LOW–TEMPERATURE HEAT CAPACITY AND STANDARD ENTHALPY OF FORMATION OF NEODYMIUM GLYCINE PERCHLORATE COMPLEX [Nd$_2$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O

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Rare-earth perchlorate complex coordinated with glycine [Nd$_2$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O was synthesized and its structure was characterized by using thermogravimetric analysis (TG), differential thermal analysis (DTA), chemical analysis and elementary analysis. Its purity was 99.90%. Heat capacity measurement was carried out with a high-precision fully-automatic adiabatic calorimeter over the temperature range from 78 to 369 K. A solid–solid phase transformation peak was observed at 256.97 K, with the enthalpy and entropy of the phase transformation process are 4.438 kJ mol^{-1} and 17.270 J K^{-1} mol^{-1}, respectively. There is a big dehydrated peak appears at 330 K, its decomposition temperature, decomposition enthalpy and entropy are 320.606 K, 41.364 kJ mol^{-1} and 129.018 J K^{-1} mol^{-1}, respectively. The polynomial equations of heat capacity of this compound in different temperature ranges have been fitted. The standard enthalpy of formation was determined to be –8023.002 kJ mol^{-1} with isoperibol reaction calorimeter at 298.15 K.

Introduction

Rare earth complex coordinated with amino acids possesses many special functions especially in biologic process, and so it has drawn more and more attention by experimentalists and theoreticians. The rare-earth perchlorate complexes have been used widely in medicine, biological diagnosis, agriculture, forestry, livestock production and fishing, etc. [1], therefore the fundamental theoretical study including thermodynamic study on such kind of complex is very significant [2, 3]. However, till now basic thermochemistry data of rare earth complexes with amino acids were rarely reported. To promote the further applications of the rare earth perchlorate complexes, the titled compound was synthesized and was studied by thermodynamic method in this paper, and some important thermochemistry data and heat decomposition mechanics have been acquired.

Experimental

Synthesis of [Nd$_2$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O

The synthesis method was designed according to [4]: 30 mmol glycine was added into 40 mmol Nd(ClO$_4$)$_3$ solution (0.998 mol L^{-1}), then distilled water was added to 200 mL, and the pH value of the final dilution was 2.9. The mixed solution was stirred for 8 h in water bath at 353 K, and then concentrated by evaporation at the same temperature. The obtained microcrystalline was redissolved in distilled water and then filtered. The filtrate was placed at room temperature, purple crystal would appear after about 20 days natural evaporation. At last the crystals were dried to constant mass, the product was 4.3 g.

Methods

Component determination of the product

The ratio analysis of C, H and N in the complex was performed with EA-1106 elementary analyzer (Carlo Erba, Italian), and the relative content of Nd was determined by EDTA titration. To confirm the component and the structure of the complex, the thermogravimetric analysis and the differential thermal analysis were also carried out with TGA/DT-20B (Shimadzu, Japan) and DTA/PCT-2 (Beijing Optical Instrument Plant). The melting point of the sample was measured with micromelting point apparatus/XT4 (Beijing Taike Instrument Company).

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 the test condition have been described in [5]. The test lasted for 36 h.

Determination of standard enthalpy of formation

The determination of standard enthalpy of formation was carried out with the solution-reaction isoperibolic calorimeter which was constructed by Thermochemistry Lab. of Wuhan University. The test condition was the same as that described in [6]. To get the final enthalpy result, the help of a new-designed chemical cycle is necessary, and the rationality of the designed chemical cycle was tested by the spectrochemical analysis performed by WZS-1 Abbe's refractometer (Beijing Optical Instrument Plant) and UV-16 ultraviolet-visible spectrometer (Beijing Purkinje General Instrument Corporation).

Results

Constitution, structure and melting point of the rare earth complex

The content of the elements in the rare earth complex was determined by elementary analysis and EDTA titration (%): Nd 19.16, C 9.59, H 3.34, N 5.58, which agree with the theoretical calculation values in $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$: Nd 19.26, C 9.62, H 3.23, N 5.61%.

It was concluded from the thermogravimetric analysis and the differential thermal analysis that the thermal decomposition process is composed of 4 steps. In the DTA curves, there exists four peaks: an endothermal peak in the temperature range of 320–372 K (the peak value is 343.4 K), two relative lower endothermal peaks which are overlapped with each other in the temperature range of 406–475 K (the peak values are 421.9 and 452.4 K, respectively), and an exothermic peak in the range of 558–658 K. The area of the two peaks in the range of 406–475 K are equal to each other and their total area is larger than that of the first peak. The TG curves show that the mass loss in the two periods, 320–372 and 558–568 K, are 10.9% and 61.5%, respectively. Based on the analysis of DTA and TG, in the thermal decomposition process of the sample, the mass loss 10.9% should correspond with the loss of 7 water molecules: 5 exterior crystallization water synchronously at first, and 2 interior crystallization water in the following two steps sequentially. The mass loss in

the range of 558–568 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.

According to [4], the sample's structure is characterized as $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$. The purity of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ in the product is determined to be 99.90% based on the analysis of EDTA titration. The melting point was scanned from room temperature to 593 K, and the melting phenomenon was observed in the range of 573–577 K when the solid began to turn to yellow vesicular matter. This observed melting point is assigned to the melting point of the decomposed product.

Heat capacity of the sample

86 sets of molar heat capacity values of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ were tested with the sample's mass 3.0809 g. The experimental results are listed in Table 1. And the variation of molar heat capacity $C_{p,m}$ along with the experimental temperature are plotted in Fig. 1.

It can be seen from Fig. 1 that the $C_{p,m}$–T curve of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ is smoothly ascending in the temperature range of 77.882–249.014 K, which indicates that there exists no magnetic heat capacity and other abnormal heat phenomenon in this range. There are two peaks in Fig. 1 whose peak values are about 260 and 330 K. Incorporated with the DTA, TG analysis and the melting point measurement, the peak at 260 K is assigned to the peak of transition of crystallographic form. The second peak at 330 K should correspond to one dehydration process of the coordination compound, and it has been confirmed that there exists one-to-one correspondence between this peak and the endothermal peak in the DTA curve which is caused
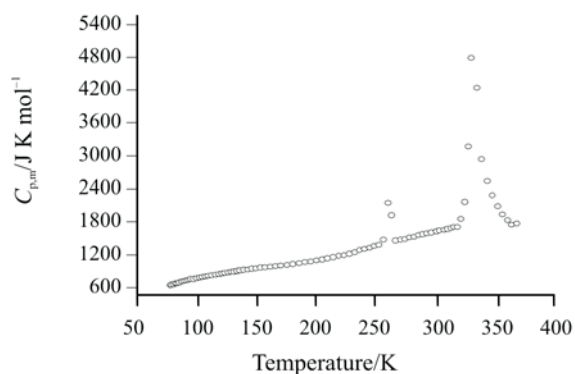
Fig. 1 Experimental molar heat capacity plotted *vs*. temperature of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$

Table 1 Experimental heat capacities of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ (M_r=1497.7224 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}
77.882	594.88	126.417	822.99	214.636	1107.13	301.153	1578.92
78.693	599.29	128.948	836.21	219.209	1129.20	303.485	1596.49
80.386	610.27	131.433	843.33	223.709	1146.05	307.695	1608.61
82.013	621.96	133.941	854.95	228.061	1169.29	310.447	1622.23
83.626	628.31	136.375	861.92	232.413	1197.18	313.182	1637.33
85.436	642.95	139.399	872.97	836.691	1233.21	315.899	1656.40
87.449	657.18	142.866	881.68	240.821	1258.19	318.788	1664.03
89.428	669.93	146.332	895.05	244.952	1280.85	321.667	1806.72
91.377	679.74	149.726	902.60	249.014	1308.69	325.002	2118.07
93.296	691.91	153.562	915.96	253.026	1334.81	327.879	3123.95
95.187	706.03	157.766	924.09	256.935	1429.51	330.303	4749.86
97.355	708.42	161.897	931.07	260.397	2105.85	335.152	4196.35
99.848	722.27	166.027	942.11	263.597	1873.83	338.939	2892.44
102.279	734.06	170.674	953.15	267.154	1411.59	343.788	2493.28
104.671	745.17	175.764	963.03	270.990	1424.37	348.030	2240.47
107.018	754.43	180.854	979.87	274.788	1440.86	352.424	2038.24
109.525	766.63	185.869	997.30	278.527	1468.42	356.520	1891.88
112.476	777.67	190.811	1016.48	282.202	1482.57	360.779	1788.09
115.722	785.81	195.679	1029.27	286.449	1509.85	364.242	1702.94
118.655	795.86	200.548	1049.02	289.652	1527.79	368.485	1718.91
121.271	805.95	205.269	1062.38	292.808	1543.05		
123.857	814.47	209.989	1086.21	297.032	1560.91		

by the loss of 5 crystallization water from $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$.

The polynomial equation of molar heat capacity $C_{p,m}$ to temperature T of complex $[Nd_2(Gly)_6(H_2O)_4] \cdot (ClO_4)_6 \cdot 5H_2O$ in the temperature range of 77.882–249.014 K have been obtained by fitting the experimental data using the least square method:

$$C_{p,m} / \text{J K}^{-1} \text{ mol}^{-1} = 935.447 + 227.986X + 13.822X^2 + 130.765X^3 + 4.971X^4$$

where $X = (T/\text{K} - 163.448)/85.566$, and the correlation coefficient of the fitting $R = 0.99983$.

From 270.990 to 318.788 K:

$$C_{p,m} / \text{J K}^{-1} \text{ mol}^{-1} = 1552.230 + 116.100X - 16.839X^2 + 5.836X^3 + 9.658X^4$$

where $X = (T/\text{K} - 296.328)/25.337$, and the correlation coefficient $R = 0.99932$.

Using area integration method [5], in the temperature range of 249.014–274.788 K, the transformation temperature, the enthalpy and the entropy of phase transition were determined to be 256.970 K, 4.483 kJ mol^{-1} and 17.270 J K^{-1} mol^{-1}, respectively. For the decomposition peak, the dehydration temperature is 320.606 K, the

decomposition enthalpy is 41.364 kJ mol^{-1}, and the decomposition entropy is 129.018 J K^{-1} mol^{-1}.

Standard enthalpy of formation at 298.15 K

The standard enthalpy of formation of the sample was determined according to the designed chemical cycle in Fig. 2 at 298.15 K and under the normal atmosphere [6]. 0.1500 g $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ was weighted for the calorimetric experiments, and the quantities of other reactants and products were determined according to the reaction equations shown in Fig. 2. The experimental temperature difference was traced by thermal resistance through DC Wheatstone Bridge and was recorded at times. The dissolution medium is 100 mL 2 mol L^{-1} HCl solution. The energy equivalent was determined using electric standardization and was corrected by Reynolds graph. Here calibration heating resistor $R = 1350.3 \, \Omega$, and calibration electric current $I = 9.997 \cdot 10^{-3}$ A. Dissolution enthalpies were calculated from the average of five experiments, and the reaction enthalpy $\Delta_r H^{\theta}$ could be calculated according to the chemical cycle in Fig. 2. Experimental data and the calculation results are listed in Tables 2 and 3, where, electric calibrated heat $Q_e = I^2 R t$, dissolution

Table 2 Dissolution enthalpies of the reactants: $Nd(NO_3)_3 \cdot 6H_2O$, Gly, $NaClO_4 \cdot H_2O$ ($n_{Nd(NO_3)_3 \cdot 6H_2O} : n_{Gly} : n_{NaClO_4 \cdot H_2O} = 2:6:6$) in 100 mL 2 mol L^{-1} HCl (298.15 K, $R=1350.3\Omega$, $I=9.997$ mA)

No.	m_1^a/g	m_2^b/g	m_3^c/g	ΔE_s/mV	ΔE_e/mV	t/s	$\Delta_s H_1$/J
1	0.0878	0.0450	0.0844	4.590	3.572	100.0	17.341
2	0.0879	0.0451	0.0845	4.640	3.580	100.1	17.508
3	0.0878	0.0451	0.0844	4.602	3.502	98.1	17.397
4	0.0878	0.0452	0.0843	4.588	3.864	108.2	17.337
5	0.0877	0.0451	0.0844	4.645	3.976	111.1	17.516
av.							$\Delta_s H_1 = 17.420 \pm 0.039$ J

a–mass of $Nd(NO_3)_3 \cdot 6H_2O$; b–mass of Gly; c–mass of $NaClO_4 \cdot H_2O$

Table 3 Dissolution enthalpies of the products: $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, $NaNO_3$ ($n_{[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O} : n_{NaNO_3} = 1:6$) in 100 mL 2 mol L^{-1} HCl+0.0162 g H_2O (298.15 K, $R=1350.3\Omega$, $I=9.997$ mA)

No.	m_4^d/g	m_5^e/g	ΔE_s/mV	ΔE_e/mV	t/s	$\Delta_s H_2$/J
1	0.1500	0.0511	5.230	5.020	142.1	19.978
2	0.1500	0.0511	5.212	5.302	150.0	19.899
3	0.1499	0.0512	5.244	5.382	152.2	20.013
4	0.1501	0.0511	5.208	4.951	140.1	19.888
5	0.1500	0.0511	5.213	5.178	146.6	19.917
av.						$\Delta_s H_2 = 19.939 \pm 0.024$ J

d–mass of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$; e–mass of $NaNO_3$

heat $Q_s = (E_s/E_e)Q_e = \Delta_s H_1$, and E_s, E_e have been corrected using Reynolds graph. The fact that the refractive index and UV spectrum of dissolved matters are similar, which would be described in detail in the next part, shows that the dissolved final states of reactants and products are identical.

According to Hess law: $\Delta_r H^\theta = \Delta_s H_1 - \Delta_s H_2 - \Delta_d H$, where $\Delta_d H$ is the enthalpy of dilution of adding 0.0162 g H_2O into 100 mL 2 mol L^{-1} HCl. According to the later calculation in the next part, the value of $\Delta_d H$ is very little and so could be omitted here. Thus, to calculate the reaction enthalpy, only the dissolution enthalpies $\Delta_s H_1$ and $\Delta_s H_2$ are needed.

Reaction enthalpy: $\Delta_r H^\theta = \Delta_s H_1 - \Delta_s H_2 - \Delta_d H = \Delta_s H_1 - \Delta_s H_2 = (17.420 - 19.939)$ J $= -2.519$ J. For that 0.1500 g $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ was

used during the measurement, after scaling, $\Delta_r H_m^\theta = -25.152$ kJ mol^{-1}.

According to thermodynamic principles: $\Delta_r H_m^\theta = \Delta_f H_m^\theta \{[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, s, 298.15 K$\} + 6\Delta_f H_m^\theta (NaNO_3, s, 298.15$ K$) + 9\Delta_f H_m^\theta (H_2O, l, 298.15$ K$) - 2\Delta_f H_m^\theta [Nd(NO_3)_3 \cdot 6H_2O, s, 298.15$ K$] - 6\Delta_f H_m^\theta (Gly, s, 298.15$ K$) - 6\Delta_f H_m^\theta (NaClO_4 \cdot H_2O, s, 298.15$ K$)$.

According to [7, 8]:
$\Delta_f H_m^\theta (NaNO_3, s, 298.15$ K$) = -467.85$ kJ mol^{-1}
$\Delta_f H_m^\theta (H_2O, l, 298.15$ K$) = -285.83$ kJ mol^{-1}
$\Delta_f H_m^\theta (Gly, s, 298.15$ K$) = -528.104$ kJ mol^{-1}
$\Delta_f H_m^\theta (NaClO_4 \cdot H_2O, s, 298.15$ K$) = -677.766$ kJ mol^{-1}
$\Delta_f H_m^\theta [Nd(NO_3)_3 \cdot 6H_2O, s, 298.15$ K$] = -3071.1$ kJ mol^{-1}
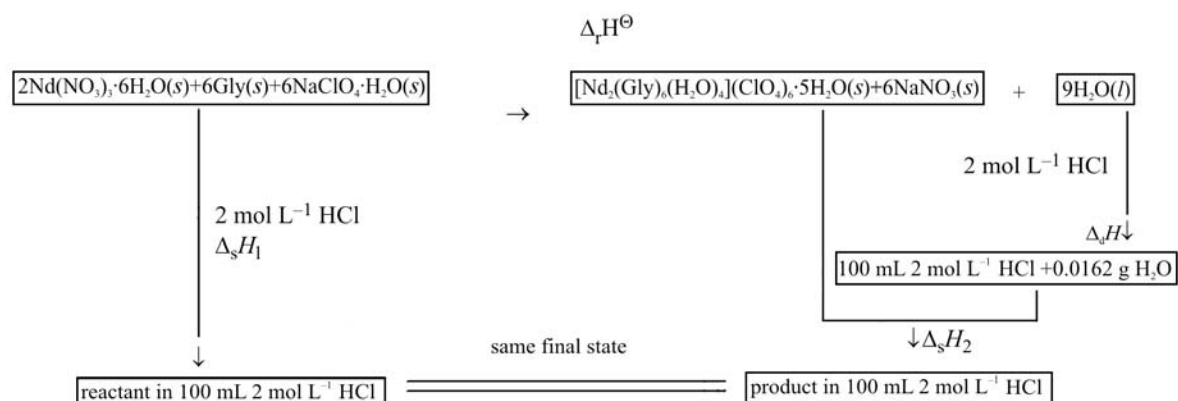
Fig. 2 Designed chemical cycle to determine the reaction enthalpy $\Delta_r H^\theta$

So the standard formation enthalpy of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ could be calculated and the value is $\Delta_f H_m^{\theta}$=[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6·5H_2O, s, 298.15 K= – 8023.002 kJ mol^{-1}.

Discussion

Estimation of dilution enthalpy $\Delta_d H$

Enthalpy of dilution of adding 0.0162 g water into 100 mL 2 mol L^{-1} HCl (the molar concentrations of mass of HCl before and after dilution are 2.1573, 2.1569 mol kg^{-1}, respectively) can be obtained by least squares fitting the data of [9] in the range from 1.5000 to 2.5000 mol kg^{-1}. The fitted linear equation is φ_L=198.11+214.04 m, and the relative coefficient R=0.99991.

$$\Delta_d H_{2.1573 \to 2.1569} = \Delta_d H_{2.1573 \to 0} - \Delta_d H_{2.1569 \to 0} =$$
$$= (\varphi_{L(2.1573)} - \varphi_{L(2.1569)}) \times 0.1 \times 4.184 \times 10^{-3} =$$
$$= -(659.8585 - 659.7702) \times 0.1 \times 4.184 \times 10^{-3} \text{ kJ} =$$
$$= -3.694 \times 10^{-5} \text{ kJ}$$

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

Testifications for the identification of the two final dissolved matters in Fig. 2

The refractive index and UV spectrum of the reactants $[2Nd(NO_3)_3 \cdot 6H_2O + 6Gly + 6NaClO_4 \cdot H_2O]$ and the products $\{[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O + 6NaNO_3 + 9H_2O\}$ dissolved in 100 mL 2 mol L^{-1} HCl had been determined by using Abbe's refractometer and uv-v_{is} spectrometer. The identity of the experimental data between the two dissolved matters shows that after dilution the reactants and the products in Fig. 2 could get the same final state. And so the designed chemical cycle is reasonable.

The standard enthalpy of formation at other temperatures

According to Kirchhoff's law, $\Delta_f H_m^{\Theta}(T)=$ $=\Delta_f H_m^{\Theta} \times (298.15 \text{ K}) + \int_{298.15}^{T} \Delta C_{p,m} \, dT$, the standard enthalpy of formation of $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ at other temperatures can be calculated with the thermodynamical data provided by this article.

References

1 J. Du, J. H. Zhang and B. Fang, Progress in Chemistry, 15 (2003) 288.

2 Y. M. Dan, Y. R. Zhao, Y. Liu Y and *et al.*, J. Therm. Anal. Cal., 84 (2006) 531.

3 G. Xie, S. P. Chen, S. L. Gao and *et al.*, J. Therm. Anal. Cal., 83 (2006) 693.

4 J. Legendziewicz, E. Huskowska, A. Waśkowska and *et al.*, Inorg. Chim. Acta, 92 (1984) 151.

5 X. M. Wu, Y. Liu, L. Li and *et al.*, Acta Chim. Sinica, 59 (2001) 1396.

6 X. M. Wu, Z. C. Tan, X. C. Lv and *et al.*,Thermochim. Acta, 441 (2006) 199.

7 J. A. Dean, Lange's Handbook of Chemistry 12th Ed, McGraw–Hill Book Co., New York 1979, pp. 9–2.

8 S. L. Gao, Y. L. Liu and Z. P. Yang, Chin. Rare Earths, 11 (1990) 23.

9 R. C. Weast, Handbook of Chemistry and Physics, CRC Press, Florida 1989, p. D-121.