

# Thermodynamic Properties of $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$ (Ala = alanine)\*

Liu Bei-Ping<sup>1,2</sup> Tan Zhi-Cheng<sup>2</sup> Yu Hua-Guang<sup>2</sup> Lan Xiao-Zheng<sup>2</sup>  
Zhang Da-Shun<sup>1</sup> Liu Ping<sup>1</sup> Sun Li-Xian<sup>2</sup>

<sup>1</sup> Department of Chemistry, Changde Normal College, Changde 415000;

<sup>2</sup> Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 110623)

**Abstract** The crystalline complex of holmium chloride with alanine,  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$ , was synthesized. Heat capacities of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  were measured by adiabatic calorimetry over the temperature range from 78 to 363 K. A solid-solid phase transition was found between 214 K and 255 K with the peak temperature of 235.09 K. The enthalpy and entropy of the transition were determined to be  $3.017 \text{ kJ} \cdot \text{mol}^{-1}$  and  $12.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , respectively. The molar heat capacities were presented by a fitted polynomial as a function of reduced temperature. The thermodynamic functions relative to the reference temperature 298.15 K were calculated based on the heat capacity data. Thermal stability of the complex was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) over the temperature range from 40 to 800 °C. From the DTG curves, two peaks were observed in the process of the thermal decompositions for the complex. The first mass-loss peak started from 80 °C and ended at 179 °C, and the second mass-loss peak started from 242 °C and ended at 479 °C. A possible mechanism of the thermal decomposition was presented.

**Keywords:** Complex of rare earth with amino acid,  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$ , Adiabatic calorimetry, Heat capacity, Thermodynamic function, Thermogravimetry, Differential scanning calorimetry

Since the 1960s, the syntheses, structures and properties of complexes of rare-earth compounds with amino acids have attracted increasing interest<sup>[1]</sup>, and the wide applications of the complexes in agriculture<sup>[2]</sup>, medicine<sup>[3]</sup>, biology<sup>[4]</sup> and light industry<sup>[5]</sup> have been successively found. In the past decades, about 200 kinds of such complexes have been prepared and over 40 kinds of complexes among them have been studied for their structure<sup>[1]</sup>. Lengendziewicz *et al.*<sup>[6]</sup> prepared and characterized the monocrystal of holmium chloride with alanine, and determined the crystal structure. However, until now, few thermodynamic properties of these complexes have been reported in the literatures. For further research on these compounds, it is necessary to determine their basic thermodynamic properties.

In this paper, we report the heat capacities and thermodynamic functions of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  over the temperature range of 80 ~ 365 K. A possible thermal decomposition mechanism is proposed for this compound on the basis of thermogravimetry (TG) and differential scanning calorimetry (DSC).

## 1 Experimental

### 1.1 Sample preparation and characterization

In accordance with the method described in Ref. [6], the crystalline  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  was synthesized. Rare earth oxide ( $\text{Ho}_2\text{O}_3$ , with a purity greater than 99.9%) was dissolved in hydrochloric acid to obtain aqueous solutions of  $\text{HoCl}_3$ . The amino acid was then added to the solution with the molar ratio of 2:1 to rare earth ion at pH=4.0. The crystal of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  precipitated from the solution. Finally, the collected crystals were desiccated in a dryer to prevent the coordination compounds from deliquescent in air.

The actual content of holmium ion in the crystalline product was determined by EDTA titrimetric analysis. The result of analysis indicated that the purity of the prepared  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  sample was greater than 99.50% (mass fraction).

### 1.2 Adiabatic calorimetry

Heat capacity measurement was carried out in an automatic small sample adiabatic calorimeter. The principle and structure of

the calorimeter were described in detail elsewhere<sup>[7-9]</sup>. The calorimeter mainly consisted of a sample cell, the inner and outer adiabatic shields, a platinum resistance thermometer, an electric heater, two sets of differential thermocouples and a high vacuum can. Briefly, the sample cell was a gold-plated copper container with an internal volume of about 6 mL. The electric heater was wound on the wall of the cell for heating the samples. A miniature platinum resistance thermometer was fixed at the bottom of the cell for measuring the temperature of sample. A small amount of helium gas was introduced into the cell to promote the heat transfer. The electric energy was introduced into the cell, and then the temperature of the cell was measured by the platinum thermometer. The calorimetric data were automatically collected by the Data Acquisition / Switch Unit (Model 34970A, Agilent, USA) and interfaced to a personal computer for processing.

In order to obtain good adiabatic conditions between the sample cell and its surroundings, two similar control circuits were used to control the temperature of the inner and outer adiabatic shields. Each control circuit consisted of a precise temperature controller and a set of thermocouples. When these control circuits were working, the temperature difference between the cell and its surroundings was kept within  $\pm 1$  mK during the entire experimental process of heat capacity measurements. The temperature drift rates of the cell were kept less than  $\pm 0.5$  mK  $\cdot$  min<sup>-1</sup> during the temperature equilibrium period. Liquid nitrogen was used as the cooling medium.

Prior to the heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified through the heat capacity measurements of the reference standard material  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The deviations of our calibration results from the recommended values reported by Ditmars *et al.*<sup>[10]</sup> of the former National Bureau of Standards are within  $\pm 0.2\%$  in the temperature range from 80 to 400 K.

The sample mass of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> used for the heat capacity measurements was 1.9901 g, which is equivalent to 1.9082 mmol, based on its corresponding molar mass of 1042.9 g  $\cdot$  mol<sup>-1</sup>.

### 1.3 Thermal analysis

The TG measurement of the sample was carried out by a thermogravimetric analysis system (Model TGA / SDTA851e, METTLER TOLEDO COMPANY, Switzerland) under high purity N<sub>2</sub>(99.999%) with a flow rate of 60 mL  $\cdot$  min<sup>-1</sup> and the heating rate was 10  $^{\circ}$ C  $\cdot$  min<sup>-1</sup>. The mass of the sample used for TG analysis was 2.410 mg.

A differential scanning calorimeter (Model SETSYS-16/18, SETARAM, France) was used to perform the thermal analysis of [Ho<sub>2</sub>(Ala)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>]Cl<sub>6</sub>. The mass of the sample used for DSC measurement was 3.000 mg, the heating rate was 10  $^{\circ}$ C  $\cdot$  min<sup>-1</sup>, and the flow rate of purge gas (N<sub>2</sub>, with a purity of

99.999%) was 20 mL  $\cdot$  min<sup>-1</sup>.

## 2 Results and discussion

### 2.1 Heat capacity

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

For [Ho<sub>2</sub>(Ala)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>]Cl<sub>6</sub> over the temperature range from 78 to 214 K:

$$C_{p,m}(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 721.31 + 293.82X - 45.119X^2 - 65.422X^3 - 6.7924X^4 + 33.737X^5 \quad (1)$$

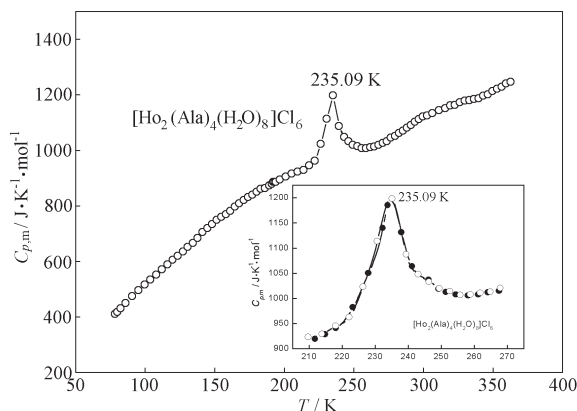
where,  $X = [T(\text{K}) - 146]/68$ ,  $T$  is the absolute temperature;  $R^2$  is the correlation coefficient of the fitted curve, and  $R^2 = 0.9998$ .

Over the temperature range of 255 to 363 K:

$$C_{p,m}(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 1140.1 + 116.42X - 87.927X^2 + 39.022X^3 + 77.236X^4 - 35.700X^5 \quad (2)$$

where,  $X = [T(\text{K}) - 309]/54$ ,  $R^2 = 0.9993$ .

From Fig. 1, it can be seen that the heat capacities of the sample [Ho<sub>2</sub>(Ala)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>]Cl<sub>6</sub> increase with increasing temperature in a smooth and continuous manner from 78 to 214 K and from 255 to 363 K. It showed that no phase transition or thermal anomaly occurred in these temperature ranges. Therefore, the sample was stable in the above ranges. However, a thermal anomaly was observed in the temperature range from 214 to 255 K with a peak temperature of 235.09 K. Two series of heat capacity experiments were carried out in the region of thermal anomaly (see Fig. 1) under the same conditions, which may verify that the thermal anomaly behavior was reversible and repeatable. No fusion phenomenon was observed in the sample after the heat capacity measurements were completed. Thus, the thermal



**Fig. 1** Experimental molar heat capacities of [Ho<sub>2</sub>(Ala)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>]Cl<sub>6</sub> as a function of temperature  
 Inserted fig. demonstrates the relationship of  $C_{p,m}$  vs  $T$  in the phase transition region

**Table 1** The experimental molar heat capacities of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  (molar mass:  $M = 1042.92$ )

$T/\text{K}$	$C_p$		$T/\text{K}$	$C_p$	
	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$			$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	
78.328	410.13	180.203	849.95	273.782	1031.6
79.952	416.66	183.250	860.69	276.705	1045.1
82.389	430.83	186.282	863.50	279.627	1050.9
86.032	449.38	189.286	873.16	282.549	1061.8
90.803	473.82	191.234	879.30	285.390	1070.6
95.361	495.72	192.127	885.45	288.231	1080.6
99.746	515.92	193.101	886.76	291.071	1090.5
103.982	534.44	194.075	887.77	293.912	1102.2
108.093	551.37	196.834	894.23	296.834	1111.8
112.090	570.42	201.136	904.77	299.756	1120.7
115.995	588.31	205.519	916.19	302.679	1125.2
119.812	605.70	209.740	923.21	306.575	1133.6
123.550	620.18	213.880	928.92	311.201	1144.1
127.218	635.11	218.019	945.17	315.747	1150.5
130.830	651.99	222.159	962.73	319.237	1161.0
134.388	666.44	226.299	1022.9	322.779	1163.8
137.906	684.46	230.601	1113.4	326.136	1172.4
141.369	705.18	235.091	1198.0	329.627	1178.6
144.806	719.92	239.367	1087.2	333.023	1180.1
148.198	733.84	243.019	1047.9	336.364	1183.8
151.551	748.79	246.266	1032.6	339.692	1187.4
154.870	759.41	249.432	1019.8	343.101	1196.3
158.152	769.45	252.597	1014.1	346.429	1201.8
161.402	781.30	255.763	1006.7	349.756	1213.2
164.615	796.77	258.795	1007.4	353.084	1221.2
167.789	807.77	261.832	1010.6	356.331	1228.3
170.931	821.15	264.846	1012.8	359.578	1240.1
174.045	831.64	267.843	1020.1	362.744	1245.6
177.136	839.15	270.829	1032.6		

anomaly may be ascribed to a solid-solid phase transition for the investigated solid complex.

The molar enthalpy of the phase transition,  $\Delta H_m$ , and molar entropy of the phase transition,  $\Delta S_m$ , of the complex were derived from the heat capacity data according to the relationship of thermodynamic functions. The  $\Delta H_m$  and  $\Delta S_m$  were determined to be  $3.017 \text{ kJ} \cdot \text{mol}^{-1}$  and  $12.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , respectively.

## 2.2 The values of thermodynamic functions

In the present study, the heat capacity near the temperature of thermodynamic zero point was difficult to obtain. Therefore, only the thermodynamic function data in the temperature range from 80 to 400 K were calculated based on the reference standard temperature 298.15 K. According to the relationship between the molar heat capacity and the thermodynamic functions (formula 3, 4) by means of numerical integrating the heat capacity polynomials, the values of thermodynamic functions,

$H_T - H_{298.15 \text{ K}}$  and  $S_T - S_{298.15 \text{ K}}$  were calculated and listed in Table 2 with the interval of 5 K.

$$H_T - H_{298.15 \text{ K}} = \int_{298.15}^T C_{p,m} dT \quad (3)$$

$$S_T - S_{298.15 \text{ K}} = \int_{298.15}^T C_{p,m} T^{-1} dT \quad (4)$$

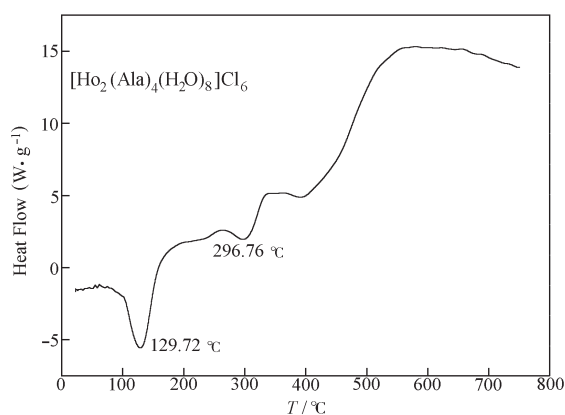
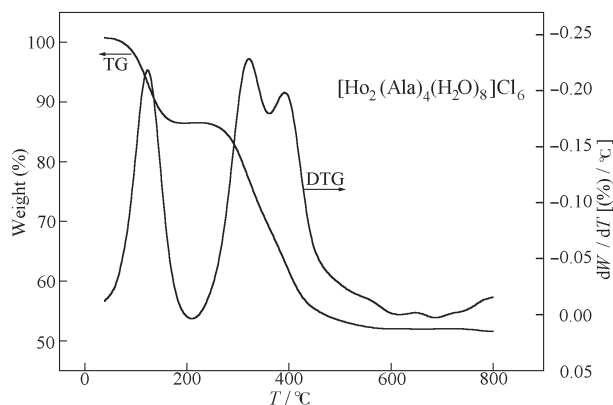
## 2.3 The results of TG/DSC analysis of the sample

The DSC results of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  are presented in Fig. 2, from which we can see that no thermal anomaly occurred below  $80 \text{ }^\circ\text{C}$ , which means that the structure of the complex was stable below this temperature. However, two exothermic peaks were observed at about  $129 \text{ }^\circ\text{C}$  and  $296 \text{ }^\circ\text{C}$ , respectively.

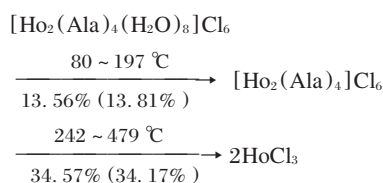
The TG/DTG curves of the complex are shown in Fig. 3. It can be seen clearly from the mass-loss curve that two steps existed in the process of the thermal decomposition for  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$ . The solid complex was stable below  $80 \text{ }^\circ\text{C}$  and started decomposi-

**Table 2** The values of the thermodynamic functions of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$ 

$T/\text{K}$	$C_p$	$H_{298.15} - H_T$	$S_{298.15} - S_T$	$T/\text{K}$	$C_p$	$H_{298.15} - H_T$	$S_{298.15} - S_T$
	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$		$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
80	418.36	182.97	1000.9	230	1100.5	72.186	275.03
85	444.66	180.82	974.77	235	1196.5	66.430	250.28
90	469.38	178.53	948.65	235.09	1206.8	66.322	249.82
95	493.01	176.12	922.63	240	1077.4	60.768	226.43
100	515.95	173.60	896.76	245	1037.8	55.501	204.71
105	538.51	170.96	871.04	250	1017.7	50.363	183.95
110	560.88	168.22	845.47	255	1034.1	45.272	163.79
115	583.23	165.36	820.05	260	1007.2	40.201	144.09
120	605.61	162.38	794.75	265	1012.6	35.154	124.87
125	628.04	159.30	769.58	270	1023.5	30.065	105.85
130	650.49	156.10	744.51	275	1037.9	24.913	86.937
135	672.87	152.79	719.54	280	1054.2	19.683	68.091
140	695.08	149.37	694.67	285	1071.2	14.369	49.283
145	716.98	145.84	669.89	290	1087.9	8.971	30.507
150	738.42	142.20	645.22	295	1103.7	3.492	11.773
155	759.25	138.46	620.67	298.15	1113.0	0.000	0.000
160	779.32	134.61	596.24	300	1118.1	-2.064	-6.901
165	798.47	130.67	571.97	305	1131.0	-7.687	-25.491
170	816.59	126.63	547.86	310	1142.2	-13.371	-43.974
175	833.58	122.50	523.94	315	1152.0	-19.107	-62.330
180	849.39	118.30	500.23	320	1160.6	-24.890	-80.542
185	864.00	114.01	476.76	325	1168.4	-30.712	-98.597
190	877.45	109.66	453.54	330	1175.8	-36.573	-116.49
195	889.85	105.24	430.58	335	1183.4	-42.471	-134.23
200	901.37	100.76	407.91	340	1191.5	-48.408	-151.82
205	912.28	96.226	385.51	345	1200.8	-54.388	-169.28
210	922.92	91.638	363.40	350	1211.6	-60.418	-186.63
215	933.88	86.994	341.55	355	1224.3	-66.507	-203.91
220	949.08	82.271	319.83	360	1239.1	-72.664	-221.13
225	999.67	77.426	298.06	365	1256.3	-78.902	-238.34

**Fig. 2** DSC curve of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  under high purity  $\text{N}_2$  atmosphere**Fig. 3** TG/DTG curves of  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  under high purity  $\text{N}_2$  atmosphere

tion at this point. The first mass-loss took place in the range of 80 ~ 197 °C, and the second mass-loss occurred in the temperature range of 242 ~ 479 °C. These results were well in accord with those obtained by DSC. The first mass-loss was 13.56 %, and the second mass-loss was 34.57 %. According to the mass-loss in each step, it was assumed that the first mass-loss peak was associated with the loss of water, and the second mass-loss peak corresponded to the decomposition of alanine. Because the two corresponding mass-losses were close to the calculated theoretical values, we considered that the final residue for thermal decomposition of the complex should be  $\text{HoCl}_3$ . Therefore, the possible mechanism of thermal decomposition for the complex was deduced as follows:



The mass-loss percentages in the brackets are the calculated theoretical values of the corresponding thermal decomposition.

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## 稀土钬丙氨酸配合物的热力学性质\*

刘北平<sup>1,2</sup> 谭志诚<sup>2</sup> 余华光<sup>2</sup> 兰孝征<sup>2</sup> 张大顺<sup>1</sup> 刘平<sup>1</sup> 孙立贤<sup>2</sup>

(<sup>1</sup> 常德师范学院化学系, 常德 415000;

<sup>2</sup> 中国科学院大连化学物理研究所热化学实验室, 大连 116023)

**摘要** 合成了稀土氯化钬丙氨酸配合物,  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$ , 的晶体. 用绝热量热法测定了其在 78 ~ 363 K 温区的热容. 在 214 ~ 255 K 温区发现一固-固相变, 相变峰温、相变焓和相变熵分别为 235.09 K, 3.017 kJ · mol<sup>-1</sup> 和 12.83 J · K<sup>-1</sup> · mol<sup>-1</sup>. 用最小二乘法将实验热容值拟合热容随温度变化的多项式方程, 利用此方程式和热力学函数关系, 计算出以 298.15 K 为参考温度的热力学函数值. 在 40 ~ 800 °C 温区, 用热重分析和差示扫描量热法研究了该配合物的热稳定性, 观察到  $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$  分两步分解, 第一步从 80 °C 开始, 179 °C 结束; 第二步从 242 °C 开始, 479 °C 结束. 从热分析结果推测出该配合物可能的热分解机理.

**关键词:** 稀土氨基酸配合物, 氯化钬丙氨酸配合物 ( $[\text{Ho}_2(\text{Ala})_4(\text{H}_2\text{O})_8]\text{Cl}_6$ ), 绝热量热, 热容, 热力学函数, 热重, 差示扫描量热

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