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CALORIMETRIC STUDY AND THERMAL ANALYSIS OF $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ (*Ala*=ALANINE)

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Abstract

A solid complex of rare-earth compounds with alanine, $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ (*Ala*=alanine), was synthesized, and a calorimetric study and thermal analysis for it was performed through adiabatic calorimetry and thermogravimetry. The low-temperature heat capacity of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ was measured with an automated adiabatic precision calorimeter over the temperature range from 78 to 377 K. A solid–solid phase transition was found between 99 and 121 K with a peak temperature at 115.78 K. The enthalpy and entropy of the phase transition was determined to be 1.957 kJ mol^{-1}, 16.90 J mol^{-1} K^{-1}, respectively. Thermal decomposition of the complex was investigated in the temperature range of 40~550°C by use of the thermogravimetric and differential thermogravimetric (TG/DTG) analysis techniques. The TG/DTG curves showed that the decomposition started from 120 and ended at 430°C, completed in three steps. A possible mechanism of the thermal decomposition was elucidated.

Keywords: adiabatic calorimetry, $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$, heat capacity, thermal decomposition

Introduction

Solid complexes of rare-earth compounds with *L*-amino acids have been extensively investigated in the last 20 years due to their significant biological effects [1]. For instance Prados *et al*. [2] and Legendziewicz et al. [3], have prepared and characterized lanthanide compounds with amino acids and holmium with *L*-α-alanine and determined their crystal structures because of the role of these complexes in studies of biological systems and the interesting properties. Nearly 200 kinds of solid complex of rare-earth compounds with *L*-amino acids have been prepared and studied in the last decade. The synthesis and application of these complexes are growing in recent years.

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In order to improve the processes of chemical synthesis of these complexes and carry out relevant application and theoretical research, the thermodynamic properties of these substances are in urgent needs both in rare-earth science and technology. Heat capacity is one of the fundamental thermodynamic properties of substances and closely related to the energetic structure, and is sensitive to the variations in other properties of substances.

In the present work, the low-temperature heat capacity of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ (*Ala*=alanine) has been measured over the temperature range from 78 to 377 K. The possible mechanism of thermal decomposition of the complex is proposed on the basis of thermogravimetric (TG) analysis.

Experimental

Sample preparation

Monocrystal of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ was prepared by mixing $Er(ClO_4)_3$ and $Y(ClO_4)_3$ in an aqueous solution of α-alanine at pH=3 with the molar ratio 1:1:4 as described in [4].

The chemical purity of the sample is proved to be higher than 99.5% according to the actual contents of the rare-earth ions in the complex sample determined by EDTA titrimetric analysis.

Adiabatic calorimetry

Heat-capacity measurements were carried out in a precision automatic adiabatic calorimetric system described in detail previously [5]. Briefly, it is an adiabatic calorimeter with intermittent energy inputs and temperature equilibrium after each input. The calorimeter consists mainly of a sample cell, an adiabatic (or inner) shield, a guard (or outer) shield, two sets of different thermocouples and a high vacuum can. Liquid nitrogen was used as the cooling medium. The evacuated chamber was kept within ca $1 \cdot 10^{-3}$ Pa during the heat-capacity measurements so as to eliminate the heat loss owing to gas convection. Six pairs of differential thermocouples (connected in series) were used to detect the temperature difference between the sample cell and the inner shield. Likewise, six pairs of differential thermocouples (connected in series) were installed between the inner and the outer shields. When the temperature in the sample cell increases due to heating, the thermocouples measure the temperature difference. This signal is used to control the heater distributed on the walls of the inner and outer shields, respectively. Both shields were heated under the control of signal and kept at the same temperatures as the sample cell. The sample cell was a gold-plated container with an internal volume of about 6 cm^3, an Y-shaped gold-plated copper vane was placed in the sample cell to promote the heat conduction between the sample and the cell. The temperature of the cell was determined by a platinum resistance thermometer that was tightly inserted in the copper sheath silver-soldered at the bottom of the sample cell. Temperature and energy data were automatically collected by use of

data acquisition/switch unit (Model: 34970A, Agilent, USA) and processed by a computer on line. The sample mass of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ used for heat capacity measurements is 3.9816 g, which is equivalent to 2.9423 mmol, based on its corresponding molar mass of 1353.23 g mol^{-1}.

Prior to the heat capacity measurements of the complex sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material α-alumina. The deviations of our calibration results from the recommended values reported by Ditmars *et al*. of the National Bureau of Standards [6] are within ±0.2% in the temperature range of 80~400 K.

TG/DTG analysis

The TG measurements of the sample were carried out by a thermogravimetric analysis system (Model: TGA/SDTA851e, Mettler Toledo Company, Switzerland) under high purity N_2 (99.999%) with a flow rate of 60 mL min^{-1}. The mass of the sample used for TG analysis was 1.2658 mg, and the heating rate was 10°C min^{-1}

Results and discussion

Heat capacity

The experimental molar heat capacities of the sample is shown in Fig. 1 and Table 1, respectively. The molar heat capacities are fitted to the following polynomial in reduced temperature (X), by means of the least square fitting.

For solid complex $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$, over the temperature range of 121 to 377 K:

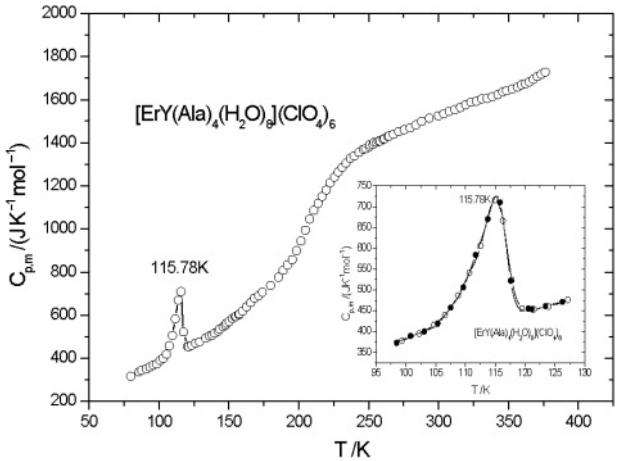

Fig. 1 Experimental molar heat capacities of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ as a function of temperature

$$C_{p,m}(J\ mol^{-1}\ K^{-1})=1363.9870+752.8456X-799.8492X^2-50.0012X^3+ +559.9095X^4-74.6321X^5 \quad (1)$$

where, $X=[T(K)-249]/128$, T is the absolute temperature. $R^2=0.9993$, where R^2 is the correlation coefficient of the fitted curve.

Table 1 The experimental molar heat capacities of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ (molar mass: M=1353.23)

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
79.926	316.76	157.500	606.09	257.224	1405.82
85.758	336.86	159.762	619.20	158.198	1407.32
87.727	344.61	162.707	639.54	260.471	1425.27
91.046	351.37	165.584	658.34	261.201	1417.77
93.552	359.84	168.372	679.80	263.718	1430.21
96.018	368.53	171.189	690.77	264.448	1433.21
98.427	373.12	173.967	707.39	267.695	1439.67
100.773	389.38	179.870	738.47	271.347	1451.61
103.080	400.10	185.552	776.79	275.562	1460.23
105.324	419.46	188.816	808.18	279.685	1468.44
107.504	457.82	192.059	833.09	283.773	1483.72
109.626	506.14	195.267	857.43	287.803	1499.88
111.687	583.76	198.434	900.03	293.263	1513.82
113.725	670.22	201.560	943.93	299.812	1525.48
115.776	710.40	204.654	994.59	303.774	1533.85
117.576	521.98	207.717	1046.37	307.710	1545.49
120.537	455.27	210.761	1086.35	311.626	1554.53
121.119	454.00	213.773	1118.83	315.519	1563.50
123.407	460.83	216.743	1151.58	319.399	1575.95
126.249	471.37	219.670	1181.17	323.253	1587.73
129.035	477.52	222.556	1214.77	327.110	1592.94
133.442	494.12	225.415	1241.46	330.902	1603.27
136.120	504.07	228.238	1264.54	334.697	1606.82
138.152	507.96	231.029	1285.83	338.485	1613.85
139.828	517.54	233.793	1305.34	342.289	1624.30
142.436	525.59	236.851	1328.19	345.698	1636.24
143.385	535.77	239.529	1339.14	348.701	1642.21
145.946	546.90	242.938	1354.57	352.516	1648.68
147.564	554.61	246.104	1369.50	356.412	1658.14
148.452	563.80	247.727	1372.98	359.253	1669.09
150.082	571.49	250.406	1381.44	362.121	1672.83
152.587	584.95	250.568	1390.90	364.935	1682.49
154.669	593.15	253.003	1391.89	367.771	1694.79
155.063	594.03	253.896	1400.84	370.583	1706.93
157.089	603.10	255.601	1402.84	373.394	1717.05
–	–	–	–	376.218	1728.42

From Fig. 1, it can be seen that the heat capacities of the solid complex $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ increase with increasing temperature in a smooth and continuous manner from 121 to 377 K, no phase transition or thermal anomaly occurred

in this temperature range. Therefore, the complex is stable in the above temperature range. However, a thermal anomaly of transition was observed in the temperature range from 99 to 121 K with a peak temperature at 115.78 K. Two series of heat capacity measurements carried out in the region of thermal anomaly (Fig. 1) under the same conditions demonstrate that the transition is reversible and repeatable. No fusion phenomenon was observed in the sample after the heat capacity measurement was completed. Thus, the thermal anomaly may be ascribed as solid phase transitions in the investigated solid complex.

The molar enthalpy, ΔH_m, and entropy, ΔS_m, of the phase transitions of the complex can be derived from the heat capacity data according to the relationship of thermodynamic functions [7, 8]: ΔH_m=1.957 kJ mol^{-1}, ΔS_m=16.90 J mol^{-1} K^{-1}, respectively.

The results of TG/DTG analysis of the sample

The TG/DTG curves of the sample is given in Fig. 2. It can be seen from the TG/DTG curves of the complex that three steps exist in the process of the thermal decomposition. According to the mass loss in each step, the possible mechanism of the thermal decomposition of the complex was deduced as follows:

$$[ErY(Ala)_4(H_2O)_8](ClO_4)_6$$

$$\xrightarrow{120\text{–}190\,^\circ C;\ 9.44\%\ (10.64\%)} [ErY(Ala)_4](ClO_4)_6$$

$$\xrightarrow{215\text{–}317^\circ C;\ 30.37\%\ (29.40\%)} Er(ClO_4)_3+Y(ClO_4)_3$$

$$\xrightarrow{317\text{–}430\,^\circ C;\ 35.10\%\ (34.64\%)} ErCl_3+YCl_3$$

The mass-loss percentage in the brackets are the calculated theoretical values corresponding to the decomposition reaction.

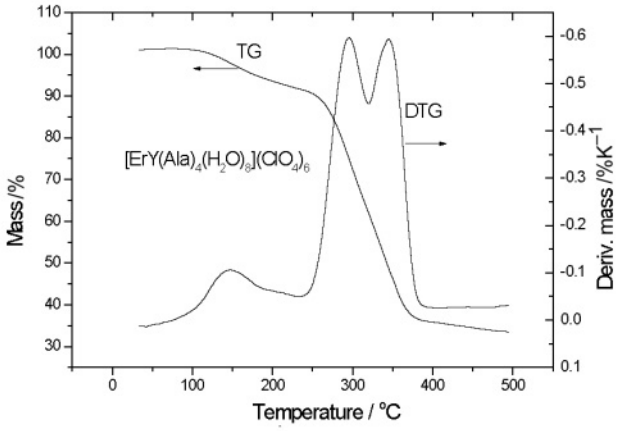

Fig. 2 TG/DTG curve of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ under high purity N_2 atmosphere

Conclusions

The low-temperature heat capacity of $[ErY(Ala)_4(H_2O)_8](ClO_4)_6$ was measured with an automated adiabatic precision calorimeter over the temperature range from 78 to 377 K. A solid–solid phase transition was found between 99 and 121 K with a peak temperature at 115.78 K. The enthalpy and entropy of the phase transition was determined to be 1.957 kJ mol^{-1}, 16.90 J mol^{-1} K^{-1}, respectively. Thermal decomposition of the complex was investigated in the temperature range of 40~550°C by TG/DTG analysis. The TG/DTG curves showed that the decomposition started from 120°C and ended at 430°C, completed in three steps. A possible mechanism of the thermal decomposition was elucidated. The mechanisms and characteristics of the solid to solid phase transition of the complex will be further studied.

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