Heat Capacities and Thermodynamic Properties of Lanthanum/Holmium Perchlorate Complexes with Glycine

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The heat capacities of the two complexes, $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$ (Gly = glycine), were measured by adiabatic calorimetry in the temperature range from 78 to 375 K. A solid-solid phase transition was found between 322.87 and 342.29 K for $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$, and the peak temperature, the enthalpy and the entropy of the transition were obtained to be 330.94 K, 11.65 kJ·mol^{-1} and 35.20 J·K^{-1}·mol^{-1}, respectively. No indication of any phase transition or thermal anomaly was observed for $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$. Thermal stabilities of the two complexes were investigated by thermogravimetry in the temperature range of 40—800 ℃. The possible mechanisms for the thermal decompositions were proposed according to the TG and DTG curves.

Keywords lanthanum/holmium perchlorate-glycine complex, adiabatic calorimetry, heat capacity, thermogravimetry, thermal decomposition

Introduction

Since Anghileri *et al.*[1] reported in 1975 that the complex of lanthanum chloride with glycine had anti-cancer effect, complexes of rare earth with amino acid have been extensively studied. In the past decades, about 200 kinds of complexes of rare-earth compounds with amino acids have been synthesized and studied.[2] They can be used as antiseptic and anticancer drugs in medicine, additives of animal forage and fertilizer in agriculture, and wool dye in textile industry.[3,4] Complexes of rare earth with amino acid were widely used in many fields, however, thermodynamic properties of the compounds have been seldom reported. For further research on the compounds, it is necessary to determine their basic thermodynamic properties.

In the present work, two complexes of rare-earth with glycine, $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$, were synthesized. Heat capacities of the two complexes were measured by a precision automatic adiabatic calorimeter with small sample in the temperature range from 78 to 375 K. A solid-solid phase transition for the complex, $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$ was found. The molar enthalpy and entropy of the phase transition were determined according to the heat capacity measurements. The possible mechanisms of the thermal decomposition were deduced on the basis of the thermogravimetry (TG).

Experimental

Sample preparation and characterization

$[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$ were synthesized as described previously.[5,6] 20 mmol of rare-earth oxides (La_2O_3, Ho_2O_3, 99.9%) were dissolved in perchloric acid ($HClO_4$, 99.5%) to obtain the aqueous solutions of the rare-earth perchlorates and 60 mmol of high purity glycine were added to the solutions under the condition of pH = 2—3. The mixed solutions were stirred in water bath at 80 ℃ for 6 h, and then were concentrated by evaporation. After they were cooled and filtered, the solutions were placed in room temperature for a month and crystals were separated out and washed three times with absolute alcohol. Finally the collected crystals were kept in a desiccator with P_2O_5 for 3 months. The crystals of $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$ were obtained. The purities of the samples of $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$, were determined by EDTA titrimetric analysis to be 99.56% and 99.38%, respectively.

Adiabatic calorimetry

The heat capacities were measured with a precision auto-

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Received October 18, 2002; revised and accepted February 11, 2003.

Project supported by the National Natural Science Foundation of China (No. 20073047) and the Natural Science Foundation of Hunan Province (No. 00JJY20115).

matic adiabatic calorimeter in the temperature range from 78 to 375 K. Its principle and structure were described in detail elsewhere.[7-9] The adiabatic calorimeter mainly consists of a sample cell, an adiabatic shield, a guard shield, a platinum resistance thermometer, an electric heater, two sets of differential thermocouples and a high vacuum can. A miniature platinum resistance thermometer was fixed at the bottom of the sample cell for measuring the sample temperature. The precision of the temperature measurement is 1 mK in the temperature range from 80 to 400 K. The electric energy introduced into the calorimetric cell and the equilibrium temperature of the cell were periodically measured by the Data Acquisition/Switch Unit (Model: 34970A, Agilent, USA). The data were automatically collected and processed by a personal computer. Programmed by the computer, the temperature of the cell increased at the rate of 0.2—0.4 $K \cdot min^{-1}$ and the interval of the temperature increment was 2—4 K for each energy input period. The temperature drift rates were less than ± 0.5 $mK \cdot min^{-1}$ during the temperature equilibrium period. The whole calorimetric system was housed in the vacuum can (1×10^{-3} Pa) to eliminate heat transfer due to convection. The vacuum can was filled with liquid nitrogen to obtain low temperature (78 K).

After the sample was loaded in the cell, the cover of the cell was sealed by epoxy. 24 h later the epoxy was solidified, the air in the cell was pumped out through a copper capillary soldered on the cover, and then the cell was filled with helium gas of 0.1 MPa to enhance the heat transfer within the cell during the heat capacity measurements. The sample amounts of $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$ used for heat capacity measurements were 2.4648 g and 1.2536 g, which were equivalent to 1.7644 and 0.8442 mmol, based on their corresponding molar mass of 1396.93 and 1484.98 $g \cdot mol^{-1}$, respectively.

Prior to the heat capacity measurements of the 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 *et al.*[10] were within $\pm 0.2\%$ in the temperature range of 80—400 K.

TG/DTG *analysis*

The TG measurements of the two complexes were carried out on a thermogravimetric analyzer (Model TGA/SDTA851e, Mettler Toledo Company, Switzerland) under high purity N_2 (99.999%) with a flow rate of 60 mL/min and a heating rate of 10 $℃ \cdot min^{-1}$. The amounts of the samples used for TG analysis were 5.891 mg and 5.617 mg for $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$, respectively.

Results and discussion

Heat capacity

The experimental molar heat capacities of the two complexes in the temperature range from 78 to 375 K are shown in Fig. 1, and tabulated in Tables 1 and 2, respectively. From Fig. 1, it can be seen that the heat capacities of the complexes increase with increasing temperature in a smooth and continuous manner for $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ over the entire measuring temperature range and for $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$ in the temperature range from 78 to 322 K, which implies that the complexes are stable and no phase transition or thermal anomaly occurred in the above temperature ranges. However, a phase transition was observed in the temperature range from 322 to 342 K with a peak temperature at (330.94 ± 0.01) K for $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$. No fusion phenomenon was observed in the sample after the heat capacitiy measurements were completed. Thus, the thermal anomalies may be ascribed to solid-solid phase transition. The molar enthalpy (ΔH_m) and entropy (ΔS_m) of the phase transition of $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$ can be derived from the heat capacity data according to the relationship of thermodynamic functions. They are $\Delta H_m = 11.648$ $kJ \cdot mol^{-1}$, and $\Delta S_m = 35.20$ $J \cdot K^{-1} \cdot mol^{-1}$, respectively.

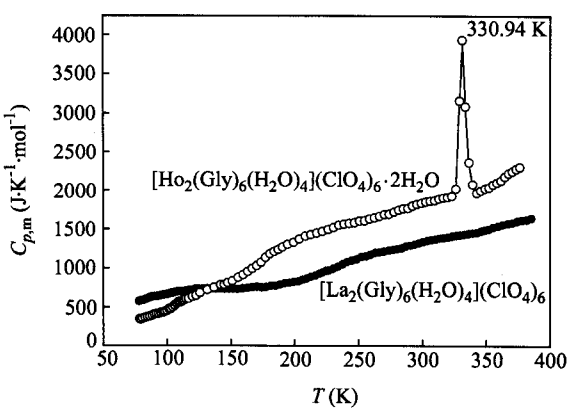

Fig. 1 Experimental molar heat capacities of $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ and $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$ as a function of temperature.

The experimental molar heat capacities of the two complexes were fitted to the following polynomials in reduced temperature (X) by means of the least square fitting.

For $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ over the temperature range of 78 to 375 K,

$$C_{p,m}(J \cdot K^{-1} \cdot mol^{-1}) = 990.1485 + 905.6827X + 272.6649X^2 - 1188.2270X^3 - 143.6193X^4 + 856.2818X^5 \quad (1)$$

where, $X = [T(K) - 213.5]/153.5$, and T is the absolute temperature. $R^2 = 0.9922$, where R^2 is the correlation coefficient of the fitted polynomial.

For $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$ over the temperature ranges of 79 to 323 K and 342 to 376 K,

$$C_{p,m}(J \cdot K^{-1} \cdot mol^{-1}) = 1524.4699 + 948.6510X - 808.8124X^2 - 168.5347X^3 + 642.1681X^4 + 225.0283X^5 \quad (2)$$

Table 1 Experimental molar heat capacities of $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ (molar mass: $M = 1396.93\ g \cdot mol^{-1}$)

T (K)	$C_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	T (K)	$C_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	T (K)	$C_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
77.922	574.23	155.126	729.51	273.505	1227.6
79.464	582.77	158.988	737.16	276.948	1236.3
81.744	589.73	162.825	744.77	280.438	1246.6
83.974	604.19	166.558	751.74	283.806	1255.9
86.149	619.94	170.292	757.89	287.182	1281.4
88.277	632.76	173.997	752.54	290.503	1292.5
90.369	637.04	177.710	757.54	293.831	1304.0
92.425	639.96	181.422	770.91	297.159	1322.0
94.450	646.76	185.046	772.24	300.406	1338.4
96.444	655.45	188.670	788.27	303.734	1353.2
98.410	660.29	192.205	806.98	306.981	1363.8
100.346	667.31	195.740	810.99	310.227	1373.2
102.259	675.35	199.275	820.34	313.474	1385.1
104.146	681.67	202.722	827.02	316.721	1390.9
106.008	689.31	206.169	849.73	319.968	1399.1
107.852	697.23	209.616	867.10	323.214	1409.7
109.674	701.44	212.886	887.14	326.380	1420.4
111.513	692.08	216.156	903.18	329.600	1429.3
113.281	701.43	219.514	928.56	332.794	1435.2
115.048	708.11	221.708	943.73	335.958	1444.6
116.816	710.78	224.729	964.63	339.123	1452.0
118.495	714.79	226.585	968.64	342.370	1458.9
120.174	714.79	230.032	990.02	345.536	1477.4
122.030	728.15	233.744	1016.7	348.620	1490.1
124.593	733.50	237.456	1048.8	351.726	1502.3
128.040	732.16	241.168	1079.5	355.184	1526.8
131.575	735.34	244.791	1096.9	358.980	1541.8
134.984	734.93	248.415	1112.9	362.780	1563.2
138.396	732.03	252.127	1141.0	366.492	1575.2
141.745	733.54	255.839	1151.7	370.204	1585.9
145.050	732.77	259.374	1171.7	373.937	1607.5
148.328	731.93	262.987	1196.1	377.635	1618.3
151.573	730.76	266.558	1204.3	381.301	1625.3
		270.036	1215.4	384.968	1645.9

Table 2 Experimental molar heat capacities of $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 2H_2O$ (molar mass: $M = 1484.98\ g \cdot mol^{-1}$)

T (K)	$C_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	T (K)	$C_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	T (K)	$C_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
78.459	348.63	147.484	810.99	273.957	1694.1
79.531	345.49	151.108	832.36	277.669	1720.8
80.933	339.20	155.615	877.79	281.381	1747.6
82.666	367.49	159.592	913.86	285.011	1763.3
84.557	376.77	163.128	956.62	288.586	1769.2
86.501	382.11	166.663	994.03	292.105	1801.0
88.269	395.47	170.189	1030.9	295.569	1820.8
90.024	394.11	173.679	1071.8	299.146	1837.1
91.716	416.85	177.139	1133.6	302.593	1853.1
93.395	420.86	180.539	1182.4	306.029	1864.9
95.074	430.21	183.897	1211.8	309.454	1870.3
96.665	435.55	187.167	1235.9	312.845	1891.9
98.256	446.24	190.437	1267.9	316.203	1906.6
99.847	455.60	194.326	1304.0	319.567	1913.1
101.438	476.97	199.099	1330.7	322.873	1927.7
102.930	480.60	203.694	1373.5	326.090	2025.8
104.440	499.82	208.290	1410.9	328.734	3160.8

Continued

T (K)	$C_{p,m}$ (J·K^{-1}·mol^{-1})	T (K)	$C_{p,m}$ (J·K^{-1}·mol^{-1})	T (K)	$C_{p,m}$ (J·K^{-1}·mol^{-1})
105.933	525.80	212.798	1429.6	330.940	3938.3
107.415	546.63	217.305	1451.0	333.380	3084.3
108.882	563.25	221.724	1471.0	336.138	2363.3
110.364	565.15	226.143	1496.4	339.098	2082.2
111.778	578.51	230.385	1523.1	342.287	1969.2
113.192	590.54	234.539	1552.5	345.457	2001.4
114.606	589.20	238.693	1565.9	348.727	2026.8
116.728	609.24	242.759	1575.2	351.849	2041.4
119.644	615.92	246.749	1585.9	354.980	2079.5
122.649	647.99	250.695	1604.5	358.096	2104.3
125.560	682.80	254.655	1609.6	361.189	2133.7
131.399	720.14	258.614	1632.2	364.194	2184.5
136.702	748.19	262.488	1647.1	367.111	2225.9
141.828	782.93	266.348	1667.0	370.115	2252.6
144.656	786.94	270.163	1690.5	373.032	2280.7
				375.860	2306.0

where, $X = [T(\mathrm{K}) - 227.5]/148.5$, $R^2 = 0.9960$.

TG/DTG *analysis*

The TG/DTG curves of the two complexes are shown in Figs. 2 and 3, respectively. From Figs. 2 and 3, it can be seen that there are two larger mass-loss peaks in the DTG curves of the two complexes, indicating that two steps exist in their thermal decomposition processes. According to the mass loss in each step, possible mechanisms of thermal decompositions for the two complexes are deduced as follows:

$$[La_2(Gly)_6(H_2O)_4](ClO_4)_6 \xrightarrow[6.1\%\ (5.2\%)]{103\text{—}234\ ^\circ\mathrm{C}}$$

$$La_2(Gly)_6(ClO_4)_6 \xrightarrow[58.0\%\ (59.7\%)]{234\text{—}476\ ^\circ\mathrm{C}} 2LaCl_3$$

$$[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O \xrightarrow[7.4\%\ (7.3\%)]{109\text{—}314\ ^\circ\mathrm{C}}$$

$$Ho_2(Gly)_6(ClO_4)_6 \xrightarrow[54.0\%\ (56.2\%)]{351\text{—}728\ ^\circ\mathrm{C}} 2HoCl_3$$

where the mass-loss percentages in the brackets are the calculated values.

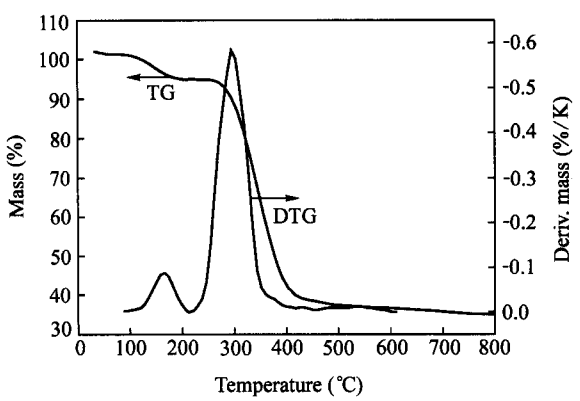

Fig. 2 TG/DTG curves of $[La_2(Gly)_6(H_2O)_4](ClO_4)_6$ under high purity N_2 atmosphere.

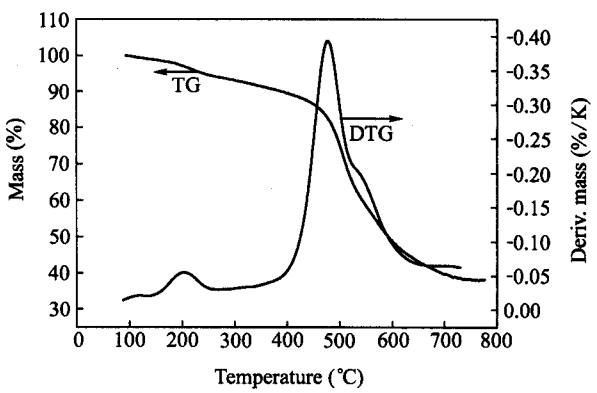

Fig. 3 TG/DTG curves of $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 2H_2O$ under high purity N_2 atmosphere.

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(E0210181 PAN, B. F.; DONG, H. Z.)