereas the bands at 1030, 919 and 901 cm<sup>-1</sup> for histidine pentaborate and 1022, 923 and 905 cm<sup>-1</sup> for arginine pentaborate are typical of asymmetric and symmetric stretching modes of B-O in BO<sub>4</sub>, respectively [29-32]. The peaks at 1188 cm<sup>-1</sup> for histidine pentaborate and 1149 cm<sup>-1</sup> for arginine pentaborate are the in-plane bending mode of B-O-H while, the out-of-plane bending modes of B-O in BO<sub>3</sub> are obtained at 703 cm<sup>-1</sup> for histidine and 707 cm<sup>-1</sup> for arginine pentaborate structures. The weak peak at 1684 cm<sup>-1</sup> and 1663 cm<sup>-1</sup> belong to bending of NH<sub>2</sub> groups [33]. Moreover, the bands at 3147 cm<sup>-1</sup> and 3230 cm<sup>-1</sup> are correspond to the N-H stretching vibrations of histidine and arginine pentaborates respectively. Finally, the O-H stretching bands are appeared

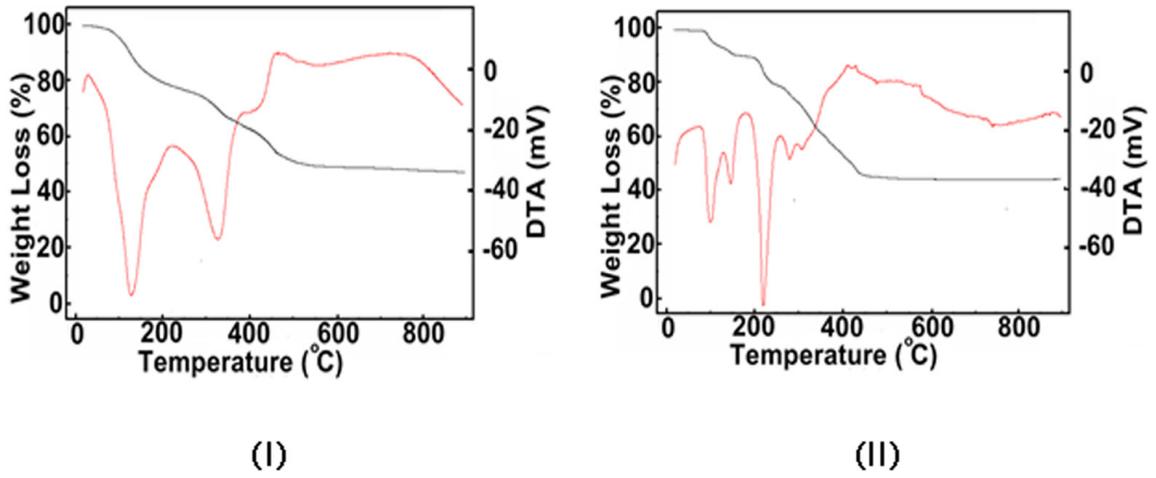
at 3412 cm<sup>-1</sup> for histidine derived pentaborate and 3455 cm<sup>-1</sup> for arginine pentaborate.

## CONCLUSION

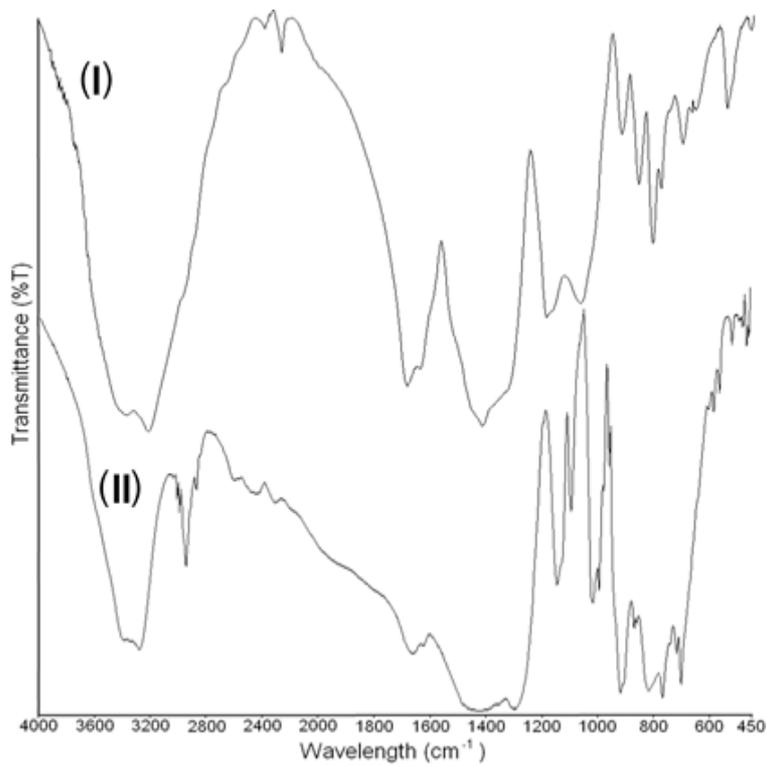
The NMC pentaborate salts derived from histidine, [C<sub>6</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>].4H<sub>2</sub>O, and arginine, [C<sub>6</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>].2.3H<sub>2</sub>O, have been synthesized and characterized by elemental analysis, spectroscopy (<sup>11</sup>B NMR and IR) and thermal (TG/DTG-DTA) methods and formulated with 4 and 3 waters of crystallization, respectively. TGA/DTA analysis showed dehydration, followed by decomposition of the amino acid fragments to leave glassy B<sub>2</sub>O<sub>3</sub> residue were obtained. Thermal stability of the samples ranged as follows: histidine pentaborate > arginine pentaborate.

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**Figure 3.** TGA/DTA curves of histidine (I) and arginine (II) pentaborate structure.



**Figure 4.** FT-IR graphic of histidine (I) and arginine (II) pentaborate structure.

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