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Short communication

Thermochemistry of dicesium calcium tetraborate octahydrate

Zhu Lixia[a,*], Yue Tao[b], Gao Shiyang[b]

[a] *School of Science, Xidian University, 2 Taibai South Road, Xi'an 710071, PR China*
[b] *Xi'an Branch, Institute of Salt Lakes, Academic, Sinica, Xi'an 710043, PR China*

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Abstract

The enthalpies of solution of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid and of CsCl(s) in aqueous (hydrochloric acid + boric acid + calcium oxide) were determined. From these results and the enthalpies of solution of $H_3BO_3(s)$ in approximately 1 mol dm^{-3} HCl(aq) and of CaO(s) in aqueous (hydrochloric acid + boric acid), the standard molar enthalpy of formation of $-(10328 \pm 6)$ kJ mol^{-1} for $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$ was obtained from the standard molar enthalpy of formation of CaO(s), CsCl(s), $H_3BO_3(s)$ and $H_2O(l)$. The standard molar entropy of formation of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$ was calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$ computed from a group contribution method.

Keywords: $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution; Aqueous hydrochloric acid solution

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1. Introduction

The best-known cesium mixed borate is $CsLiB_6O_{10}$ [1,2] because it has no absorbance in a wide UV region. Its properties, structure and Raman spectrum were investigated by Mori and co-workers in 1995 [3] and Wang et al. in 1999 [4]. In previous papers, thermochemical properties of calcium mixed pentaborate Ulexite ($NaCaB_5O_6(OH)_6\cdot 5H_2O$) [5], calcium mixed tetraborate $K_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ [6] and $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ [7] have been reported. In this paper, calcium mixed tetraborate $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ was synthesized for the first time. The standard molar enthalpy of formation $\Delta_f H_m^0$ of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$ has been determined by solution calorimetry, and other thermochemical parameters have been calculated.

2. Experimental

All the reagents used in the synthesis of the compound were analytic grade. 32.1 g of a Cs_2CO_3 (Jiangxi Lithium Factory, China) and 26.5 g of a H_3BO_3 were dissolved in approximately 150 ml H_2O. After CO_2 evolution, the above solution was mixed with 11.5 g of $CaCl_2$ to form an amorphous precipitate, the mixture was stirred during 20 min at 75 °C and following by the resting of the mixture at room temperature. The crystallization begins in a few days. Large single crystals are obtained after 60 days. The product was analyzed according to standard methods as follows: calcium was titrated by a standard solution of Na–EDTA in a basis medium by the addition of a buffer solution (pH 9.56). Boron was determined by titration with a standard solution of NaOH in the presence of mannitol. Cesium was determined as $CsB(C_6H_5)_4$ by a gravimetric method. H_2O content was determined by thermal dehydration. The powder X-ray diffraction data (Fig. 1) of the synthesized compound was obtained with a Rigaku D/MAX-2400 with Cu Kα radiation ($\lambda = 1.5418$ Å). Thermogravimetric analysis (TGA) and DSC were conducted on a NETZSCH-Geratebau STA 449c in a flow of N_2 with a heating rate of 10 °C min^{-1}. FT-IR spectra (Fig. 2) was recorded in the 4000–400 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer using KBr pellets. The analytical data, observed/calculated (mass%): Cs_2O 33.80/33.86, CaO 6.76/6.73, B_2O_3 33.45/33.46, H_2O 25.87/25.95, showed that the compound obtained is pure and has the general formula $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ and is suitable for calorimetric measurements.

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[*] Corresponding author. Tel.: +86 29 88202635.
E-mail address: zhulx@isl.ac.cn (Z. Lixia).

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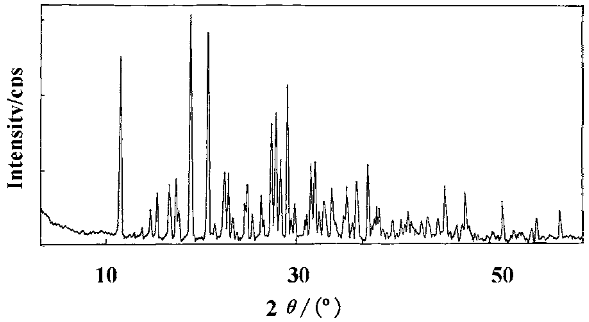

Fig. 1. The XRD of synthetic $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$.

Thermochemical reaction derivation for $\Delta_f H_m^0$ of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ was:

$$Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(cr) + 4HCl(aq) = 2CsCl(aq) + CaCl_2(aq) + 8H_3BO_3(aq) + 2H_2O(l) \quad (1)$$

The standard molar enthalpy of formation of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ was obtained by solution calorimetry in combination with the standard molar enthalpies of formation of CsCl(s), CaO(s), H_3BO_3(s) and H_2O(l). Approximately 6 mg of H_3BO_3(s) and 10 mg of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$(s) were each dissolved in 2 cm^3 of 0.9972 mol dm^{-3} aqueous hydrochloric acid, 0.7 mg of CaO(s) was dissolved in aqueous (hydrochloric acid + boric acid) which consisted of 0.9972 mol dm^{-3} HCl(aq) and 6.16 mg of H_3BO_3, and then 4.20 mg of CsCl(s) was dissolved in this latter solution (hydrochloric acid + boric acid + calcium oxide).

High-purity CaO (mass fraction >0.9999, PR China) was heated at 1098 K during 3 h, and stored in a desiccator. The CaO was sealed in glass ampoules inside a glove box containing P_2O_5 as a drying agent. Before sealing, high-purity Ar gas was admitted to the glove box to expel the air. The CsCl (mass fraction >0.9999, PR China) was heated at 873 K during 3 h and stored in a desiccator. The H_3BO_3 (mass fraction >0.9999, PR China) was used without further purification. The HCl standard solution was prepared from azeotropic hydrochloric acid and deionized water, and its concentration determined by titration with standard borax. An RD496-III Microcalorimeter was used [8].

3. Results and discussion

To check the performance of the RD496-III microcalorimeter, the enthalpy of solution of KCl (mass fraction >99.99%) in deionized water at 295.15 K was measured. The experimental value 17.24 ± 0.06 kJ mol^{-1} is in good agreement with the value 17.241 ± 0.018 kJ mol^{-1} reported in the literature [9].

The measured heats of solution are $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$,112.68 ± 0.19 kJ mol^{-1} ($n = 5$) and CsCl, 17.63 ± 0.04 kJ mol^{-1} ($n = 5$) where the uncertainty is twice the standard deviation of the mean. Table 1 gives the thermochemical cycle for the derivation of the standard molar enthalpies of formation of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$(s). The molar enthalpies of solution of H_3BO_3(s), 21.83 ± 0.08 kJ mol^{-1} in approximately 1 mol dm^{-1} HCl(aq) and of CaO(s), −(188.63 ± 0.88) kJ mol^{-1} in the mixture of HCl and H_3BO_3 were taken from our previous work [10,11]. The standard molar enthalpies of formation of H_2O(l), CaO(s), and H_3BO_3(s) were taken from CODATA Key Values [12], namely −(285.830 ± 0.04), −(643.9 ± 0.9) and −(1094.8 ± 0.8) kJ mol^{-1}, respectively. The standard molar enthalpies of dilution of HCl(aq) and enthalpies of formation of CsCl(s) and HCl(aq) were taken from the NBS tables [13]. The calculated standard molar enthalpies of formation of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$(s) is −(10328 ± 6) kJ mol^{-1}. Applying a group contribution method developed by Li et al. [14] for the calculation of thermodynamic properties of hydrated borates, we calculated $\Delta_f H_m^0$ of the $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$(s) to be −10311.67 kJ mol^{-1}, which agrees with the experimental result. Because no experimental data on $\Delta_f G_m^0$ of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$(s) are available, we used a group contribution method to calculate $\Delta_f G_m^0$ of the $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$(s), −9227.80 kJ mol^{-1}.

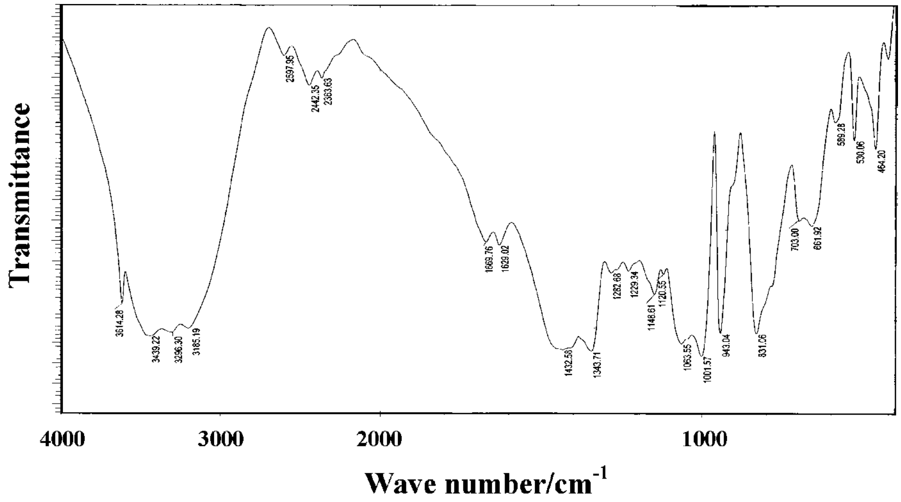

Fig. 2. The FT-IR spectrum of synthetic $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$.

Table 1
Thermochemical cycle and results $\Delta_f H_m^0$ of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$, $T = 298.15\,K$

Reaction	$\Delta_r H_m$ ($kJ\,mol^{-1}$)
1. $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s) + 156.73(HCl\cdot 55.828H_2O) = 2Cs^+(aq) + Ca^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 152.73(HCl\cdot 57.303H_2O)$	112.68 ± 0.19
2. $8H_3BO_3(aq) + 156.73(HCl\cdot 55.828H_2O) = 8H_3BO_3(s) + 156.73(HCl\cdot 55.828H_2O)$	−174.64 ± 0.64
3. $Ca^{2+}(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 154.73(HCl\cdot 56.556H_2O) = CaO(s) + 8H_3BO_3(aq) + 156.73(HCl\cdot 55.828H_2O)$	188.63 ± 0.88
4. $2Cs^+(aq) + Ca^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 154.73(HCl\cdot 56.556H_2O) = 2CsCl(s) + Ca^{2+}(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 154.73(HCl\cdot 56.556H_2O)$	−35.26 ± 0.08
5. $152.73(HCl\cdot 57.303H_2O) = 152.73(HCl\cdot 56.556H_2O) + 114.089H_2O(l)$	2.24 ± 0.08
6. $H_2(g) + Cl_2(g) + 113.112H_2O(l) = 2(HCl\cdot 56.556H_2O)$	−330.86 ± 0.20
7. $2CsCl(s) = 2Cs(s) + Cl_2(g)$	886.08 ± 0.32
8. $CaO(s) = Ca(s) + (1/2)O_2(g)$	634.92 ± 0.90
9. $8H_3BO_3(s) = 8B(s) + 12H_2(g) + 12O_2(g)$	8758.40 ± 6.40
10. $H_2O(l) = H_2(g) + (1/2)O_2(g)$	285.83 ± 0.04
11. $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s) = 2Cs(s) + Ca(s) + 8B(s) + 12H_2(g) + 13O_2(g)$	10328.02 ± 6.57

Combining with the standard molar enthalpy of formation of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$, the standard molar entropy of formation of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$ is $-3690.16\,JK^{-1}\,mol^{-1}$.

This latter value allows estimation of the standard molar entropy of $Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s)$, $801.50\,JK^{-1}\,mol^{-1}$ on the basis of the following reaction.

$$2Cs(s) + Ca(s) + 8B(s) + 12H_2(g) + 13O_2(g) = Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s) \qquad (2)$$

The standard molar entropies of the elements were taken from CODATA Key Values as 85.23, 41.59, 5.90, 130.571, and $205.043\,JK^{-1}\,mol^{-1}$ for Cs(s), Ca(s), B(s), $H_2(g)$, and $O_2(g)$, respectively.

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