Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 441 (2006) 199–202

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Synthesis, heat capacity and enthalpy of formation of $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O$

Xin-Min Wu[a], Zhi-Cheng Tan[b,*], Xue-Chuan Lv[b], Song-Sheng Qu[c]

[a] *Department of Materials and Chemical Engineering, Beijing Institute of Petro-chemical Technology, Beijing 102617, PR China*
[b] *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*
[c] *Department of Chemistry, College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, PR China*

Received 11 May 2005; received in revised form 9 November 2005; accepted 14 November 2005
Available online 20 December 2005

Abstract

A complex of holmium perchlorate coordinated with L-glutamic acid, $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O$, was prepared with a purity of 98.96%. The compound was characterized by chemical, elemental and thermal analysis. Heat capacities of the compound were determined by automated adiabatic calorimetry from 78 to 370 K. The dehydration temperature is 350 K. The dehydration enthalpy and entropy are $16.34\,\mathrm{kJ\,mol^{-1}}$ and $16.67\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. The standard enthalpy of formation is $-6474.6\,\mathrm{kJ\,mol^{-1}}$ from reaction calorimetry at 298.15 K.

Keywords: Solution-reaction calorimetry; Complexes of rare earth; L-Glutamic acid; $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O$; Heat capacity; Standard enthalpy of formation

1. Introduction

Rare earth complexes have been extensively investigated in recent decade. However, basic thermochemistry data on rare earth complexes with amino acids were rarely reported. In this work, crystals of $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O$ have been synthesized and characterized. The standard molar enthalpies of formation, $\Delta_f H_m^{\Theta}$, and reaction, $\Delta_r H^{\Theta}$, of the complexes have been determined with reaction calorimetry. Molar heat capacity, $C_{p,m}$, was measured with a high-precision automated, adiabatic calorimeter.

2. Experimental

2.1. Synthesis and characterization of the complex

2.1.1. $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O$

Twenty millimoles Ho_2O_3 (99.95%) was dissolved in $HClO_4$ (analytic grade), and distilled water was added to 100 mL. Then L-glutamic acid (20 mmol) was added and stirred with pH = 3.5. The mixed solution was stirred for 3 h at 313 to 323 K, concentrated by evaporation, cooled, and filtered. Crystals appeared after a month of natural evaporation at room temperature. The crystals were dried till constant weight [1]. The product $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O$ was 5.5 g, with a purity of 98.96%.

2.1.2. $HoCl_3$

Ho_2O_3 (2.103 g) was dissolved in HCl at the mole ratio 1:1. After concentrating by evaporation, the rare-earth chloride was filtered, crystallized, washed with alcohol, and re-crystallized. Finally, the collected crystals were desiccated in a dryer until the mass became constant [2].

Relative content of C, H, N in the complexes was determined by elemental analysis and relative content of element Ho was determined by EDTA titration. Thermal analysis was done with a TGA/SDTA851^e (Mettler Toledo, Sweden) and a DTA-1700 (P.E. Perkia-Elmer, American). Melting point of the sample was obtained with binocular melting point stereometer (XT4, Taike, Beijing). $HoCl_3$ was also analyzed by thermogravimetry and differential thermal analyzer. The rare-earth content was measured with EDTA titration.

From the result of five groups data obtained by using EDTA titration in the same condition, the purity was known as 98.96%. The solid complex did not have a fixed melting point from room

---

[*] Corresponding author. Tel.: +86 411 84379199; fax: +86 411 84691570.
E-mail address: tzc@dicp.ac.cn (Z.-C. Tan).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.11.021

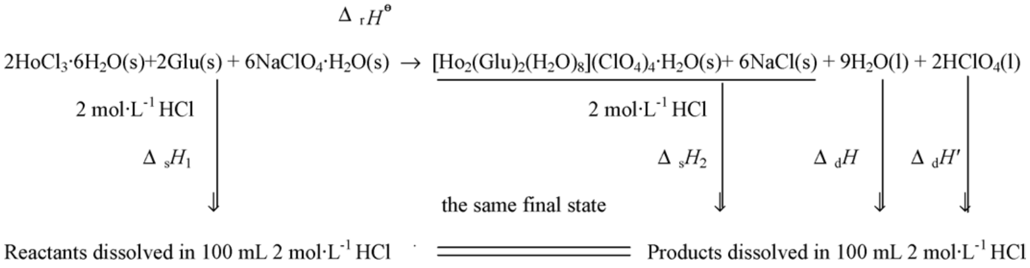

Fig. 1. The thermochemical cycles for measuring the standard molar enthalpy of reaction ($\Delta_r H^\Theta$).

temperature to 593 K. The color of the complex was bright yellow at room temperature, but at the range of 533–553 K it changed to be saffron and charred above 593 K. The constitution found was Ho (27.62%), C (10.16%), N (2.37%) and H (2.89%), in agreement with theoretical calculated result, Ho (27.91%), C (10.11%), N (2.89%) and H (2.92%). By TG and DTA, two endothermal peaks at 341–372 K (peak value at 357.7 K) and 383–473 K (peak value at 441.7 K) and an exothermal one at 483–533 K (peak value at 521.9 K) were observed with weight loss of 6.26, 7.83 and 42.89%, respectively. The total weight loss of the first two steps, 14.09%, corresponds with loss of nine water molecules, four at first and five at second. The weight loss in the third period was possibly the oxidation of L-glutamic acid by perchlorate.

The synthesized $HoCl_3$ was analyzed by TG and chemical analysis to give 27.8% water in the sample, i.e. $HoCl_3 \cdot 6H_2O$.

2.2. *Calorimetric methods*

2.2.1. $\Delta_f H^\Theta$ *at 298 K*

2.2.1.1. Thermodynamic cycle. Reaction scheme for the $\Delta_f H^\Theta$ of $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4 \cdot H_2O$ at 298.15 K at atmospheric pressure was designed as follows:

$$2HoCl_3\cdot 6H_2O(s) + 2\text{l-Glu}(s) + 6NaClO_4\cdot H_2O(s) \rightarrow [Ho_2(\text{l-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O(s) + 6NaCl(s) + 9H_2O(l)$$

It was found that the reactants and products could be dissolved in 2 mol L^{-1} HCl to give the same final state. If the dissolution enthalpies of reactants and products were determined, $\Delta_r H^\Theta$ and $\Delta_f H^\Theta$ of $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4 \cdot H_2O$ can be obtained by the chemical cycle in Fig. 1.

According to the Hess law:

$$\Delta_r H^\Theta = \Delta_s H_1 - \Delta_s H_2 - \Delta_d H - \Delta_d H'$$

where $\Delta_d H$ is enthalpy of dilution of 0.0205 g water added into 100 mL 2 mol L^{-1} HCl. $\Delta_d H'$ is enthalpy of dilution of 0.0255 g $HClO_4$ added into the solution of 100 mL 2 mol L^{-1} HCl and 0.0205 g H_2O.

2.2.1.2. Enthalpies of solution, $\Delta_s H_1$, $\Delta_s H_2$. A solution-reaction isoperibol calorimeter constructed in the Thermochemistry Lab. of Wuhan University was used to determine the enthalpies of dissolution. To verify the reliability of the calorimeter, the molar enthalpy of solution of KCl (Standard Reference Material 1655, the National Institute of Standard and Technology), in double-distilled water was measured at 298.15 K. The uncertainty and inaccuracy were within ±0.5% [3].

Reactants and products according to their ratio in the chemical reaction equation, $HoCl_3 \cdot 6H_2O$: 0.0961 g, L-Glu: 0.0373 g, $NaClO_4 \cdot H_2O$: 0.106 g, NaCl: 0.0444 g and $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4 \cdot H_2O$: 0.1500 g, were weighed and put into sample cell under normal pressure at 298.15 K. The temperature change was monitored with dc electronic bridge and recorder, energy equivalent was by electrical standardization [4].

2.2.2. $C_{p,m}$ *at 78–370 K*

The low-temperature heat capacity of the complex was measured with an adiabatic calorimeter, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The instrument has been described in detail elsewhere [5]. The working temperature was 78–370 K. The reliability of the calorimeter was verified by measuring the molar heat capacity of α-Al_2O_3. The deviation of the calibration data from those of NIST was within ±0.1%. The temperature increments of the experiment point were between 2 and 4 K; the heating duration was 25 min and the temperature drift rates in an equilibrium period were within 10^{-4} K min^{-1}[6].

3. Results and discussion

3.1. $\Delta_f H^\Theta$ *at 298 K*

3.1.1. *Enthalpy of dilution,* $\Delta_d H$

Dilution enthalpy of 0.0205 g water added into 100 mL 2 mol L^{-1} HCl (the mol concentration of mass is 2.1573 mol kg^{-1}) was obtained from [7].

$\Delta_d H_{2.1573\rightarrow 2.1568} = \Delta_d H_{2.1573\rightarrow 0} - \Delta_d H_{2.1568\rightarrow 0} = (\varphi_{L(2.1573)} - \varphi_{L(2.1568)}) \times 0.2 \times 4.184 = -(659.8585\text{–}659.7488) \times 0.2 \times 4.184 \times 10^{-3}$ kJ = −0.092 J.

3.1.2. *Enthalpy of dilution,* $\Delta_d H'$

The $HClO_4$ concentration is 0.00274 mol kg^{-1} when 0.0255 g $HClO_4$ was added into the solution of 100 mL 2 mol L^{-1} HCl and 0.0205 g H_2O. According to [7], $\Phi_L = 91.838$ J mol^{-1}, and $\Delta_d H_m{}' = -\Phi_L = -91.838$ J mol^{-1}.

$\Delta_f H_m^\Theta$ $HClO_4(l) = -40.585$ kJ mol^{-1}, $\Delta_f H_m^\Theta$ $HClO_4(aq, \infty) = -129.327$ kJ mol^{-1}, and $\Delta H(l)$ $[-129.327 - (-40.585) \times 10^3]$ J $mol^{-1} = -88.742 \times 10^3$ J mol^{-1}, and $\Delta_d H' = [(-88.742 \times 10^3 + 91.838) \times 0.0255/100.4586]$ J = −22.503 J.

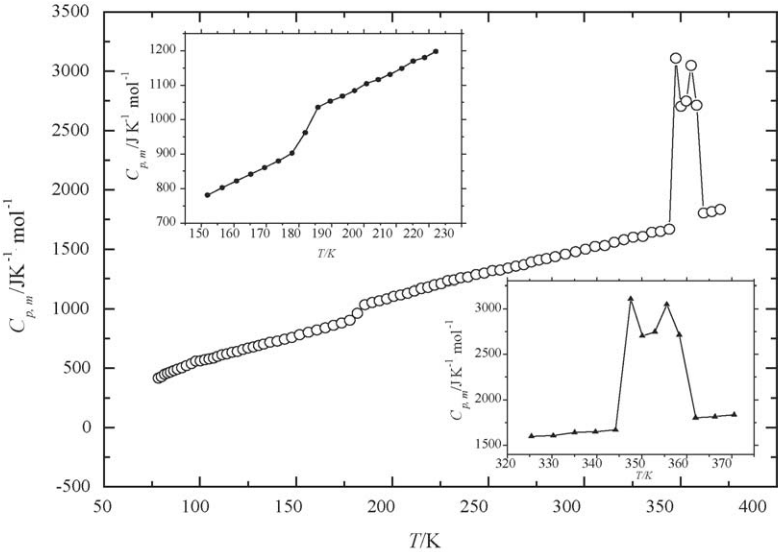

Fig. 2. Experimental molar heat capacity plotted against temperature of $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$.

3.1.3. Enthalpies of solution, $\Delta_s H_1$, $\Delta_s H_2$

Dissolution enthalpies of the reactants, $\Delta_s H_1$, $HoCl_3{\cdot}6H_2O$, L-Glu, $NaClO_4{\cdot}H_2O$ ($n_{HoCl_3\cdot 6H_2O} : n_{\text{L-Glu}} : n_{NaClO_4\cdot H_2O}$ = 2:2:6); in 100 mL, 2 mol L^{-1} HCl (298.15 K, R = 1350.3 Ω, I = 9.997 mA) were calculated to be $\Delta_s H_1 = (12.566 \pm 0.019)$ J from the average of five experiments.

Dissolution enthalpies of the products, $\Delta_s H_2$, $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$, NaCl($n_{[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4\cdot H_2O} : n_{NaCl}$ = 1:6) in 100 mL, 2 mol L^{-1} HCl + 0.0205 g H_2O (298.2 K, R = 1350.3 Ω, I = 9.997 mA) $\Delta_s H_2 = (3.773 \pm 0.014)$ J from the average of five experiments.

$$\begin{aligned}\Delta_r H^{\Theta} &= \Delta_s H_1 - \Delta_s H_2 - \Delta_d H - \Delta_d H' \\ &= [12.566 - 3.773 + 0.092 + 22.503]\,\text{J} \\ &= 31.388\,\text{J}.\end{aligned}$$

If 0.1500 g $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$ was used in the measurement, then $\Delta_r H_m^{\Theta} = 247.348$ kJ mol^{-1}.

$\Delta_r H_m^{\Theta} = \Delta_f H_m^{\Theta}$ ($[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$, s, 298.15 K) + $6\Delta_f H_m^{\Theta}$ (NaCl, s, 298.15 K) + $9\Delta_f H_m^{\Theta}$ (H_2O, l, 298.15 K) + $2\Delta_f H_m^{\Theta}$ ($HClO_4$, l, 298.15 K) − $2\Delta_f H_m^{\Theta}$ ($HoCl_3{\cdot}6H_2O$, s, 298.15 K) − $2\Delta_f H_m^{\Theta}$ (L-Glu, s, 298.15 K) − $6\Delta_f H_m^{\Theta}$ ($NaClO_4{\cdot}H_2O$, s, 298.15 K).

From [8], the values listed in Table 1, $\Delta_f H_m^{\Theta}$ was determined to be $\Delta_f H_m^{\Theta}$ ($[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$, s, 298.15 K) = (−6474.6 ± 6.4) kJ mol^{-1}.

Table 1
$\Delta_f H_m^{\Theta}$ (kJ mol^{-1}) of the pure substances at 298.15 K

NaCl (s)	−411.12
H_2O (l)	−285.83
$HClO_4$ (l)	−40.585
$HoCl_3{\cdot}6H_2O$ (s)	−2878.2
L-Glu (s)	−1009.7
$NaClO_4{\cdot}H_2O$ (s)	−677.77

3.2. $C_{p,m}$ at 78–370 K

A plot of experimental $C_{p,m}$ against temperature (T) is shown in Fig. 2 and listed in supplementary data tables. The curve was smooth and ascending over the temperature range from 78 to 344 K, except where a structure change occurred from 177 to185 K. The endothermic peak from 344 to 362 K was caused by loss of four coordinated water molecules from $[Ho_2(\text{L-Glu})_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$ molecule.

Two polynomials equations were obtained from the molar heat capacities by the least square fitting.

From 78 to 177 K
$C_{p,m}$ (J K^{-1} mol^{-1}) = $679.724 + 200.909x + 10.083x^2 + 40.029x^3 - 30.299x^4$, where $x = (T - 128)/50$, and relative coefficient R = 0.9994.

From 185 to 344 K
$C_{p,m}$ (J K^{-1} mol^{-1}) = $1362.083 + 295.923x + 1.8507x^2 + 23.556x^3 - 13.244x^4$, where $x = (T - 265)/79$, and relative coefficient R = 0.9995.

The compound dehydration temperature was 350 K, dehydration enthalpy change and dehydration entropy change were determined to be 16.34 kJ mol^{-1} and 46.69 J mol^{-1} K^{-1}, respectively, by integrating the dehydration peak.

Thermodynamic functions $[H_T - H_{298.15}]$ and $[S_T - S_{298.15}]$ were calculated in the temperature range from T = 80 to 370 K with a temperature interval of 5 K and listed in supplementary data tables.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (NSFC No. 20373072) and the Elitist financial support of Beijing Organization of Chinese (Z03-10).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.tca.2005.11.021.

References

[1] I. CsÖregh, M. Czugler, P. Kierkegaard, et al., Acta Chem. Scand. 43 (1989) 735–747.

[2] W. Zeng-Lin, N. Chun-Ji, H. Ning-Hai, et al., J. Chin. Rare Earth Soc. 12 (1) (1994) 1–5.

[3] W. Chen-Xin, S. Zhou-Hua, X.ET-AL> Win-Gao, Acta Phys.-Chim. Sinica 7 (5) (1991) 586–588.

[4] W. Xin-Ming, L. Yi, L. Lin, L. Ping, et al., Acta Chim. Sinica 59 (9) (2001) 1396–1400.

[5] T. Zhi-Cheng, Z. Li-Xing, C. Su- Xia, et al., Sci. China Ser. B 6 (1983) 497–503.

[6] T. Zhi-Cheng, T. Matsuo, H. Suga, et al., Sci. China Ser. B 27 (2) (1997) 170–180.

[7] R.C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Florida, 1989, D-121.

[8] J.A. Dean, Lange’s Handbook of Chemistry, vol. 9–2, 12th ed., McGraw-Hill Book Co., New York, 1979, pp. 9–71.