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Low-temperature heat capacity and thermodynamic properties of crystalline $[Re_2(Ala)_4(H_2O)_8](ClO_4)_6$ (Re = Eu, Er; Ala = alanine)

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Abstract

$[Re_2(Ala)_4(H_2O)_8](ClO_4)_6$ (Re = Eu, Er; Ala = alanine) were synthesized, and the low-temperature heat capacities of the two complexes were measured with a high-precision adiabatic calorimeter over the temperature range from 80 to 370 K. For $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$, two solid–solid phase transitions were found, one in the temperature range from 234.403 to 249.960 K, with peak temperature 243.050 K, the other in the range from 249.960 to 278.881 K, with peak temperature 270.155 K. For $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$, one solid–solid phase transition was observed in the range from 270.696 to 282.156 K, with peak temperature 278.970 K. The molar enthalpy increments, ΔH_m, and entropy increments,ΔS_m, of these phase transitions, were determined to be 455.6 J mol^{-1}, 1.87 J K^{-1} mol^{-1} at 243.050 K; 2277 J mol^{-1}, 8.43 J K^{-1} mol^{-1} at 270.155 K for $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$; and 4442 J mol^{-1}, 15.92 J K^{-1} mol^{-1} at 278.970 K for $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$. Thermal decompositions of the two complexes were investigated by use of the thermogravimetric (TG) analysis. A possible mechanism for the thermal decomposition is suggested.

Keywords: Alanine rare earth compounds; Heat capacity; Thermal decomposition; Adiabatic calorimeter; TG analysis

1. 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, Dao and co-workers [2,3] 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. Rare-earth ions have peculiar physiological and biochemical activities in animals, and their effects of anti-inflammation and anti-cancer have been gradually recognized [4]. Nearly 200 kinds of solid complexes of rare-earth compounds with L-amino acids have been prepared and studied in the last decade.

In order to improve the processes of chemical synthesis of these complexes and carry out relevant application and theoretical research, the thermodynamic

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properties of these substances are needed both in rare-earth science and technology. However, the thermodynamic data of these complexes have not been measured previously.

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 capacities of $[Re_2(Ala)_4(H_2O)_8](ClO_4)_6$ (Re = Eu, Er; Ala = alanine) have been measured over the temperature range from 80 to 370 K. A possible mechanism of thermal decomposition of the two complexes are proposed on the basis of thermogravimetric (TG) data.

2. Experimental

2.1. Sample preparation

Rare-earth oxides (Eu_2O_3, Er_2O_3, 99.9%), perchloric acid (99%) and L-α-alanine were used to prepare the calorimetric experimental samples in accordance with the method described in [3]. First, the rare earth oxides were dissolved in perchloric acid to obtain aqueous solutions of the rare-earth perchlorates, then after mixing the aqueous solutions with L-α-alanine at the mole ratio 1:3, the mixed solutions were stirred (in a 80 °C water bath) for 6 h. The mixed solutions were concentrated by evaporation, and the solutions were subsequently cooled and filtered. The filtrates were placed into a desiccator with P_2O_5 until crystalline products were separated out from the solutions. The crystals were filtered out and washed with absolute alcohol for three times. Finally, the collected crystals were desiccated in a dryer until the mass of the crystals became constant.

The molecular compositions and structures of the two complexes have already been reported in [3]. The actual contents of the rare-earth ions in our complex samples were determined by EDTA titrimetric analysis. The experimental results are very close to the theoretical contents of rare-earth metals in the samples calculated according to the molecular compositions and structures of the complexes. The results of EDTA titrimetric analysis demonstrated that the chemical purities of the two samples are all higher than 99.8%.

2.2. 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 differential thermocouples and a high vacuum can. Liquid nitrogen was used as the cooling medium. The evacuated can was kept within ca. 1×10^{-3} Pa during the heat capacity measurements so as to eliminate the heat loss owing to gas convection. Six pairs of copper–constantan 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 of the sample cell increases due to heating, the differential thermocouples detect the temperature differences. These signals are used to control the current through the heater wounded on the inner and outer shields. Both shields were heated under the control of the signals and kept at the same temperatures as the sample cell. The sample cell was a gold-plated copper container with an internal volume of about 6 cm^3. A 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 miniature platinum resistance thermometer tightly inserted in a copper sheath that was silver-soldered at the bottom of the sample cell. The calorimetric data were automatically collected by use of the Data Acquisition/Switch Unit (Model: 34970A, Agilent, USA) and processed on line by a computer. The sample mass of $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ and $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$ used for the heat capacity measurements are 1.9043 and 2.6361 g, which are equivalent to 1.359 and 1.841 mmol, based on their corresponding molar mass 1400.96 and 1431.58 g mol^{-1}, respectively. In order to demonstrate the repeatability of the experimental results, two series of heat capacity measurements were performed under the same conditions for $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$.

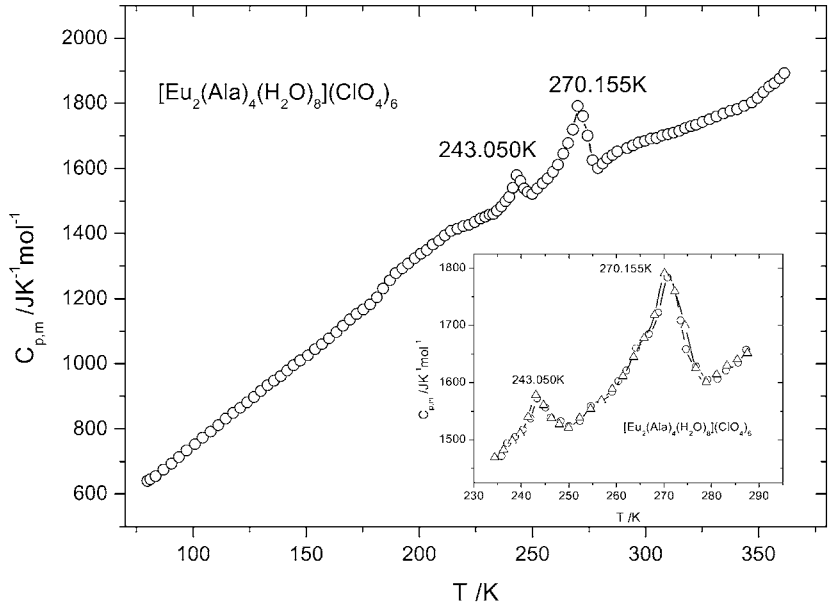

Fig. 1. Experimental molar heat capacities $C_{p,m}$ of $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ as a function of temperature.

Prior to the heat capacity measurements of the solid complex samples, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material α-Al_2O_3. The deviations of our calibration results from the recommended values reported by Ditmars of the National Bureau of Standards [6] are within $\pm 0.2\%$ in the temperature range of 80–400 K.

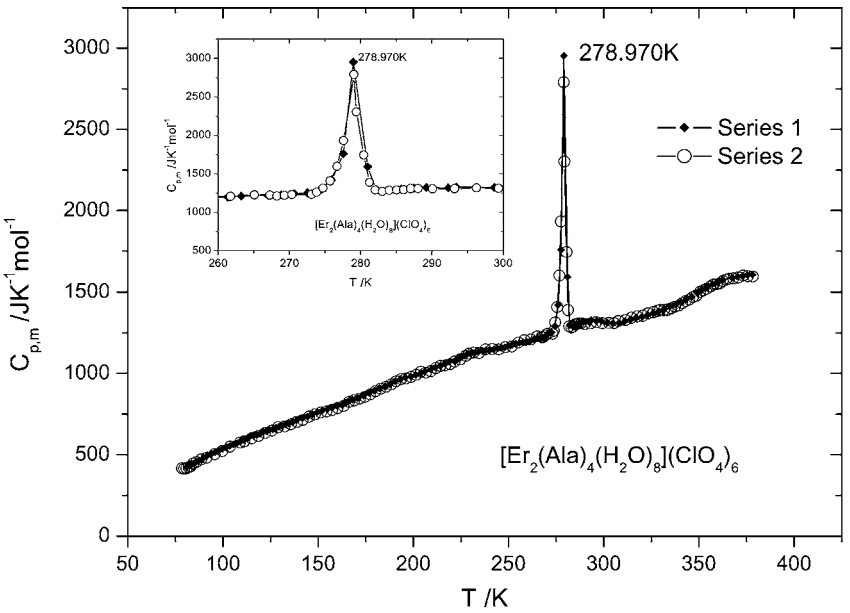

Fig. 2. Experimental molar heat capacities $C_{p,m}$ of $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$ as a function of temperature.

2.3. TG/DTG analysis

The TG measurements of the two samples were carried out by a TG analyzer (Model: TGA/SDTA851e, Metter- ToLedo, Switzerland) under high purity nitrogen (99.999%) with the flow rate of 60 ml min^{-1}. The mass of the sample used for TG analysis was 1.0134 and 1.6351 mg for $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ and $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$, respectively. The heating rate was 10 °C min^{-1}.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacities of the two solid complex of rare-earth compound with L-amino acid are shown in Figs. 1 and 2, and tabulated in Tables 1 and 2, respectively. The molar heat capacities are fitted to the following polynomials in reduced temperature (X), by means of the least square fitting.

Table 1
The experimental molar heat capacities of $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ (molar mass: $M = 1400.96$ g mol^{-1})

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
79.931	639.58	189.706	1277.87	270.155	1790.99
81.198	644.93	192.511	1292.79	272.312	1759.60
83.580	654.53	195.262	1307.91	274.436	1700.18
87.099	673.85	197.995	1323.54	276.686	1625.21
90.494	692.85	200.700	1337.41	278.881	1600.70
93.783	712.57	203.388	1348.91	281.078	1614.43
97.247	732.84	206.055	1365.81	283.255	1630.15
100.877	752.95	208.708	1377.84	285.403	1640.25
104.409	772.38	211.338	1393.91	287.545	1651.58
107.851	791.05	214.104	1407.35	291.948	1661.33
111.209	810.61	216.909	1413.93	294.519	1670.02
114.494	830.49	219.481	1421.57	297.130	1678.45
117.714	848.02	222.045	1426.53	299.701	1683.72
120.873	864.69	224.596	1434.46	302.263	1690.33
123.977	881.20	227.078	1445.02	304.805	1692.42
127.029	897.11	229.221	1450.56	307.370	1701.28
130.034	915.50	231.013	1457.93	309.909	1704.54
132.994	933.53	232.727	1459.25	312.403	1709.81
135.915	947.61	234.403	1469.26	314.935	1714.81
138.796	962.03	236.273	1482.70	317.437	1723.20
141.640	978.40	238.095	1498.31	319.961	1728.78
144.449	994.16	239.779	1511.68	322.442	1733.74
147.481	1010.06	241.415	1540.04	325.235	1741.77
150.734	1025.76	243.050	1578.31	328.299	1750.38
153.942	1044.59	244.688	1560.69	331.386	1759.33
157.114	1060.41	246.325	1537.76	334.455	1768.03
160.245	1078.37	247.976	1527.21	337.532	1775.67
163.344	1096.41	249.960	1521.19	340.571	1781.47
166.401	1116.30	252.247	1538.29	343.571	1791.74
169.425	1134.89	254.584	1554.10	347.000	1802.55
172.419	1152.36	256.856	1568.96	349.494	1816.25
175.384	1166.26	259.124	1588.70	352.087	1833.96
178.318	1181.97	261.364	1611.01	354.597	1850.76
181.222	1203.27	263.602	1644.90	357.052	1861.12
184.093	1230.63	265.817	1677.85	359.266	1876.11
186.955	1255.74	268.000	1718.45	361.413	1892.04

Table 2
The experimental molar heat capacities of $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$ (molar mass: $M = 1431.58\ g\ mol^{-1}$)

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
80.797	422.10	146.958	749.12	226.450	1108.55	289.205	1323.40
83.075	439.92	149.604	764.53	228.052	1116.74	292.289	1319.60
85.300	453.50	152.222	774.61	230.433	1127.28	293.425	1328.16
87.477	466.90	154.814	780.28	232.697	1132.72	296.281	1324.43
89.610	479.98	157.382	791.04	234.265	1134.62	298.770	1322.34
91.703	494.20	159.927	803.29	236.234	1140.16	301.857	1313.04
93.758	507.02	162.457	804.14	238.225	1143.68	304.929	1308.99
95.779	516.22	164.407	820.02	240.173	1146.31	307.988	1311.63
97.766	524.78	165.784	830.22	242.121	1149.53	311.039	1322.25
99.724	537.23	167.941	839.72	244.088	1155.07	314.069	1333.96
101.653	548.58	170.842	849.32	246.038	1157.52	317.061	1342.60
103.555	555.79	173.717	866.55	247.981	1161.75	320.055	1348.24
105.430	564.03	176.565	880.17	249.917	1170.63	323.032	1360.06
107.283	572.69	179.384	895.04	251.844	1176.10	325.992	1369.94
109.113	582.07	182.175	908.64	253.764	1182.72	328.935	1382.18
110.922	591.78	184.939	919.57	255.676	1189.09	331.860	1394.64
112.710	601.64	187.679	934.16	257.579	1191.34	334.768	1411.48
114.479	617.68	190.394	953.24	259.475	1195.22	337.657	1422.62
115.901	620.88	193.085	964.45	261.364	1199.88	340.527	1436.71
117.639	622.66	195.766	976.38	263.247	1209.30	343.377	1455.15
119.359	630.60	198.458	981.92	265.122	1216.83	346.203	1470.80
121.062	640.77	201.156	990.62	266.988	1220.12	349.005	1495.30
122.748	644.81	203.826	1002.51	268.847	1225.97	351.775	1516.04
124.421	652.06	205.974	1013.11	270.696	1242.93	354.502	1531.85
126.079	657.09	209.058	1024.64	272.533	1253.92	357.186	1546.19
127.724	665.48	211.598	1039.18	274.363	1291.13	359.827	1557.32
129.353	673.22	214.081	1046.88	275.934	1419.36	362.468	1574.00
130.968	677.35	216.560	1060.61	277.583	1760.18	367.489	1586.30
132.573	687.03	219.038	1073.59	278.970	2928.74	370.303	1594.50
134.400	695.33	221.515	1076.93	281.006	1605.97	372.900	1599.18
136.447	701.64	223.117	1088.64	282.156	1298.65	375.456	1603.43
138.844	715.83	223.967	1096.17	283.900	1288.91	378.095	1606.21
141.582	726.18	224.805	1099.18	285.682	1301.66		
144.285	735.06	225.628	1104.16	287.453	1313.47		

For solid complex $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$, over the temperature range of 79–234 K:

$$C_{p,m}(J\,K^{-1}\,mol^{-1}) = 1060.1169 + 452.4446\,X + 76.6044\,X^2 + 18.4897X^3 - 93.0282\,X^4 - 57.2763\,X^5 \quad (1)$$

where $X = (T - 156.5)/77.5$, and T is the absolute temperature. The correlation coefficient of the fitted curve, $R^2 = 0.9997$.

Over the temperature range of 278–362 K:

$$C_{p,m}(J\,K^{-1}\,mol^{-1}) = 1728.2331 + 100.7472\,X + 23.7906\,X^2 - 1.2947\,X^3 - 4.9575\,X^4 + 53.4252\,X^5 \quad (2)$$

where $X = (T - 320)/42$; $R^2 = 0.9992$.

For solid complex $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$, over the temperature range of 80–271 K:

$$C_{p,m}(J\,K^{-1}\,mol^{-1}) = 879.0532 + 450.3532\,X + 17.9161\,X^2 - 138.9800\,X^3 - 71.7120\,X^4 + 93.8387\,X^5 \quad (3)$$

where $X = (T - 176)/95$, $R^2 = 0.9997$.

Over the temperature range of 282–378 K:

$$C_{p,m}(J\,K^{-1}\,mol^{-1}) = 1383.9620 + 237.2587\,X + 189.7223\,X^2 - 147.4266\,X^3 - 124.4560\,X^4 + 66.3432\,X^5 \quad (4)$$

where $X = (T - 330)/48$; $R^2 = 0.9968$.

From Figs. 1 and 2, it can be seen that the heat capacities of the samples of $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ and $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$ increase with increasing temperature in a smooth and continuous manner from 79 to 234 K, and from 278 to 362 K for $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$, from 81 to 271 K, and from 282 to 378 K for $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$, respectively. No phase transition or thermal anomaly was observed in these temperature ranges. Therefore, the two samples are stable in the above ranges. However, the thermal anomalies were found in the temperature ranges from 234 to 278 K for $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ and from 271 to 282 K for $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$, respectively. The peak temperatures of these thermal anomalies were found to be 243.050 K, 270.155 K for $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$; 278.970 K for$[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$, respectively. Two series of heat capacity measurements carried out in the regions of thermal anomaly (see Figs. 1 and 2) may verify that the thermal anomalies are reversible and repeatable. No fusion phenomenon was observed in the sample after the heat capacity measurements were completed. Thus, these thermal anomalies may be ascribed to solid–solid phase transitions in the investigated complex. So far no study on the phase transitions of these complexes has been reported in literature.

The molar enthalpies, $\Delta_{trs}H_m$, and the entropies, $\Delta_{trs}S_m$, of the phase transitions of the two complexes can be derived from the heat capacity data according to thermodynamic function relationship as [7], $\Delta_{trs}H_m = 460\ J\ mol^{-1}$, $\Delta_{trs}S_m = 1.87\ J\ K^{-1}\ mol^{-1}$ at 243.050 K; $\Delta_{trs}H_m = 2280\ J\ mol^{-1}$, $\Delta_{trs}S_m = 8.43\ J\ K^{-1}\ mol^{-1}$ at 270.155 K for $[Eu_2(Ala)_4(H_2O)_8](ClO_4)$; $\Delta_{trs}H_m = 4440\ J\ mol^{-1}$, $\Delta_{trs}S_m = 15.92\ J\ K^{-1}\ mol^{-1}$ at 278.970 K for $[Er_2(Ala)_4(H_2O)_8](ClO_4)$, respectively.

3.2. The results of TG/DTG analysis of the complexes

The TG/DTG curves of the two solid complexes of rare-earth compounds with alanine are shown in Figs. 3 and 4, respectively. It can be seen from the TG/DTG curves that the thermal decompositions takes place in three stops. According to the mass loss in each step, possible mechanisms for the thermal decompositions are as follows

$$[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$$

$$\xrightarrow[9.82\%(10.28\%)]{104-203\,^{\circ}C} [Eu_2(Ala)_4](ClO_4)_6$$

$$\xrightarrow[24.18\%(25.44\%)]{259-304\,^{\circ}C} Eu_2(ClO_4)_6$$

$$\xrightarrow[28.53\%(27.30\%)]{319-422\,^{\circ}C} 2\,EuCl_3$$

$$[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$$

$$\xrightarrow[9.27\%(10.05\%)]{104-190^{\circ}C} [Er_2(Ala)_4](ClO_4)_6$$

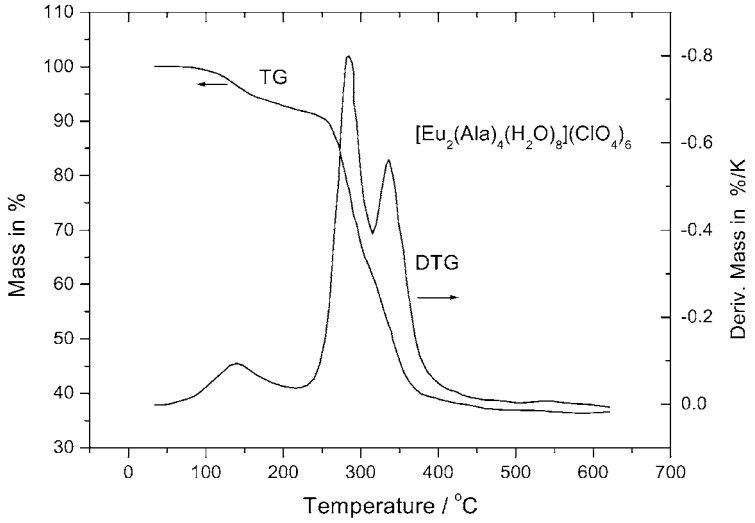

Fig. 3. TG/DTG curve of $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ under nitrogen atmosphere.

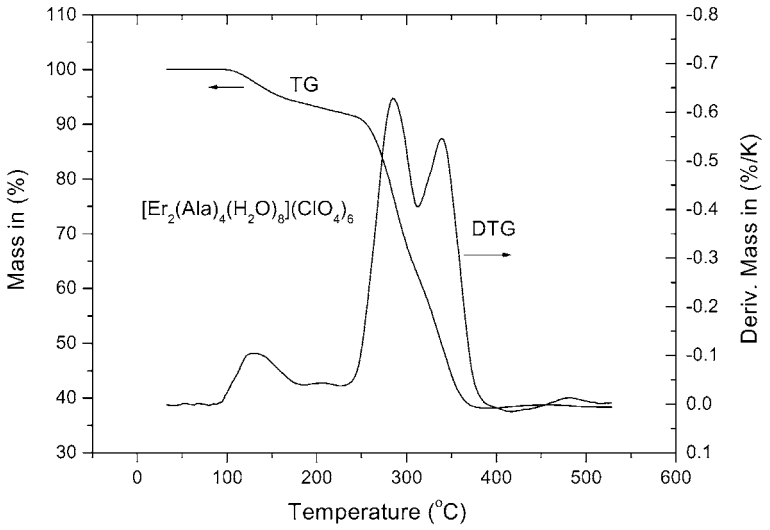

Fig. 4. TG/DTG curve of $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$ under nitrogen atmosphere.

$$\underset{25.80\%(24.91\%)}{\overset{227-312\,^{\circ}C}{\longrightarrow}} 2\,Er(ClO_4)_3$$

$$\underset{28.34\%(29.97\%)}{\overset{312-412^{\circ}C}{\longrightarrow}} 2\,ErCl_3$$

The mass-loss (in %) in the brackets are calculated theoretical values.

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