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Low-temperature heat capacity and thermal decomposition of crystalline $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$

Xiaozheng Lan, Zhi-Cheng Tan*, Beiping Liu, Zhaodong Nan, Lixian Sun, Fen Xu

Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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Abstract

The heat capacities of rare earth complex with amino acid histidine, $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$, were measured with an automatic adiabatic calorimeter from 79 to 320 K. It was found that there was a sudden increment in heat capacity within the temperature range 182–190 K. Thermal decomposition behavior of the complex in nitrogen atmosphere was studied by thermogravimetric (TG) analysis, and a possible decomposition mechanism was suggested according to TG–DTG results.

Keywords: Adiabatic calorimeter; Heat capacity; Histidine rare earth complex; TG analysis; Thermal decomposition

1. Introduction

Rare earth elements have found their applications in many areas nowadays because of their unique properties, and they are used as the main components of permanent magnets, catalysts, glass ceramics and so on [1]. In recent years, they are also being introduced into microfertilizer, pesticide [2] and antibacterial agent [3]. Accompanying these applications, rare earth elements inevitably spread into the food chain, the biological chain and then into the bodies of human beings. This leads people to care about and study the influence and the long-term effect of rare earth elements on themselves [4]. Rare earth complexes formed with amino acid were then synthesized for this purpose, because amino acid is the basic unit comprising protein and enzyme, the functional materials in the body of animals. In the last 20 years, nearly 200 kinds of these complexes have been synthesized, and about 50 kinds of them have their own crystallograms [5]. However, low-temperature heat capacities and thermodynamic properties of these compounds have seldom been reported. As we all know, only with these data can we quantitatively from energetics describe their characteristics, for example, stable forms in different temperature range, melting process, thermal anomaly and so on. Comparisons of these data for a series of complexes comprised by the same RE (or ligands) with different ligands (or RE) may enable us to have a deeper understanding of their properties.

In the present study, we report the low-temperature heat capacities of the complex $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ in the temperature range 79–320 K. The thermal stability of the complex was studied by TG analysis in the range 25–870 °C. The possible decomposition mechanism of the complex was suggested according to TG–DTG analysis.

2. Experimental

2.1. Sample synthesis and characterization

$[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ was synthesized by using the reported procedure [6]: rare earth oxide (Er_2O_3, ≥99.9% pure) was dissolved in perchloric acid to form the aqueous solution of the rare earth perchlorate. Then histidine was added to the solution with the molar ratio of 1:2 with rare earth element at pH 6.5. The crystalline product was obtained by slow evaporation of the solvent at room temperature. After being washed with water and dried in the air, the product was obtained and its composition was determined by elemental analysis.

The purity of the crystalline compound was proved to be more than 99.90% by EDTA titrimetric analysis.

* Corresponding author. Tel.: +86-411-4379215; fax: +86-411-4691570.
E-mail address: tzc@dicp.ac.cn (Z.-C. Tan).

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2.2. Adiabatic calorimeter

A precision adiabatic calorimeter was used to determine the molar heat capacity. The performance of this calorimeter and the details of its constitution have been previously described [7]. The data were automatically collected using a Data Acquisition/Switch Unit (Model 34970A; Aglient, USA) and processed by a computer.

The sample mass of $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ used for heat capacity measurement was 1.3029 g, which was equivalent to 1.000 mmol based on molar mass of 1302.5616 g mol^{-1}.

Calibration of the adiabatic calorimeter was performed with reference to standard material α-Al_2O_3 (1.6382 g, 0.016 mol). The deviations of the results from the recommended values of the former National Bureau of Standards (NBS) [8] were within ±0.2% in the experimental range from 80 to 350 K.

2.3. Thermal analysis

TG test on a thermal analyzer, model Setsys 16/18, Setaram, France, was performed under high-purity nitrogen (99.99%) atmosphere with a flowing rate 30 ml min^{-1} and a heating rate of 10 °C min^{-1}. The mass of sample used was 3.5 mg.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacities of $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ are shown in Fig. 1 and Table 1. The heat capacity data are fitted to the following polynomial in reduced temperature (X) by means of the least-squares fitting.

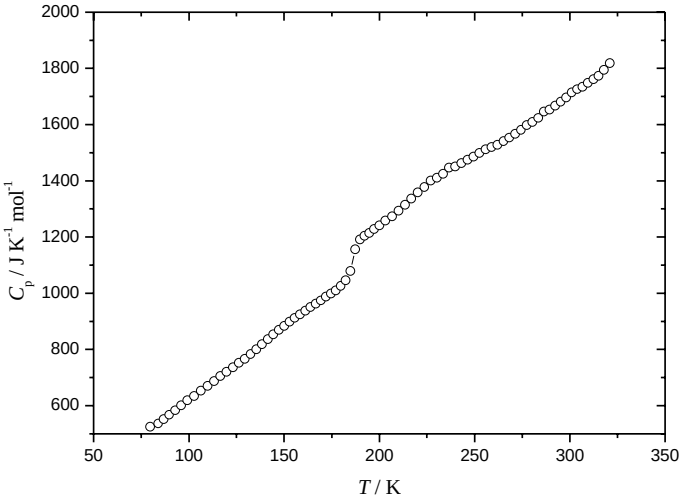

Fig. 1. Experimental molar heat capacities of $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ as a function of temperature.

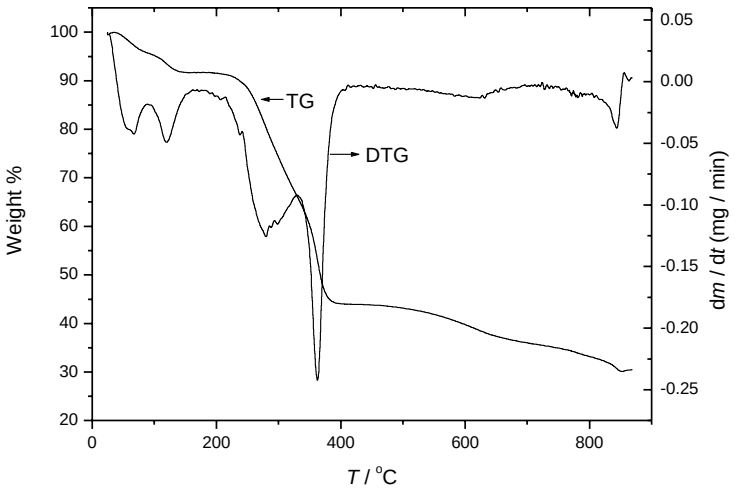

Fig. 2. TG–DTG curve of $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ under nitrogen atmosphere.

Table 1
Experimental molar heat capacities of $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ ($M = 1302.5616\,g\,mol^{-1}$)

T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)
79.700	524.61
83.963	536.31
86.794	552.14
89.741	567.68
92.801	583.06
96.012	601.05
99.344	619.16
102.808	634.34
106.391	652.40
109.885	670.91
113.296	687.44
116.634	705.07
119.903	720.57
123.116	736.54
126.284	752.01
129.402	766.25
132.474	782.87
135.506	800.10
138.499	818.89
141.455	836.93
144.376	853.30
147.259	869.16
150.102	883.44
152.901	898.44
155.674	912.15
158.446	924.32
161.204	938.23
163.938	950.7
166.644	963.1
169.326	974.4
171.970	987.9
174.587	999.5
177.182	1009.6
179.756	1026.1
182.315	1046.4
184.852	1079.1
187.340	1156.7
189.786	1190.8
192.220	1204.6
194.632	1214.2
197.249	1228.0
200.093	1241.6
203.254	1258.1
206.705	1273.5
210.130	1293.4
213.527	1314.5
216.896	1336.7
220.253	1358.9
223.600	1377.1
226.923	1400.1
230.202	1410.5
233.450	1424.8
236.681	1446.7
239.914	1450.7
243.116	1462.7
246.304	1474.2
249.487	1485.6
252.654	1498.9
255.806	1511.2
258.940	1520.0
262.059	1527.9
265.161	1541.0
268.252	1553.4
271.324	1566.4
274.381	1581.2
277.418	1597.7
280.438	1609.2
283.436	1623.7
286.415	1645.9
289.367	1653.0
292.284	1667.0
295.185	1681.0
298.085	1696.3
300.966	1713.8
303.829	1726.0
306.681	1734.2
309.515	1747.9
312.332	1760.8
315.136	1773.6
317.920	1794.2
320.989	1818.2

In the temperature range 80–182 K

$$C_{p,m}\,(J\,K^{-1}\,mol^{-1}) = 779.78 + 271.41X + 1.3487X^2 - 12.817X^3 - 1.2839X^4$$

where $X = (T - 131.007)/51.308$, T is the absolute temperature. The average deviation of the fitting is 0.3%.

In the temperature range 190–321 K

$$C_{p,m}\,(J\,K^{-1}\,mol^{-1}) = 1506.8 + 238.98X + 52.994X^2 + 166.53X^3 - 195.22X^4 - 97.974X^5 + 141.01X^6$$

where $X = (T - 255.388)/65.601$. The average deviation of the fitting is 0.2%.

In the above two temperature ranges, the curve of heat capacity of $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ is roughly smooth, indicating that the complex is stable. But between the above two ranges, from 182 to 190 K, the heat capacity increases more rapidly than in the other two ranges.

3.2. Decomposition mechanism

TG–DTG curve of $[Er_2(His{\cdot}H^+)(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ is shown in Fig. 2 and the final residue in the crucible is a pink solid. According to these results, the possible thermal decomposition mechanism of the complex is deduced as follows:

$$[Er_2(His\cdot H^+)(H_2O)_8](ClO_4)_6\cdot 4H_2O \xrightarrow[95.7\%\ (95.9\%)]{29\text{–}89.1\,^\circ C} [Er_2(His\cdot H^+)(H_2O)_8](ClO_4)_6\cdot H_2O$$

$$\xrightarrow[91.7\%\ (91.7\%)]{89.1\text{–}159.6\,^\circ C} [Er_2(His\cdot H^+)(H_2O)_6](ClO_4)_6$$

$$\xrightarrow[66.2\%\ (66.1\%)]{174.9\text{–}339.8\,^\circ C} 6Er(ClO_4)_3\cdot ErOCl$$

$$\xrightarrow[44\%\,(43.1\%)]{339.8\text{–}402.3\,^{\circ}C} Er(ClO_4)_3 \cdot 3ErOCl$$

$$\xrightarrow[37.3\%\,(37.8\%)]{402.3\text{–}651.7\,^{\circ}C} ErOCl \cdot ErCl_3 \xrightarrow[30.1\%\,(29.4\%)]{651.7\text{–}853.6\,^{\circ}C} Er_2O_3$$

The data (%) in brackets are calculated values.

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