Low-Temperature Heat Capacity and Thermal Decomposition of Crystalline $[Ho(Thr)(H_2O)_5]Cl_3$

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Rare earth elements have been widely used in many areas. Rare earth complex bearing an amino acid was synthesized to study the influence and the long-term effect of rare earth elements on environment and human beings, because amino acid is the basic unit of the living things. Previous work on these kinds of complex is focused on synthesis and characterization of them. But their thermodynamic data have seldom been reported. Here we present the thermodynamic study of $[Ho(Thr)(H_2O)_5]Cl_3$. The heat capacity of Holmium complex with threonine, $[Ho(Thr)(H_2O)_5]Cl_3$, was measured with an automatic adiabatic calorimeter in the temperature range from 79 K to 330 K and no thermal anomaly was found in this range. Thermodynamic functions relative to standard state 298.15 K were derived from the heat capacity data. Thermal decomposition behavior of the complex in nitrogen atmosphere in the range from 300 K to 900 K was studied by thermogravimetric (TG) technique and a possible decomposition mechanism was proposed according to the TG-DTG results.

Keywords RE complex of threonine, heat capacity, thermal decomposition, adiabatic calorimetry, thermodynamic function, TG analysis

Introduction

Rare earth elements (RE) have found their applications in many areas nowadays because of their unique properties: used as the main components of permanent magnet, catalysts, glass ceramics and so on.[1] In recent years, they are also introduced into micro fertilizer, pesticide[2] and antibacterial agent.[3] Accompanying these applications, rare earth elements inevitably spread into food chain, 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 bodies of human beings. In the past 20 years, about 200 kinds of these complexes were synthesized, and about 50 kinds have their own crystallograms.[5] However, for most of this kind of complex till now, no thermodynamic data are available in the literature. As we know, only with these data can we quantitatively describe their properties from energetics, for example, the stable forms in different temperature range, or melting temperature and the energy changes in physical processes or chemical reactions and so on. Comparisons of thermodynamic properties of a series of complexes comprised by the same RE (or ligands) with different ligands (or RE) may make us have deeper understanding characteristics of these complex.

In the present study, the low-temperature heat capacities of complex $[Ho(Thr)(H_2O)_5]Cl_3$ in the range of 79 K to 320 K were directly measured by a precise adiabatic calorimeter. Thermal decomposition behavior of the complex was examined by TG-DTG analysis and a possible decomposition mechanism was presented.

Experimental

Synthesis of sample

$[Ho(Thr)(H_2O)_5]Cl_3$ was synthesized according to the reported procedure.[6] Rare-earth oxide (Ho_2O_3, 99.9% pure) was dissolved in hydrogen chloride acid to get the aqueous solution of the rare-earth chlorates. Then threonine was added into the solution with the molar ratio of 1:1 with rare earth element at pH = 4—5. Crystal was obtained by slow evaporation of the solvent at room temperature. After being washed with water and dried by air, the product was obtained and the composition was determined by elemental analysis.

The purity of the crystal was proved to be more than 99.9% through EDTA titrimetric analysis.

Heat capacity measurements

A precision adiabatic calorimeter was used to deter-

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mine the molar heat capacity. The structure and performance of the calorimeter, and the procedures of heat capacity measurements have been described in detail elswere.[7-10] The data were automauically collected by using a Data Acquisition/Switch Unit (Model 34970A, Agilent, USA) and processed by a computer.

The mass of [Ho(Thr)$(H_2O)_5$]Cl_3 used for heat-capacity measurement was 2.3278 g, which was equivalent to 4.845 mmol based on molar mass of 480.485 g·mol^{-1}.

Calibration of the adiabatic calorimeter was performed with reference standard material α-Al_2O_3 (1.6382 g, 16.067 mmol). The deviations of the measured heat capacities of α-Al_2O_3 from the recommended values of the former National Bureau of Standards[11] were within ±0.2% in the temperature range of 80 K to 400 K.

Thermal analysis

Thermogravimetric (TG) analysis was carried out on a thermal analyzer, model setsys 16/18 SETARAM, France, in the temperature range of 300 K to 900 K under nitrogen (99.9% pure) atmosphere with a flowing rate of N_2 gas of 25 mL·min^{-1} and a heating rate of 10 K·min^{-1}. The amount of sample used was 3.2 mg.

Results and discussion

Heat capacity

The low-temperature experimental molar heat capacities of [Ho(Thr)$(H_2O)_5$]Cl_3 are shown in Fig. 1 and Table 1. The results are fitted as a function of reduced temperature (X) by least-squares, where $X = (T - T_1)/T_2$, $T_1 = (T_h + T_l)/2$, $T_2 = (T_h - T_l)/2$, T_h and T_l are

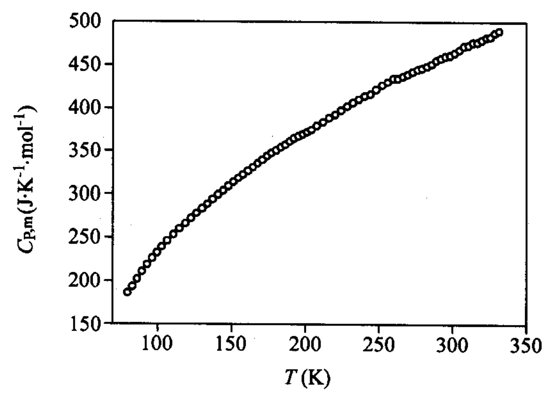

Fig. 1 Molar heat capacities of [Ho(Thr)$(H_2O)_5$]Cl_3.

Table 1 Experimental molar heat capacities of [Ho(Thr)$(H_2O)_5$]Cl_3 (M = 480.485 g·mol^{-1})

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})
82.823	193.54	173.942	344.60	263.390	437.21
86.035	202.30	177.065	348.00	266.041	437.19
89.382	210.86	180.159	350.99	269.365	439.57
92.858	218.96	183.227	354.63	272.670	442.41
96.228	226.53	186.271	357.66	275.958	444.82
99.501	232.77	189.287	361.36	279.224	446.60
102.686	239.25	192.282	365.09	282.472	448.73
106.387	246.26	195.255	367.47	285.700	451.33
110.575	253.47	198.205	369.71	288.899	455.58
114.649	260.29	201.134	372.07	292.066	457.99
118.624	266.31	204.042	374.91	295.217	460.38
122.506	272.34	207.615	379.67	298.361	461.46
126.309	278.20	211.847	383.89	301.493	464.13
130.039	283.77	216.031	388.78	304.608	467.92
133.704	288.96	220.169	392.97	307.709	472.20
137.306	294.41	224.268	397.82	310.793	472.98
140.853	299.66	228.326	402.65	313.860	476.29
144.348	304.39	232.299	406.61	316.900	476.56
147.793	309.35	236.249	410.48	319.894	479.32
151.194	314.41	240.198	414.28	322.803	482.00
154.554	318.43	244.12	416.58	325.714	482.85
157.871	322.74	248.027	421.81	328.640	487.57
161.154	326.87	251.907	426.87	331.548	490.13
164.399	331.27	255.761	430.62		
167.612	335.93	259.588	434.81		

the highest and the lowest temperature in the fitting temperature range, respectively. The following polynomial equation in the temperature range of 79 K to 320 K is obtained:

$$C_{p,m}(J \cdot K^{-1} \cdot mol^{-1}) = 378.7 + 137.57X - 27.256X^2 - 8.0108X^3 - 14.725X^4 + 22.225X^5 + 11.3177X^6$$

where $X = (T - 205.520)/126.028$, T is the absolute temperature. The average deviation of the fitting is 0.24%.

As shown in Fig. 1, the heat capacity curve is smooth and continuous, indicating that the complex in the testing temperature range is stable and no thermal anomaly takes place.

Thermodynamic functions

The smoothed heat capacities can be obtained from the above polynomial from 80 K to 330 K with a temperature intervals of 5 K. Thermodynamic functions relative to the standard reference temperature (298.15 K), $H_T - H_{298.15}$, $S_T - S_{298.15}$, are calculated on the basis of the polynomial by using following thermodynamic relationships:

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m} dT$$

$$S_T - S_{298.15} = \int_{298.15}^{T} C_{p,m} T^{-1} dT$$

The values of the above functions are actually the sum of integrity in different temperature range plus the changed value during phase transition. All data are tabulated in Table 2.

Decomposition mechanism

TG-DTG curve of $[Ho(Thr)(H_2O)_5]Cl_3$ is shown in Fig. 2. The residue remained in the crucible was a small solid ball with spongy pale yellow. On the bases of experimental and calculated results, the possible decomposition mechanism of the compound is postulated as follows[12]

Table 2 Smoothed heat capacities and thermodynamic functions relative to 298.15 K of $[Ho(Thr)(H_2O)_5]Cl_3$ ($M = 480.485$ g·mol^{-1})

T (K)	$C_{p,m}$ (J·K^{-1}·mol^{-1})	$S_T - S_{298.15}$ (J·K^{-1}·mol^{-1})	$H_T - H_{298.15}$ (kJ·mol^{-1})	T (K)	$C_{p,m}$ (J·K^{-1}·mol^{-1})	$S_T - S_{298.15}$ (J·K^{-1}·mol^{-1})	$H_T - H_{298.15}$ (kJ·mol^{-1})
80	187.59	-422.91	-76.489	210	383.57	-148.40	-37.524
85	200.15	-411.16	-75.519	215	388.90	-139.31	-35.593
90	211.89	-399.39	-74.489	220	394.14	-130.30	-33.635
95	222.87	-387.64	-73.402	225	399.29	-121.37	-31.651
100	233.19	-375.95	-72.261	230	404.33	-112.53	-29.642
105	242.92	-364.33	-71.071	235	409.27	-103.78	-27.608
110	252.10	-352.81	-69.833	240	414.10	-95.100	-25.550
115	260.82	-341.40	-68.550	245	418.81	-86.510	-23.468
120	269.12	-330.11	-67.225	250	423.41	-78.000	-21.362
125	277.05	-318.95	-65.860	255	427.90	-69.570	-19.234
130	284.66	-307.93	-64.455	260	432.27	-61.220	-17.083
135	291.98	-297.04	-63.014	265	436.53	-52.950	-14.911
140	299.06	-286.30	-61.536	270	440.68	-44.760	-12.718
145	305.92	-275.68	-60.023	275	444.74	-36.650	-10.504
150	312.59	-265.20	-58.477	280	448.70	-28.600	-8.2710
155	319.10	-254.85	-56.898	285	452.59	-20.630	-6.0180
160	325.46	-244.63	-55.286	290	456.42	-12.730	-3.7450
165	331.70	-234.52	-53.644	295	460.21	-4.9000	-1.4530
170	337.82	-224.54	-51.970	298.15	462.60	0	0
175	343.84	-214.67	-50.265	300	464.00	2.8700	0.8570
180	349.77	-204.90	-48.531	305	467.79	10.570	3.1870
185	355.61	-195.24	-46.768	310	471.64	18.220	5.5350
190	361.37	-185.69	-44.975	315	475.57	25.800	7.9030
195	367.04	-176.23	-43.154	320	479.64	33.330	10.291
200	372.63	-166.86	-41.305	325	483.89	40.810	12.700
205	378.14	-157.59	-39.428	330	488.38	48.220	15.130

$$[Ho(Thr)(H_2O)_5]Cl_3 \xrightarrow[84.8\%\ (85\%)]{25—191.3\ ℃}$$

$$[Ho(Thr)(H_2O)]Cl_3 \xrightarrow[80.6\%\ (81.3\%)]{236—255.4\ ℃}$$

$$[Ho(Thr)]Cl_3 \xrightarrow[60.3\%\ (60.3\%)]{258—553\ ℃}$$

$$2[Ho(Thr)]Cl_3 \cdot Ho_2O_3 \xrightarrow[52.7\%\ (52.7\%)]{503—684.8\ ℃}$$

$$2HoCl_3 \cdot HoOCl \xrightarrow[39.9\%\ (39.3\%)]{684.8—841.1\ ℃} Ho_2O_3$$

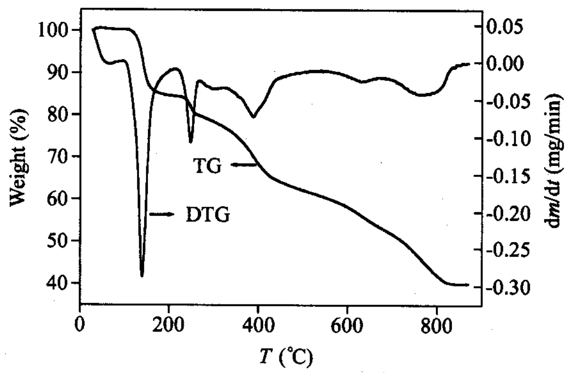

Fig. 2 TG and DTG curves of $[Ho(Thr)(H_2O)_5]Cl_3$.

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12 The data (%) in brackets are the calculated values.

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