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Short communication

Synthesis, characterization and thermodynamic properties of $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$

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ABSTRACT

The crystalline form of a new tetraborate, $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$ was synthesized and characterized. The enthalpies of solution of $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$ in approximately 1 mol dm^{-3} HCl(aq) and of CsCl in aqueous ($HCl + H_3BO_3 + NaCl$) were determined. From these results and the enthalpy of solution of H_3BO_3 in approximately 1 mol dm^{-3} HCl(aq), the enthalpy of solution of NaCl(s) in aqueous ($HCl + H_3BO_3$) and the standard molar enthalpies of formation of NaCl(s), CsCl(s), H_3BO_3(s) and H_2O(l), the standard molar enthalpy of formation for $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$ as being $-(5140.55 \pm 1.94)$ kJ mol^{-1}. The standard molar entropy of formation of $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$ was calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$ computed from a group contribution method.

1. Introduction

Since the discovery of the promising second harmonic generation properties of β-BaB_2O_4(BBO) [1] and LiB_3O_5(LBO) [2], the chemistry of borates has become of great interest to scientists due to their diverse industrial uses and rich structural chemistry. The studies of borate hydrates have been extensively explored in recent years and many new tetraborate hydrates have also been synthesized, the structure and thermal behavior being described [3–7]. All these compounds contain the $[B_4O_5(OH)_4]^{2-}$ tetraborate anion which is the same founding as the compound borax. Recently, our research group [8] synthesized a new hydrated double metal tetraborate $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$ and determined its crystal structure and studied its thermal behavior. But its physicochemical properties have not been studied.

Thermodynamic properties play very important roles in scientific researches and industrial applications. In previous work [9–15], the standard molar enthalpies of formation of some hydrated alkali metals borates and hydrated alkali earth metals borates were reported. The thermodynamic properties of some hydrated double metals borates were also studied [16–20]. As part of the systematic study of the thermochemistry of hydrated borates and hydrated double borates of alkali metals and alkali earth metals, this paper reports the standard molar enthalpies of formation, the calculated entropy of formation of $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$.

2. Experimental

2.1. Synthesis and characterization of $NaCs[B_4O_5(OH)_4]\cdot 4H_2O$

All chemical reagents used in synthesis were of analytical grade. Crystals of hydrated sodium cesium tetraborate were obtained from an aqueous solution of $CsB_5O_6\cdot 4H_2O$ and NaOH in a molar relation of 1/1, by slow evaporation of the solution at 30 °C (30 days) [8]. The uncolored and transparent crystals obtained were filtered and washed with redistilled water and ether, respectively, and dried at room temperature. The composition of the crystals was determined as follows: Na and Cs were analyzed by atomic absorption spectroscopy (Hitachi Z5000 atomic absorption spectrometer); B was determined by titration with a standard solution of NaOH in the presence of mannitol; H_2O content was determined by thermal dehydration. The powder X-ray diffraction data of the synthesized compound was obtained by using a Bruker D8 Advance equipment with Cu Kα radiation. TG–DTA curves were obtained on a Shimadzu DT-40 thermal analyzer in an air atmosphere with a heating rate of 10 °C/min. FT-IR spectra was recorded on a FTS-40 FT-IR spectrometer (Bio-Rad) using KBr pellets.

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Table 1
The powder X-ray diffraction data for compound.

d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
8.5611	29.4	4.1069	34.5	2.6269	19.6
8.2312	34.2	3.7411	19.9	2.5783	18.7
6.4397	17.7	3.3653	32.0	2.5468	28.5
6.0018	42.4	3.2045	82.0	2.5091	14.6
5.6123	18.4	3.0698	77.2	2.3517	15.5
5.2421	15.5	3.0298	100.0	2.0877	19.0
4.6976	32.6	2.9582	31.0	2.0577	17.4
4.5722	19.6	2.8266	16.8	2.0108	20.3
4.4441	94.3	2.7403	34.2	1.9515	35.4
4.3948	36.4	2.6743	17.1		

2.2. Calorimetric measurements

Thermochemical reaction used for getting the derivation of $\Delta_f H^{\circ}_m$ of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ is as follows:

$$NaCs[B_4O_5(OH)_4]{\cdot}4H_2O(s) + 2HCl(aq)$$

$$= NaCl(aq) + CsCl(aq) + 4H_3BO_3(aq) + H_2O$$

The standard molar enthalpy of formation of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of CsCl(s), NaCl(s), H_3BO_3(s) and H_2O(l). The H_3BO_3(s) and $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$(s) were each dissolved in approximately 1 mol dm^{-3} aqueous hydrochloric acid, the calculated amount of NaCl(s) was dissolved in aqueous ($HCl + H_3BO_3$) which consisted of approximately 1 mol dm^{-3} HCl(aq) and the calculated amount of H_3BO_3 and then the calculated amount of CsCl was dissolved in the former mixed solution ($HCl + H_3BO_3 + NaCl$).

The enthalpies of solution of H_3BO_3(s) in HCl(aq), and NaCl(s) in aqueous ($HCl + H_3BO_3$) were determined previously [21,13]. In this paper, we only determine $\Delta_f H^{\circ}_m$ of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ in HCl(aq) and of CsCl in aqueous ($HCl + H_3BO_3 + NaCl$). Both CsCl and NaCl (99.99% pure) were heated at 873 K for 3 h and stored in a desiccator. The H_3BO_3 (99.99% pure) was used as obtained. The HCl solution was prepared from azeotropic hydrochloric acid and redistilled water, and its concentration was determined by titration with standard sodium carbonate.

A RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used. The sensitivity of the instrument was measured through electrical calibration and the accuracy and precision were determined by chemical calibration. The calibration was repeated after each experiment and the average calibration constant was used. The temperature of the calorimetric experiments was 298.15 ± 0.005 K. A detailed description is found elsewhere [15,22]. The total time required for the complete reaction was about 1 h, depending on the samples. No solid residues were observed in the solution after the calorimetric experiments.

3. Results and discussion

3.1. Characterization of the synthetic sample

The analytical data of the compound is (calc.): Na_2O 7.46%(7.39%), Cs_2O 33.54%(33.62%), B_2O_3 33.18%(33.22%), H_2O 25.82%(25.77%). The data is consistent with the calculated values for the chemical formula can be written as $H_{12}NaCsB_4O_{13}$. The characteristic d values (I/I_0) are presented in Table 1. The IR spectrum of the compound is shown in Fig. 1. The absorption bands observed at 3584 and 3389 cm^{-1} are assigned to the stretching mode of the OH group. The band at 1630 cm^{-1} is due to the bending mode of this group. Thus, the compound contains crystallization water. The absorption bands observed at 1439, 1350 and 942 cm^{-1} are, respectively, attributed to the antisymmetric and symmetric stretching modes of the group B(3)–O [23]. The absorption bands observed in the region 1267–1133 cm^{-1} are due to the in-plane bending mode of the group B–O–H [23]. The absorption bands at 1066, 1002, 836 and 809 cm^{-1} are assigned to the antisymmetric and symmetric stretching modes of the group B(4)–O [23]. The bands at 711 and 685 cm^{-1} are due to the out-of-plane bending mode of the group B(3)–O [23]. The band observed at 601 cm^{-1} is characteristic for the tetraborate anion and the bands at 522 and 462 cm^{-1} are due to the bending mode of the group B(4)–O [23].

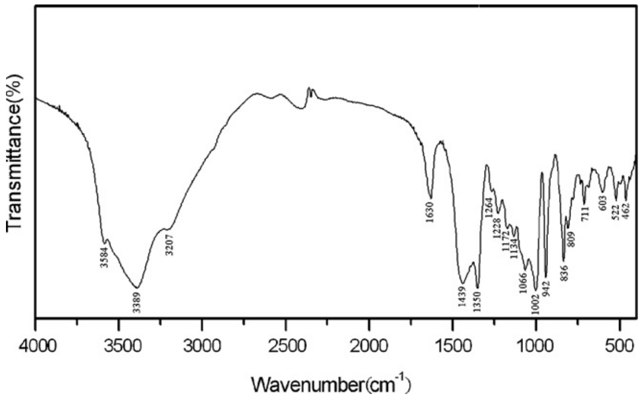

Fig. 1. The FT-IR spectrum of synthetic $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$.

TG–DTA curves (Fig. 2) show the weight loss (17.25%) in the range of 30–180 °C temperature range corresponded to the loss of four molecules of crystallization water (calculated, 17.18%). The total weight loss (25.82%) in the 30–400 °C temperature range corresponded to the loss of six water molecules (calculated, 25.77%).

All these results showed that the synthesized compound is pure and has the general formula $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ and it is suitable for calorimetric measurements.

3.2. Results of the calorimetric experiment

The molar enthalpies of solution of CsCl in aqueous ($HCl + H_3BO_3 + NaCl$) measured at 298.15 K was 17.23 ± 0.25 kJ mol^{-1} ($n = 5$) (Table S1 in Supplementary data files), where the uncertainty is twice the standard deviation of the mean. The molar enthalpies of solution of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ in approximately 1 mol dm^{-3} HCl(aq) at 298.15 K was 59.69 ± 0.22 kJ mol^{-1} ($n = 5$) (Table S2 in Supplementary data files). Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpies of formation of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$. The molar enthalpies of solution of H_3BO_3(s) of (21.83 ± 0.08) kJ mol^{-1} in approximately 1 mol dm^{-3} HCl(aq), and of NaCl(s) of $-(5.14 \pm 0.02)$ kJ mol^{-1} in

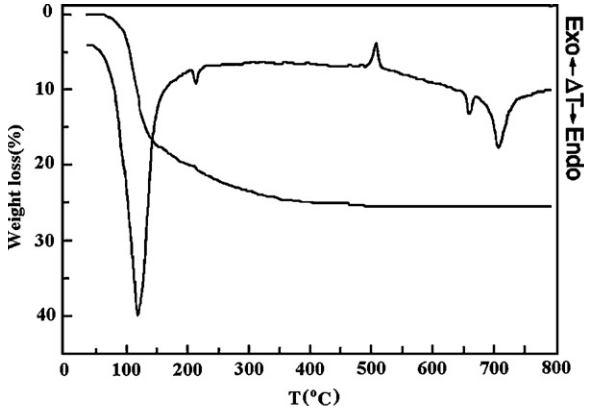

Fig. 2. DTA and TG curves for $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$.

Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H^\circ_m$ ($NaCsB_4O_7{\cdot}6H_2O$, 298.15 K).

Reaction		$\Delta_f H_m$ ($kJ\,mol^{-1}$)
$NaCsB_4O_7{\cdot}6H_2O(s) + 81.776(HCl{\cdot}53.230H_2O) = Na^+(aq) + Cs^+(aq) + 2Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl{\cdot}54.577H_2O)$	(1)	59.69 ± 0.22
$4H_3BO_3(aq) + 79.776(HCl{\cdot}54.577H_2O) = 4H_3BO_3(s) + 79.776(HCl{\cdot}54.577H_2O)$	(2)	−87.32 ± 0.32
$Na^+(aq) + Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl{\cdot}54.577H_2O) = NaCl(s) + 4H_3BO_3(aq) + 79.776(HCl{\cdot}54.577H_2O)$	(3)	−5.14 ± 0.02
$Na^+(aq) + Cs^+(aq) + 2Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl{\cdot}54.577H_2O) = CsCl(s) + Na^+(aq) + Cl^-(aq) + 4H_3BO_3(aq) + 79.776(HCl{\cdot}54.577H_2O)$	(4)	−17.23 ± 0.25
$81.776(HCl{\cdot}54.577H_2O) = 81.776(HCl{\cdot}53.230H_2O) + 110.154H_2O(l)$	(5)	2.19 ± 0.04
$H_2(g) + Cl_2(g) + 109.154H_2O(l) = 2(HCl{\cdot}54.577H_2O)$	(6)	−330.86 ± 0.20
$CsCl(s) = Cs(s) + (1/2)Cl_2(g)$	(7)	443.04 ± 0.10
$NaCl(s) = Na(s) + (1/2)Cl_2(g)$	(8)	411.15 ± 0.10
$4H_3BO_3(s) = 4B(s) + 6H_2(g) + 6O_2(g)$	(9)	4379.20 ± 3.20
$H_2O(l) = H_2(g) + (1/2)O_2(g)$	(10)	285.83 ± 0.04
$NaCsB_4O_7{\cdot}6H_2O(s) = Na(s) + Cs(s) + 4B(s) + 6H_2(g) + (13/2)O_2(g)$	(11)	5140.55 ± 1.94[a,b]

[a] $\Delta_f H^\circ{}_m = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \Delta_r H_4 + \Delta_r H_5 + \Delta_r H_6 + \Delta_r H_7 + \Delta_r H_8 + \Delta_r H_9 + \Delta_r H_{10}$.

[b] Uncertainty is twice the standard deviation of the mean.

the mixture of HCl and H_3BO_3 were taken from our previous works [21,13]. The standard molar enthalpies of formation of $H_2O(l)$, NaCl(s), CsCl(s) and $H_3BO_3(s)$ were taken directly from the CODATA Key Values [24], namely −(285.83 ± 0.04), −(411.15 ± 0.10), −(443.04 ± 0.10) and −(1094.8 ± 0.80) $kJ\,mol^{-1}$, respectively. The standard molar enthalpy of formation of HCl(aq) and the enthalpy of dilution of HCl(aq) were calculated from the data in NBS tables [25], respectively. From these data, applying Hess's law, the standard molar enthalpy of formation of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ was calculated to be −(5140.55 ± 1.94) $kJ\,mol^{-1}$, according to the following equation:

$$\Delta_f H^\circ_m = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \Delta_r H_4 + \Delta_r H_5 + \Delta_r H_6 + \Delta_r H_7 + \Delta_r H_8 + \Delta_r H_9 + \Delta_r H_{10}$$

The enthalpy of formation of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ can also be estimated by a group contribution method [23], which can be expressed as shown in following equation: $\Delta_f H^\circ{}_m(NaCs[B_4O_5(OH)_4]\cdot 4H_2O, s) = \Delta_f H^\circ_m(Na^+, aq) + \Delta_f H^\circ_m(Cs^+, aq) + \Delta_f H^\circ{}_m([B_4O_5(OH)_4]^{2-}, aq) + 4\Delta_f H^\circ{}_m(H_2O)$in which, the $\Delta_f H^\circ{}_m$ for $[B_4O_5(OH)_4]^{2-}$ and H_2O have the values of −3464.46 and −290.42 $kJ\,mol^{-1}$, respectively [21]. The $\Delta_f H^\circ{}_m$ of −240.12 and −251.17 $kJ\,mol^{-1}$ for Na^+ and Cs^+, respectively were taken from the NBS tables [25]. The calculated standard molar enthalpy of formation is −5124.54 $kJ\,mol^{-1}$. The relative error is 0.311%.

We also used a group contribution method to calculate $\Delta_f G^\circ{}_m$ of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ to be −4599 $kJ\,mol^{-1}$ according to the following equation:

$$\Delta_f G^\circ{}_m(NaCs[B_4O_5(OH)_4]\cdot 4H_2O, s) = \Delta_f G^\circ{}_m(Na^+, aq) + \Delta_f G^\circ{}_m(Cs^+, aq) + \Delta_f G^\circ{}_m([B_4O_5(OH)_4]^{2-}, aq) + 4\Delta_f G^\circ{}_m(H_2O)$$

in which the values −3095.99 and −237.28 $kJ\,mol^{-1}$ for the $\Delta_f G^\circ{}_m$ of $[B_4O_5(OH)_4]^{2-}$ and H_2O, respectively were taken from the literature [26], and the $\Delta_f G^\circ{}_m$ of −261.91 and −292.02 $kJ\,mol^{-1}$ for Na^+ and Cs^+, respectively were taken from the NBS tables [25]. Combining the $\Delta_f H^\circ{}_m$ of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$, the standard molar entropy of formation of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ has been calculated to be −1816.300 $J\,mol^{-1}\,K^{-1}$ according to following equation:

$$\Delta_f S^\circ{}_m = \frac{\Delta_f H^\circ_m - \Delta_f G^\circ_m}{T}$$

Finally, the standard molar entropy of $NaCs[B_4O_5(OH)_4]{\cdot}4H_2O$ was calculated otherwise to be 459.94 $J\,mol^{-1}\,K^{-1}$ according to reaction (11) in Table 2. The standard molar entropies of the elements were taken from the NBS tables [25] to be (51.21, 85.23, 5.86, 130.68, and 205.14) $J\,mol^{-1}\,K^{-1}$ for Na(s), Cs(s), B(s), $H_2(g)$, and $O_2(g)$, respectively.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.11.003.

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