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Low-Temperature Heat Capacity and Enthalpy of Formation of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$

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A crystalline complex of erbium perchlorate coordinated with glycine, $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, has been synthesized. No melting point is observed above room temperature. The heat capacity of the complex was measured by adiabatic calorimetry from 79 K to 369 K, and two peaks centered at 233 K and 325 K were found. The first peak centered at 233 K was a phase transformation peak, and the second was decomposition. The temperature, enthalpy change, and entropy change of the phase transformation were 219.47 K, 17.51 $kJ \cdot mol^{-1}$, and 79.77 $J \cdot K^{-1} \cdot mol^{-1}$, and those of the decomposition process were 312.576 K, 94.86 $kJ \cdot mol^{-1}$, and 303.49 $J \cdot K^{-1} \cdot mol^{-1}$. The polynomial equations of heat capacity in different temperature ranges, 79.091 K to 217.424 K and 255.606 K to 306.143 K, have been obtained by least-squares fitting. The standard enthalpy of formation was determined to be $\Delta_f H_m^\theta$ ($[Er_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, s, 298.15 K) = -7911.13 ± 2.77 $kJ \cdot mol^{-1}$ by isoperibol reaction calorimetry.

Introduction

Rare earth complexes coordinated with amino acids are of interest for several reasons.[1−4] On the basis of our previous work and experiences,[5,6] erbium perchlorate coordinated with glycine, $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, was synthesized, and the composition was analyzed. The heat capacity of the complex was measured by adiabatic calorimetry from 79 K to 369 K, and the polynomial equations of heat capacity were obtained by least-squares fitting. The enthalpy of formation was determined by isoperibol reaction calorimetry at 298.15 K.

Experimental

Synthesis of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$. Following the synthesis method described in ref 7, 2.252 g of glycine was added into 30.36 mL of 0.988 $mol \cdot L^{-1}$ $Er(ClO_4)_3$ solution, and then distilled water was added to 150 mL with the final pH of 3.0. The mixed solution was stirred for 2 h in a water bath at 353 K, then concentrated to 25 mL by evaporation at the same temperature. The concentrated solution was placed at room temperature, and pink crystals appeared after about 23 days of natural evaporation. The constant weight is 2.7 g.

Synthesis of Rare Earth Nitrate. Following the synthesis method of ref 8, about 2 g of Er_2O_3 was put into a heating strong nitric acid solution and dissolved into the solution gradually (quantity of oxide is excessive). The excessive Er_2O_3 was separated from the solution after the completion of the reaction. By cooling the solution, the crystal of nitrate appeared. The crystal was then put into a vacuum desiccator at room temperature, and after 48 h desiccation, it was transferred to the desiccator with desiccant of 45 % H_2SO_4 and was dried to constant weight. At last, the pink erbium nitrate crystal was obtained.

Component Determination. Analysis of C, H, and N in the rare earth complex was performed with an EA-1106 elementary analyzer (Carlo Erba, Italy), and the relative content of Er was determined by EDTA titration. Thermogravimetric analysis (TG) (static air atmosphere, 10 $K \cdot min^{-1}$, 6.00 mg sample) and differential thermal analysis (DTA) (room temperature to 773 K, N_2 atmosphere with 40 $mL \cdot min^{-1}$, 3 $K \cdot min^{-1}$, sample 12.80 mg) were carried out with TGA/DT-20B (Shimadzu, Japan) and DTA/DTA-1700 (Perkin-Elmer Co. Ltd., U.S.A.).

The melting point of the sample was measured using a micromelting point apparatus/XT4 (Beijing Taike Instrument Company).

The Er component of rare earth nitrate was determined by thermogravimetric analysis using TGA/DT-20B (Shimadzu, Japan) and by EDTA titration.

Determination of Low-Temperature Heat Capacity. Low-temperature heat capacity was measured with the high-precision, fully automatic, adiabatic calorimeter manufactured by Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The instrument and procedure are described in ref 9. The reliability of the calorimeter was verified by measuring the molar heat capacity of standard α-Al_2O_3, and the accuracy is ± 0.1 %. The temperature precision was 10^{-4} K; the temperature step was 2 K to 4 K; the step period was 25 min; and the continuous testing time was 34 h.

Determination of Enthalpy of Formation. The determination of enthalpy of formation was carried out with an isoperibol reaction calorimeter which was modified by Thermochemistry Laboratory of Wuhan University based on the instrument provided by London University.[10] The temperature control precision is $\pm 1 \cdot 10^{-3}$ K, and the detection limit for measuring the temperature is $\pm 1 \cdot 10^{-4}$ K. To verify the reliability of the calorimeter, the molar enthalpy of KCl was measured at 298.20 K, and the results were within ± 0.5 % of the literature values (17.536 ± 0.009 $kJ \cdot mol^{-1}$).[11]

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Table 1. Experimental Heat Capacities of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O$ (M_r = 1543.7624 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}	T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}
79.091	571.42	136.764	944.37	217.424	1542.85	306.143	1948.07
81.727	592.59	140.145	958.40	223.485	1809.52	310.094	2112.60
84.600	624.74	144.125	980.28	229.394	2471.42	313.854	2397.98
87.386	641.53	148.039	1001.59	233.234	3756.53	317.343	2846.80
90.097	670.09	151.891	1021.56	236.790	2134.94	320.449	3701.42
92.736	689.65	155.684	1044.44	241.212	1585.71	323.050	5246.83
95.531	702.90	159.423	1058.78	246.061	1490.47	325.111	7401.13
98.476	730.40	163.113	1082.23	250.887	1446.03	327.273	4752.38
101.364	738.09	166.756	1094.02	255.606	1461.90	330.152	3238.09
104.242	758.09	170.355	1118.30	259.848	1485.71	333.636	2333.33
107.189	781.05	173.912	1129.06	263.636	1514.28	337.424	2104.76
110.393	799.11	177.431	1150.03	267.424	1547.62	341.061	2100.00
113.529	821.72	180.908	1170.58	271.992	1567.44	344.697	2109.52
116.601	843.83	184.343	1194.84	276.515	1604.76	348.182	2157.14
119.615	860.73	188.182	1233.33	280.909	1676.19	351.818	2238.09
122.578	875.69	192.727	1300.00	285.289	1697.89	358.636	2385.72
125.496	889.13	197.727	1328.57	289.545	1761.90	362.121	2442.85
128.373	901.82	202.576	1409.52	293.788	1795.24	365.455	2500.00
131.207	922.45	207.424	1461.90	298.030	1842.85	368.788	2595.24
134.002	932.35	212.273	1504.76	302.082	1891.41		

The standard enthalpy of formation of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O$ was determined according to a designed chemical cycle at 298.15 K and under a normal atmosphere. The reaction equation

$$2Er(NO_3)_3\cdot 6H_2O + 6Gly + 6NaClO_4\cdot H_2O = [Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O + 6NaNO_3 + 9H_2O \quad (1)$$

was designed first, whose reaction enthalpy was $\Delta_r H_m^\theta$. Then the reactants $\{2Er(NO_3)_3\cdot 6H_2O + 6Gly + 6NaClO_4\cdot H_2O\}$ and the products $\{[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O + 6NaNO_3\}$ not including H_2O were dissolved in 100 mL of 2 mol·L^{-1} HCl solution, respectively, and the corresponding dissolution enthalpies were $\Delta_s H_1^\theta$ and $\Delta_s H_2^\theta$. If the two dissolved materials are identical, the chemical cycle would be completed, and then the standard enthalpy of formation of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O$ could be calculated from the standard enthalpies of formation of other complexes in reaction 1, $\Delta_r H_m^\theta$, $\Delta_s H_1$, and $\Delta_s H_2$, and the dilution enthalpy, $\Delta_d H$, of the mixing process between 2 mol·L^{-1} HCl solution and H_2O, which is the only liquid-phase member in the products.

The final states of dissolution systems were determined and compared with Abbe's refractometer WZS-1 (Shanghai instrument plant, China) and UV-16 visible spectroscopy (Shimadzu, Japan).

Results and Discussion

Constitution, Structure, and Melting Point of the Rare Earth Perchlorate Complex. The composition of the synthesized rare earth perchlorate complex was C 9.11 %, H 3.43 %, N 5.34 %, Er 21.63 %, which agrees with the theoretical values for $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O$: C 9.34 %, H 3.13 %, N 5.44 %, Er 21.67 %.

There were four peaks in the DTA curves. The first one is an endothermal peak centered at 339.4 K. The second and the third endothermal peaks are overlapped with each other, with peaks at 419.4 K and 469.1 K. The area of the two peaks is approximately equal, and their total area is a little smaller than that of the first peak. The fourth peak is an exothermic peak at 539.2 K. The TG results show that the weight loss in the two periods, 313 K to 484 K and 505 K to 540 K, is 11.3 % and 55.7 %, respectively. The DTA results together with the TG results show the thermal decomposition process of the sample is composed of four steps: five exterior crystallization water at first, and two interior crystallization water in the following two steps sequentially. The weight loss in the high-temperature range of 505 K to 540 K is probably caused by the loss of amino acid and the simultaneous oxidation of the amino acid by perchlorate and some other decomposition processes. The DTA and TG analysis provide further information for determining the structure of the product.

The purity of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O$ in the synthesized product was determined to be 99.82 % by EDTA complexometric titration of the Er element. The melting point of the rare earth complex coordinated with amino acid was scanned from room temperature to 593 K, and no definite melting point was observed. The complex exhibits as a light pink solid at room temperature and begins to soften and to turn yellow gradually from 547 K, and its color turns to dark yellow at 593 K.

The constitution of the synthesized rare earth nitrate was determined to be $Er(NO_3)_3\cdot 6H_2O$ by EDTA titration and thermal analysis.

Heat Capacity of the Sample. 79 sets of molar heat capacity values of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O$ were tested with the sample's weight of 2.6707 g. The experimental results are listed in Table 1, and the variation of molar heat capacity, $C_{p,m}$, along with the experimental temperature is pictured in Figure 1.

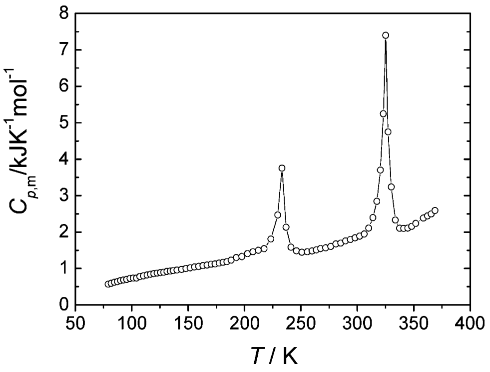

Figure 1. Experimental molar heat capacity plotted against temperature of $[Er_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot 5H_2O$.

It can be seen from Figure 1 that the $C_{p,\mathrm{m}}-T$ curve of $[\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O}$ is smoothly ascending over the temperature range from 79.091 K to 217.424 K, which indicates that there exists no magnetic heat capacity and other abnormal heat phenomenon in this range. There are two peaks in Figure 1 with the peak values of about 233 K and 325 K. Incorporated with the results of DTA, TG analysis, and the melting point measurement, the peak at 233 K is probably induced by the transition of the crystallographic form, and the second peak at 325 K is assigned to be the dehydration peak corresponding to the loss of five crystallization water from $[\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O}$.

The polynomial equation of molar heat capacity, $C_{p,\mathrm{m}}$, to temperature, T, of complex $[\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O}$ over the temperature range from 79.091 K to 217.424 K has been obtained by fitting the experimental data using the least-squares method

$$C_{p,\mathrm{m}}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 998.688 + 337.336X + 53.454X^2 + 162.664X^3 + 18.025X^4$$

where $X = (T/\mathrm{K} - 148.258)/69.167$ and the correlation coefficient of the fitting $R = 0.99923$.

From 255.606 K to 306.143 K

$$C_{p,\mathrm{m}}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = 1660.339 + 257.571X + 37.055X^2 - 10.742X^3 + 6.936X^4$$

where $X = (T/\mathrm{K} - 280.875)/25.269$ and the correlation coefficient $R = 0.99869$.

Using the area integration method,[9] in the temperature range of 217.424 K to 255.606 K, the transformation temperature, the enthalpy, and the entropy of phase transition were determined to be 219.47 K, 17.51 $\mathrm{kJ\cdot mol^{-1}}$, and 79.77 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, respectively. For the decomposition process that occurs in the temperature range of 306.143 K to 341.061 K, the dehydration temperature is 312.576 K; the decomposition enthalpy is 94.86 $\mathrm{kJ\cdot mol^{-1}}$; and the decomposition entropy is 303.49 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

Standard Enthalpy of Formation at 298.15 K. A portion of 0.1500 g of $[\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O}$ was weighted for the calorimetric experiments, and the quantities of other reactants and products were determined according to the stoichiometric relationship of reaction 1. The experimental temperature difference was traced by thermal resistance through a DC Wheatstone Bridge, and the temperature value was conversed to the electromotive force E. The energy equivalent was determined using electric standardization and was corrected by the Reynolds graph.[12] The calibration heating resistor is $R = 1350.3\ \Omega$, and the calibration electric current is $I = 9.997\cdot 10^{-3}$ A. The electric calibration heat, $Q_\mathrm{e} = I^2Rt$, the dissolution heat $Q_\mathrm{s} = (E_\mathrm{s}/E_\mathrm{e})Q_\mathrm{e} = \Delta_\mathrm{s}H$, and E_s and E_e have been corrected using the Reynolds graph.

The dissolution enthalpy, $\Delta_\mathrm{s}H^\theta$, was calculated from the average of five experiments. The average dissolution enthalpy of the reactants dissolved in 100 mL of 2 $\mathrm{mol\cdot L^{-1}}$ HCl solution was $\overline{\Delta_\mathrm{s}H_1} = 13.71 \pm 0.16$ J, and that of the products not including $\mathrm{H_2O}$ was $\overline{\Delta_\mathrm{s}H_2} = 16.34 \pm 0.21$ J.

According to the Hess law, $\Delta_\mathrm{r}H^\theta = \Delta_\mathrm{s}H_1 - \Delta_\mathrm{s}H_2 - \Delta_\mathrm{d}H$, where $\Delta_\mathrm{d}H$ is the enthalpy of dilution of 0.0158 g of $\mathrm{H_2O}$ adding into 100 mL of 2 $\mathrm{mol\cdot L^{-1}}$ HCl. According to the latter calculation in the following part, the value of $\Delta_\mathrm{d}H$ is very small and so could be omitted here. Thus, to calculate the reaction enthalpy, only the dissolution enthalpies $\Delta_\mathrm{s}H_1$ and $\Delta_\mathrm{s}H_2$ are needed.

Reaction enthalpy:

$$\Delta_\mathrm{r}H^\theta = \overline{\Delta_\mathrm{s}H_1} - \overline{\Delta_\mathrm{s}H_2} - \Delta_\mathrm{d}H = \overline{\Delta_\mathrm{s}H_1} - \overline{\Delta_\mathrm{s}H_2} = (13.71 - 16.34)\ \mathrm{J} = -2.63 \pm 0.27\ \mathrm{J}$$

For that, 0.1500 g of $[\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O}$ participated in the reaction, and after scaling, $\Delta_\mathrm{r}H_\mathrm{m}{}^\theta = -27.08 \pm 2.76\ \mathrm{kJ\cdot mol^{-1}}$.

$$\Delta_\mathrm{r}H_\mathrm{m}{}^\theta = \Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ ([\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O},\ \mathrm{s},\ 298.15\ \mathrm{K}) + 6\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{NaNO_3},\ \mathrm{s},\ 298.15\ \mathrm{K}) + 9\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{H_2O},\ \mathrm{l},\ 298.15\ \mathrm{K}) - 2\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{Er(NO_3)_3\cdot 6H_2O},\ \mathrm{s},\ 298.15\ \mathrm{K}) - 6\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{Gly},\ \mathrm{s},\ 298.15\ \mathrm{K}) - 6\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{NaClO_4\cdot H_2O},\ \mathrm{s},\ 298.15\ \mathrm{K})$$

According to ref 13

$$\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{NaNO_3},\ \mathrm{s},\ 298.15\ \mathrm{K}) = -467.85\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{Gly},\ \mathrm{s},\ 298.15\ \mathrm{K}) = -528.10\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{NaClO_4\cdot H_2O},\ \mathrm{s},\ 298.15\ \mathrm{K}) = -677.77\ \mathrm{kJ\cdot mol^{-1}}$$

According to ref 14

$$\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{H_2O},\ \mathrm{l},\ 298.15\ \mathrm{K}) = -285.83 \pm 0.04\ \mathrm{kJ\cdot mol^{-1}}$$

According to ref 8

$$\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ (\mathrm{Er(NO_3)_3\cdot 6H_2O},\ \mathrm{s},\ 298.15\ \mathrm{K}) = -3014.2\ \mathrm{kJ\cdot mol^{-1}}$$

So, the standard formation enthalpy of $[\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O}$ could be calculated

$$\Delta_\mathrm{f}H_\mathrm{m}{}^\theta\ ([\mathrm{Er_2(Gly)_6(H_2O)_4}](\mathrm{ClO_4})_6\cdot 5\mathrm{H_2O},\ \mathrm{s},\ 298.15\ \mathrm{K}) = -7911.13 \pm 2.77\ \mathrm{kJ\cdot mol^{-1}}$$

Estimation of Dilution Enthalpy Δ_dH. The enthalpy of dilution of 0.0158 g of water adding into 100 mL of 2 $\mathrm{mol\cdot L^{-1}}$ HCl (the molar concentrations of mass of HCl before and after dilution are 2.1573 $\mathrm{mol\cdot kg^{-1}}$ and 2.1569 $\mathrm{mol\cdot kg^{-1}}$, respectively) can be obtained by least-squares fitting of the data of ref 14 over the range from 1.5000 $\mathrm{mol\cdot kg^{-1}}$ to 2.5000 $\mathrm{mol\cdot kg^{-1}}$. The fitted linear equation is $\varphi_\mathrm{L} = 198.11 + 214.04m$, and the relative coefficient $R = 0.99991$. And then

$$\Delta_\mathrm{d}H_{2.1573\ \mathrm{mol/kg}\rightarrow 2.1569\ \mathrm{mol/kg}} = \Delta_\mathrm{d}H_{2.1573\ \mathrm{mol/kg}\rightarrow 0} - \Delta_\mathrm{d}H_{2.1569\ \mathrm{mol/kg}\rightarrow 0}$$

$$= (\varphi_{\mathrm{L}(2.1573\ \mathrm{mol/kg})} - \varphi_{\mathrm{L}(2.1569\ \mathrm{mol/kg})})\cdot 0.1\cdot 4.184\cdot 10^{-3}$$

$$= -(659.8585 - 659.7722)\cdot 0.1\cdot 4.184\cdot 10^{-3}\ \mathrm{kJ}$$

$$= -3.611\cdot 10^{-5}\ \mathrm{kJ}$$

This calculation result shows that it is feasible to ignore the dilution enthalpy in the calculation of reaction enthalpy.

Identification Test for the Final Dissolved Material. The identity of the final dissolved material of the reactants and the products of reaction 1 is the key step of the designed chemical cycle for the calculation of standard enthalpy of formation of

$[Er_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$. The refractive index and UV spectrum of reactants $[2Er(NO_3)_3 \cdot 6H_2O + 6Gly + 6NaClO_4 \cdot H_2O]$ and products $\{[Er_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O + 6NaNO_3 + 9H_2O\}$ dissolved in 100 mL of 2 $mol \cdot L^{-1}$ HCl had been determined by using WZS-1 Abbe's refractometer and UV-16 ultraviolet−visible spectrometer. The experimental data of the two solutions are identical. The designed chemical cycle is reasonable.[15]

Supporting Information Available:

The experimental data for calculating the dissolution enthalpy $\Delta_s H^\theta$ are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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