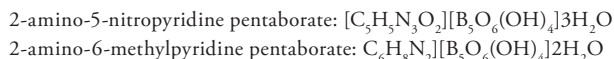


Synthesis, Spectroscopic and Thermal Characterization of Non-Metal Cation (NMC) Pentaborates Salts Containing 2-amino-5-nitropyridine and 2-amino-6-methylpyridine as Cation

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ABSTRACT

The pyridine derivatives, 2-amino-5-nitropyridine and 2-amino-6-methylpyridine (6-aminopicolin), were used for the synthesis of two new non-metal cation (NMCs) pentaborate structures. The NMCs pentaborate molecules were characterized using ^{11}B -NMR, elemental analysis, BET, FT-IR, P-XRD and melting point technics. The thermal properties had been investigated by TGA/DTA/DTG methods. 2-amino-5-nitropyridine and 2-amino-6-methyl pyridine (NMC)s pentaborates showed different thermal stabilities among each other, but degradation of the dehydration of the following organic both NMC pentaborate structure as part away and decomposition products of B_2O_3 occurs by having glassy structure. The trigonal (BO_3) and tetragonal (BO_4) moieties were determined in ^{11}B NMR spectrums. According to P-XRD methods each of the compound structures are in crystalline form. The peaks of pentaborate anion $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ were seen in FT-IR spectra. Lastly, the hydrogen storage properties of these molecules were studied. The estimated molecular formulas of the complexes are as follows:



Key Words:

Boron; Non-metal Cation Borate Structure; Pentaborate; P-XRD; Thermal Investigation; ^{11}B -NMR.

INTRODUCTION

Boron is a chemical element with symbol B and atomic number 5. Because boron is produced entirely by cosmic ray spallation and not by stellar nucleosynthesis, it is a low-abundance element in both the Solar system and the Earth's crust [1]. In biology, borates have low toxicity in mammals (similar to table salt), but are more toxic to arthropods and are used as insecticides. Boric acid is mildly antimicrobial, and a natural boron-containing organic antibiotic is known [2]. The earliest routes to elemental boron involved reduction of boric oxide with metals such as magnesium or aluminum. However the product is almost always contaminated with metal borides. Pure boron can be prepared by reducing volatile boron halides with hydrogen at high temperatures. Ultrapure boron for use in the semiconductor industry is produced by the decomposition of diborane at high temperatures

and then further purified with the zone melting or Czochralski processes [3]. Elemental boron is rare and poorly studied because the material is extremely difficult to prepare. Most studies on "boron" involve samples that contain small amounts of carbon. Chemically, boron behaves more similarly to silicon than to aluminum. Crystalline boron is chemically inert and resistant to attack by boiling hydrofluoric or hydrochloric acid. When finely divided, it is attacked slowly by hot concentrated hydrogen peroxide, hot concentrated nitric acid, hot sulfuric acid or hot mixture of sulfuric and chromic acids [4]. Boron is always found in nature combined with oxygen as anhydrous mixed metal oxides or as hydrated metal borates, with more than 200 borate minerals known and more than 100 were structurally characterized [5–7]. Borate materials have attracted a great deal of attention in the past decades because of their

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rich structural chemistry and potential applications in mineralogy and industry [8-10]. The large family of borate materials have provided an expansive area of research in the last decades owing to their rich structural chemistry and important applications as nonlinear optical (NLO) crystals, luminescent host materials, lithium battery electrodes and porous open-frameworks for catalysis and separation [11]. From the structural point of view, boron atoms may coordinate with oxygen atoms not only in three-fold coordination (triangular, BO_3), but also in four-fold coordination (tetrahedral, BO_4). The BO_3 and 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 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 [12-17]. Some structures display 'isolated' borate or polyborate anions, but the vast majority display more condensed anions comprising infinite chains, sheets or networks. Generally, the boroxole (B_3O_3) ring in various guises is a reoccurring structural motif, with the Lewis acidity of the metal counter-ions influencing the observed structures: strongly Lewis acidic metals being commonly found in structures with a high proportion of four-coordinate boron sites [18,19]. The only minerals that do not contain metal counter-ions are ammonioborate, $[\text{NH}_4]_3[\text{B}_{15}\text{O}_{20}(\text{OH})_8] \cdot 4\text{H}_2\text{O}$ [20] and larderellite $[\text{NH}_4]_3[\text{B}_5\text{O}_7(\text{OH})_2] \cdot \text{H}_2\text{O}$ [21] and these polyborate minerals have anionic structures exclusively paired with the ammonium cation. 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 nonspherical and may have H-bond donor sites [22]. These properties may lead to previously

unobserved borate structural moieties and further offers the opportunity to explore structure directing H-bond relationships. Indeed, 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 [23]. More recently some template complexed metal cation/ pentaborate anion salts have been characterized [24]. 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

0,02 mol 2-amino-5-nitropyridine and 2-amino-6-methylpyridine (Sigma-Aldrich) were solved in a mixture of acetonitrile (50/50 mL). Then (5.5 mL) methyl iodide (Sigma-Aldrich) was added on both of them to occur cationic form for 2-amino-5-nitropyridine and 2-amino-6-methylpyridine ligands. The solution was heated using heating basket about two hours at 85°C under reflux unit. Then formed colour different crystals were collected with filtration. Then the crystals were solved in 100 mL distillation water and the ion-exchange resin was added on it (double amount of crystals). The purpose of this step is to change iodine ion in 2-amino-5-nitropyridine and 2-amino-6-methylpyridine with hydroxy ion in resin. The solution with ion exchanger resin was remained about 24 hours at room temperature. After the filtration of resin, 0.1 mol (6.2 g) boric acid (Sigma-Aldrich) was added on the ion-exchanged solution. The last solution was stirred about two hours on magnetic stirrer. Then the solution was evaporated until drying with rotatory evaporator and the precipitate samples was collected and dried at 50°C in a vacuum stove.

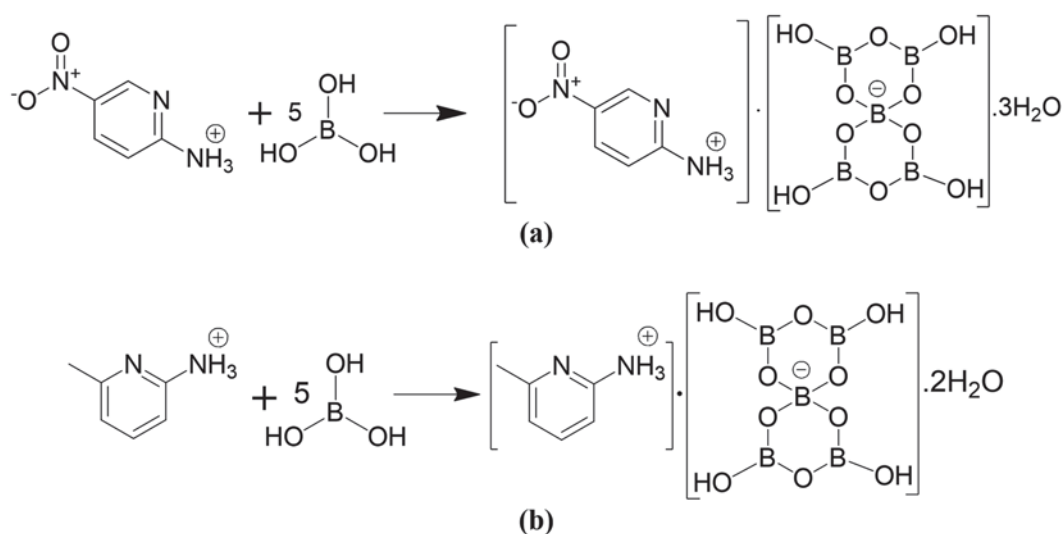


Figure 1. Synthesis scheme of 2-amino-5-nitropyridine pentaborate (a) and 2-amino-6-methylpyridine pentaborate (b) salts..

Table 1. Analytical results of 2-amino-5-nitropyridine and 2-Amino-6-methylpyridine derived pentaborates.

Molecular Formula	M.W. (g/mol)	Yield (%)	Melting Point (°C)	C (%) Exp.Calc	H (%) Exp.Calc	N (%) Exp.-Calc.
$C_5H_{16}B_5N_3O_{25}$	412.25	90	110	13.55-14.57	4.23-3.91	10.12-10.19
$C_6H_{16}B_5N_2O_{12}$	362.25	88	136	18.62-19.89	4.02-4.45	7.52-7.73

The synthesis reactions of 2-amino-5-nitropyridine and 2-amino-6-methylpyridine pentaborate were described below and obtained in a 88% and 90% overall yield respectively. Analytical data are shown in Table 1.

RESULTS AND DISCUSSION

The Figure 2 shows that FT-IR spectrum curves of 2-amino-5-nitropyridine pentaborate (red line) and 2-amino-6-methylpyridine pentaborate (black line) salts. The strong and broad bands at $3600-3000\text{ cm}^{-1}$ for each of the salt compounds are attributed to $-\text{OH}$ stretching [25]. While, the peaks at the range of 3398 and 3391 cm^{-1} belong to N-H groups, at the 3197 and 3191 cm^{-1} refer to C-H groups of organic cations, respectively. The bands of $\text{C}=\text{C}$ and bending N-H group appear at range of the 1468 , 1399 cm^{-1} and 1457 , 1407 cm^{-1} , consecutively [26]. The peaks at the 1230 , 1200 cm^{-1} for 2-amino-5-nitropyridine pentaborate salt are concerned to B-O stretchings of triangular BO_3 , while B-O stretchings of tetragonal BO_4^- are come out at the range of 1137 , 1050 cm^{-1} [27]. The same group peaks of 2-amino-6-methylpyridine pentaborate salt are appeared at the range of 1238 , 1207 cm^{-1} for triangular BO_3 and 1140 , 1055 cm^{-1} for tetragonal BO_4^- . The most important peak for pentaborate structures is $\text{B}_5\text{O}_6(\text{OH})_4^-$ anion group peak [28] that is obtained at the range of 530 cm^{-1} for 2-amino-5-nitropyridine pentaborate salt and 529 cm^{-1} for 2-amino-6-methylpyridine pentaborate salt.

^{11}B NMR spectra (400 MHz, D_2O) of 2-amino-5 nitropyridine (Figure 3a) and 2-amino-6-methylpyridine pentaborate (Figure 3b) derived pentaborates were given Figure 3. The 2-aminopyridine pentaborate spectrum has three peaks that are at 19.07 ppm attributed to trigonal free boric acid, at 13.10 ppm attributed to triborate structure and at 1.13 ppm tetrahedral center of pentaborate structure. The 2-amino-5nitropyridine pentaborate spectrum has three peaks that are at 19.39 ppm attributed to trigonal free boric acid, at 12.77 ppm attributed to triborate structure and at 1.16 ppm tetrahedral center of pentaborate structure. These results agree with previous literature [25,29-31].

The ^{11}B NMR spectra of the 2-amino-5 nitropyridine and 2-amino-6-methylpyridine pentaborate salts are complex but explainable in terms of a complex series of equilibria existing in aqueous solution which link

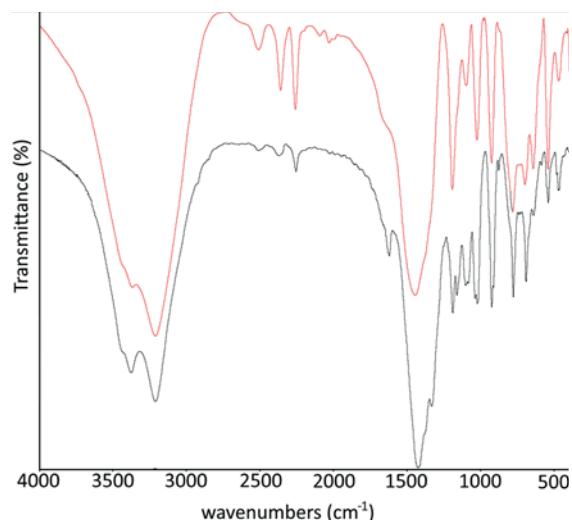
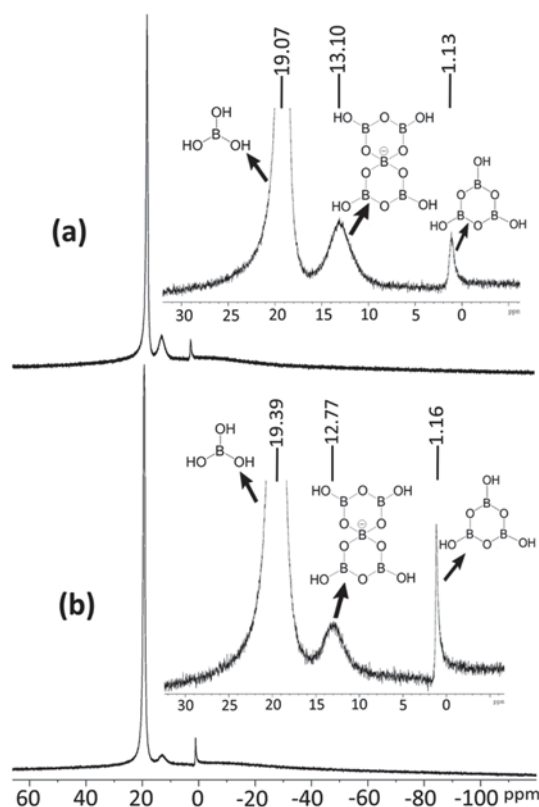
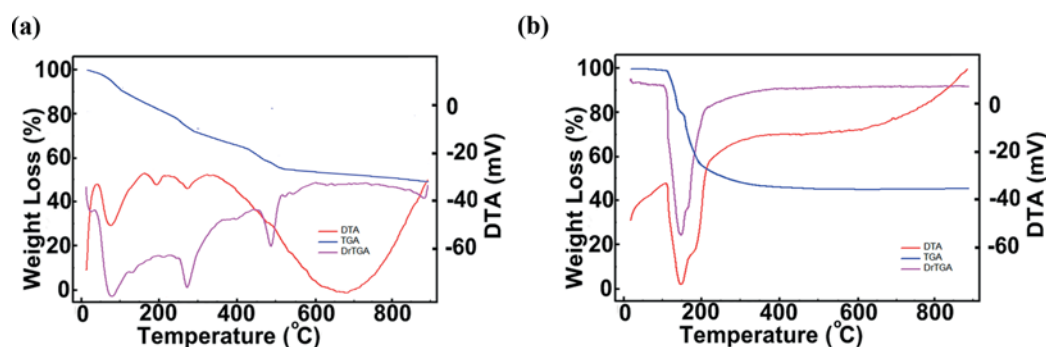
**Figure 2.** FT-IR spectrum curves of 2-amino-5-nitropyridine pentaborate (red line) and 2-amino-6-methylpyridine pentaborate (black line) salts.**Figure 3.** ^{11}B NMR curves of a) 2-amino-5 nitropyridine and b) 2-amino-6-methylpyridine pentaborate salts.

Table 3. Thermal degradation steps and temperatures details.

Complex	Temp. Range/ (°C)	DTA _{max} (°C)	Removed Group	Weight Change/%		Total Loss / %		Decom. Prod.	Colour
				Found	Calc.	Found	Calc.		
$[C_5H_5N_3O_2][B_5O_6(OH)_4]3H_2O$ 412.25 g/mol	1	65-147	81	$3H_2O$	13.25	13.10			White
	2	149-241	197	$2H_2O$	8.73	9.22			
	3	243-567	275,471	$C_5H_6N_3O_2$	31.12	33.99	46.41	44.39	
$[C_5H_8N_3][B_5O_6(OH)_4]2H_2O$ 362.25 g/mol	1	68-162	146	$4H_2O$	18.92	19.88			White
	2	164-493	177	$C_6H_9N_2$	29.61	30.13	51.47	50.53	B_5O_6

**Figure 4.** TGA/DTA/DTG curves of a) 2-amino-5-nitropyridine and b) 2-amino-6-methylpyridine pentaborate salts.

monomeric and oligomeric borate species [3].

Thermal analysis curves of 2-amino-5-nitropyridine (Figure 4a) and 2-amino-6-methylpyridine (Figure 4b) pentaborate salts are shown in Figure 4. TGA data for NMCs pentaborates were recorded in the temperature range of 25–900°C in a nitrogen atmosphere. Thermal decompositions occur in three stages. The first stage is attributed to the dehydration of each compound, followed by the removal of pentaborate hydroxyl groups as aqua molecules. Subsequently, the organic portions are decomposed and removed as CO/CO₂/NO/NO₂. Finally, a glassy B₅O₆ residue remains as the degradation product of the pentaborate salts. The thermal degradation steps and temperature ranges are detailed in Table 3.

The powder XRD patterns are shown in Figure 5. The red line curve represents 2-amino-5-nitropyridine pentaborate and the black line curve represents 2-amino-6-methylpyridine pentaborate. According to P-XRD data, the products are mostly crystalline, but the structures contain some amorphous regions. They include the main components boric acid and pentaborate salts. The compounds contain an amorphous residue in proportion of 9.4% and 8.9%, respectively. Similar results are seen in the ¹¹B NMR spectra of the compounds.

According to single-point BET analysis data, the surface area of 2-amino-5-nitropyridine pentaborate is 5.47 m²/g and 2-amino-6-methylpyridine

pentaborate is 3.15 m²/g.

Lastly, the hydrogen storage capacity of each compound was measured experimentally, and the results are shown in Figure 6 as graphical data and summarized in Table 4. Eventually, the storage capacities of the materials were 0.043 for 2-amino-5-nitropyridine pentaborate and 0.060 for 2-amino-6-methylpyridine pentaborate wt.%, while the values were 0.092 and 0.102 within the unit of g hydrogen/L adsorbent, respectively.

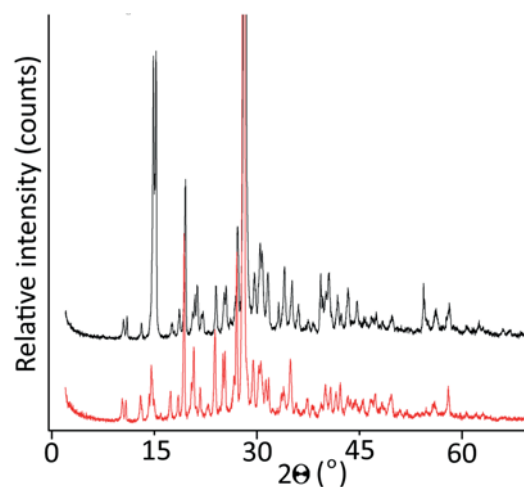
**Figure 5.** The powder XRD pattern of pentaborate salts: 2-amino-5-nitropyridine pentaborate (red line) and 2-amino-6-methylpyridine pentaborate (black line).

Table 4. The hydrogen storage data of pentaborate salts.

Hydrogen Storage	2-amino-5 nitropyridine pentaborate	2-amino-6-methylpyridine pentaborate
Mass (%)	0,043	0,06
Volumetric (g/ml)	0,092	0,102

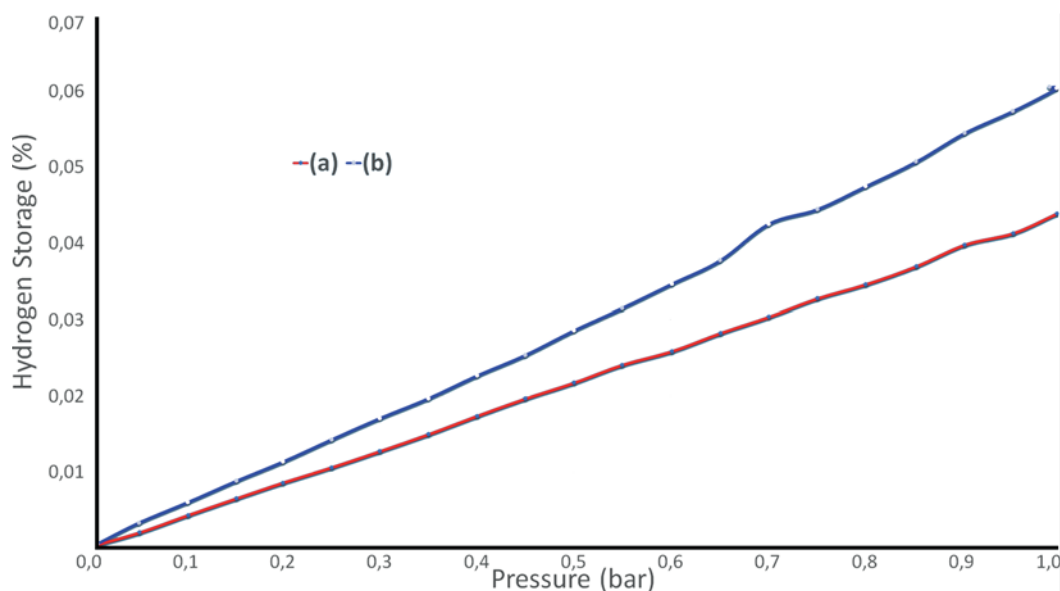


Figure 6. The hydrogen storage (mass %) graphic, (a) 2-amino-5 nitropyridine pentaborate and (b) 2-amino-6-methylpyridine pentaborate salts.

CONCLUSION

NMC pentaborate salts using amino pyridine derivatives, $[C_5H_5N_3O_2][B_5O_6(OH)_4]3H_2O$ and $[C_6H_8N_2][B_5O_6(OH)_4]2H_2O$, have been synthesized and characterized. The ^{11}B NMR spectra support to powder XRD pattern that the molecules include boric acid and pentaborate salt with organic cation. The final product, as a result of decomposition of pentaborate salts was obtained B_5O_8 . Thermal stability of these two salts is as follows: 6-aminopicoline pentaborate > 2-amino-5-nitropyridine pentaborate. The surface area of 2-amino-5-nitropyridine pentaborate is $5.47 \text{ m}^2/\text{g}$ and 6-aminopicoline pentaborate is $3.15 \text{ m}^2/\text{g}$ according to single point BET analysis.

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