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CALORIMETRIC AND THERMAL DECOMPOSITION KINETIC STUDY OF $Tb(Tyr)(Gly)_3Cl_3 \cdot 3H_2O$

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The solid-state ternary complex of terbium chloride with *L*-tyrosine and glycine, [$Tb(Tyr)(Gly)_3Cl_3 \cdot 3H_2O$], was synthesized and characterized. Using a solution-reaction isoperibol calorimeter, the enthalpy of reaction for the following reaction, $TbCl_3 \cdot 6H_2O(s)+Tyr(s)+3Gly(s)=Tb(Tyr)(Gly)_3Cl_3 \cdot 3H_2O(s)+3H_2O(l)$, was determined to be (5.1±0.6) kJ mol^{-1}. The standard enthalpy of formation of $Tb(Tyr)(Gly)_3Cl_3 \cdot 3H_2O$ at T=298.15 K has been derived as –(4267.3±2.3) kJ mol^{-1}. The thermal decomposition kinetics of the complex was studied by non-isothermal thermogravimetry in the temperature range of 325–675 K. Two main mass loss stages existed in the process of the decomposition of the complex, the kinetic parameters for the second stage were analyzed by means of differential and integral methods, respectively. Comparing the results of differential and integral methods, mechanism functions of the thermal decomposition reaction for its second stage were proposed. The kinetic equation can be expressed as: $d\alpha/dt=A\exp(-E/RT)(1-\alpha)^2$. The average values of the apparent activation energy E and pre-exponential factor A were 213.18 kJ mol^{-1} and $2.51 \cdot 10^{20}$ s^{-1}, respectively.

Keywords: *glycine, L-tyrosine, standard enthalpy of formation, terbium chloride, thermal decomposition kinetics*

Introduction

Since Anghileri [1] reported that the tumor inhibitory activity of lanthanum was enhanced when it was complexed by glycine in 1975, complexes of rare earths with amino acids have been extensively studied due to their unique physiological and biochemical effects [2–9]. About 200 kinds of such complexes have been reported and different structures have been proposed. But few studies on the thermodynamic properties about the rare earth–amino acid–amino acid type complexes have been reported.

In this paper, the ternary solid-state complex of terbium chloride with *L*-tyrosine and glycine was synthesized and the standard enthalpy of reaction for the following reaction, $TbCl_3 \cdot 6H_2O(s)+Tyr(s)+3Gly(s)=Tb(Tyr)(Gly)_3Cl_3 \cdot 3H_2O(s)+3H_2O(l)$, was determined by solution-reaction calorimetry. According to Hess's law, we designed a thermochemical cycle and derived the standard enthalpy of formation of $Tb(Tyr)(Gly)_3Cl_3 \cdot 3H_2O(s)$. In addition, the thermal stability of the complex was investigated by thermogravimetry, based on the analysis of the data of its non-isothermal decomposition, a possible mechanism of the thermal decomposition of the complex was proposed.

Experimental

Apparatus and reagents

KCl (mass fraction 0.9999) was purchased from Shanghai No. 1 Reagent Factory, Shanghai, P. R. China. It was dried in a vacuum oven at T=500 K for 6 h prior to use. Tb_4O_7 (mass fraction 0.9995) was commercially obtained from Baotou Institute of Rare Earth, Baotou, P. R. China. *L*-tyrosine (abbreviated as *Tyr*, mass fraction 0.995) and glycine (abbreviated as *Gly*, mass fraction 0.995) were supplied by Shanghai Chemical Reagent Co., Shanghai, P. R. China. Hydrochloric acid (analytical grade) and double-distilled water were used to prepare all of the calorimetric solutions.

Elemental analysis (C, H and N) was carried out with an Elemental Analyzer (Model 1106, Carlo Erba Strumentazione, Italy) and Tb^{3+} content was determined by EDTA titration. IR spectrum was measured with a FT-IR Spectrometer (Perkin Elmer Spectrum One, USA). Thermogravimetric analysis was performed on a Thermal Analyzer (Model WCT-1, Beijing Optical Instrument Factory, Beijing, P. R. China), at a nitrogen flow rate of 45 cm^3 min^{-1}, with the temperature range of 325–675 K and a linear heating rate of 10 K min^{-1}.

A solution-reaction isoperibol calorimeter constructed in the laboratory was used to determine the enthalpy of dissolution. The volume of the reaction vessel is 100 cm^3. During the experiments, the water thermostat was maintained at T=298.15 K. The stability of temperature control of the water thermostat was $\pm 1 \cdot 10^{-3}$ K, and the resolution of the temperature measurement was $\pm 1 \cdot 10^{-4}$ K. A more comprehensive description and detailed procedure of the calorimeter can be found in [10]. Before the calorimetric tests, the reliability of the calorimeter was confirmed by measuring the enthalpy of

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dissolution of KCl (Standard Reference Material 1655, the National Institute of Standards and Technology) in double-distilled water at T=298.15 K. The average enthalpy of solution of KCl in double-distilled water was (17586±20) J mol^{-1}, which was well in conformity with the published values [11, 12]. The uncertainty and inaccuracy of the experimental results were within ±0.3% compared with the recommended reference data.

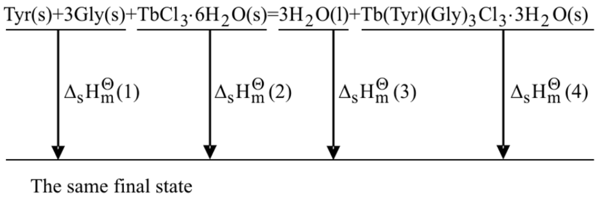

Fig. 1 Thermochemical cycle

Synthesis and characterization of the sample

Sample of $\mathrm{TbCl_3{\cdot}6H_2O}(s)$ used for synthesis and calorimetric determination was prepared from the oxide as previously described in detail elsewhere [2].

$\mathrm{Tb(Tyr)(Gly)_3Cl_3{\cdot}3H_2O}(s)$ was synthesized and characterized according to the method given in [4].

Determination of the standard enthalpies of dissolution

The calorimetric solvent must dissolve the chemicals in the sample cell of the calorimeter completely and relatively rapidly. In our experiments, 2 mol L^{-1} HCl solution was chosen as the calorimetric solvent.

According to Hess's law, the standard enthalpy of reaction for the coordination reaction can be obtained through the thermodynamic cycle depicted in Fig. 1.

$$\Delta_\mathrm{r} H_\mathrm{m}^\ominus = \Delta_\mathrm{s} H_\mathrm{m}^\ominus(1) + \Delta_\mathrm{s} H_\mathrm{m}^\ominus(2) - \Delta_\mathrm{s} H_\mathrm{m}^\ominus(3) - \Delta_\mathrm{s} H_\mathrm{m}^\ominus(4)$$

The mixture of 0.1709 g *Tyr* and *Gly* at mole ratio of n(Tyr) : n(Gly)=1 : 3 was dissolved in 100 cm^3 2 mol L^{-1} HCl at T=298.15 K.

$$\{\mathrm{Tyr}(s)+3\mathrm{Gly}(s)\}+\text{solution A}\rightarrow\text{solution B}$$

where solution A was the calorimetric solvent.

0.1571 g $\mathrm{TbCl_3{\cdot}6H_2O}(s)$ was dissolved in 100 cm^3 solution B at T=298.15 K

$$\mathrm{TbCl_3{\cdot}6H_2O}(s)+\text{solution B}\rightarrow\text{solution C}$$

where solution B was the calorimetric solvent.

0.3053 g $\mathrm{Tb(Tyr)(Gly)_3Cl_3{\cdot}3H_2O}(s)$ was dissolved in 100 cm^3 solution D at T=298.15 K

$$\mathrm{Tb(Tyr)(Gly)_3Cl_3{\cdot}3H_2O}(s)+\text{solution D}\rightarrow\text{solution C}$$

where solution D was the calorimetric solvent.

The above experiments were repeated at least five times and the results of the calorimetric measurements are listed in Table 1.

The verification of the same thermodynamic final state: we determined the UV-Vis spectra and refractive indexes of dissolution of the reactants and products in 100 cm^3 2 mol L^{-1} HCl and discovered that both had the same UV-Vis spectrum and refractive index. Moreover, no enthalpy change was detected when releasing

Table 1 Enthalpies of dissolution at T=298.15 K[a]

System	Solvent	No.	m/g	Q_s/J	$\Delta_\mathrm{s}H_\mathrm{m}^\ominus$/kJ mol^{-1}
$\mathrm{Tyr}(s)+3\mathrm{Gly}(s)$	A	1	0.1709	–19.600	–46.667
		2		–19.511	–46.455
		3		–19.929	–47.450
		4		–19.197	–45.706
		5		–20.026	–47.682
Mean	$\Delta_\mathrm{s}H_\mathrm{m}^\ominus(1)$=(–46.792±0.356) kJ mol^{-1}				
$\mathrm{TbCl_3{\cdot}6H_2O}(s)$	B	1	0.1571	8.065	19.202
		2		8.109	19.308
		3		8.163	19.436
		4		8.578	20.424
		5		8.721	20.765
Mean	$\Delta_\mathrm{s}H_\mathrm{m}^\ominus(2)$=(–19.827±0.320) kJ mol^{-1}				
$\mathrm{Tb(Tyr)(Gly)_3Cl_3{\cdot}3H_2O}(s)$	D	1	0.3053	–13.466	–32.062
		2		–13.802	–32.862
		3		–13.246	–31.538
		4		–13.143	–31.292
		5		–13.731	–32.693
Mean	$\Delta_\mathrm{s}H_\mathrm{m}^\ominus(4)$=(–32.089±0.308) kJ mol^{-1}				

[a] m was the mass of sample, Q_s was the heat of dissolution and $\Delta_\mathrm{s}H_\mathrm{m}^\ominus$ was the standard enthalpy of dissolution. Solvent A was 100.0 cm^3 2 mol L^{-1} HCl(aq), B was [100.0 cm^3 2 mol L^{-1} HCl(aq)+1.26 mmol Gly+0.42 mmol Tyr], and D was [100.0 cm^3 2 mol L^{-1} HCl(aq)+1.26 mmol $\mathrm{H_2O}$].

the sample cell containing the final solution from the dissolution of the reactants into the final solution from the products in the calorimeter.

Results and discussion

Standard enthalpy of reaction

$$\Delta_r H_m^\Theta = \Delta_s H_m^\Theta(1) + \Delta_s H_m^\Theta(2) - \Delta_s H_m^\Theta(3) - \Delta_s H_m^\Theta(4)$$

where $\Delta_s H_m^\Theta(3)$ was the enthalpy of dilution of 0.023 g H_2O in 100 cm^3 2 mol L^{-1} HCl, its value is very small [13] and can be neglected.

$$\Delta_r H_m^\Theta = \Delta_s H_m^\Theta(1) + \Delta_s H_m^\Theta(2) - \Delta_s H_m^\Theta(3) - \Delta_s H_m^\Theta(4)$$

$$=(-46.792)+(19.827)-0-(-32.089)$$
$$=(5.1\pm0.6)\ \text{kJ mol}^{-1}$$

Standard enthalpy of formation

From the standard enthalpy of reaction for the reaction and various ancillary data listed in Table 2, the standard enthalpy of formation of the complex was calculated.

$$\Delta_f H_m^\Theta[Tb(Tyr)(Gly)_3Cl_3{\cdot}3H_2O(s)]$$
$$=\Delta_f H_m^\Theta[TbCl_3{\cdot}6H_2O(s)]+\Delta_f H_m^\Theta[Tyr(s)]$$
$$+3\Delta_f H_m^\theta[Gly(s)]-3\Delta_f H_m^\Theta[H_2O(l)]+\Delta_r H_m^\Theta$$
$$=[-2859.3]+[-685.1]+3[-528.5]-3[-285.830]+[5.1]$$
$$=-(4267.3\pm2.3)\ \text{kJ mol}^{-1}$$

Kinetics of the thermal decomposition

The TG-DTG-DTA curves of the complex are shown in Fig. 2. From the TG-DTA curves, it can be clearly seen that two main mass loss stages existed in the process of thermal decomposition for the complex. The first mass loss took place in the temperature of 365–415 K and the percentage of the mass loss was 7.58%; the second mass loss step occurred in the temperature of 518–593 K and the percentage of mass loss was 19.3%. According to mass loss in each stage, it was assumed that the first mass loss stage corresponded to the loss of three water molecules and the second is the loss of three carboxyl groups. Because the two corresponding mass loss were close to the calculated theoretical values.

Table 2 Ancillary data[b]

$\Delta_f H_m^\Theta$	Unit	Value	Ref.
$TbCl_3{\cdot}6H_2O(s)$	kJ mol^{-1}	–(2859.3±0.1)	[13]
Tyr(*s*)	kJ mol^{-1}	–(685.1±1.67)	[14]
Gly(*s*)	kJ mol^{-1}	–(528.5±0.5)	[14]
$H_2O(l)$	kJ mol^{-1}	–(285.83±0.042)	[13]

[b] was the standard enthalpy of formation.

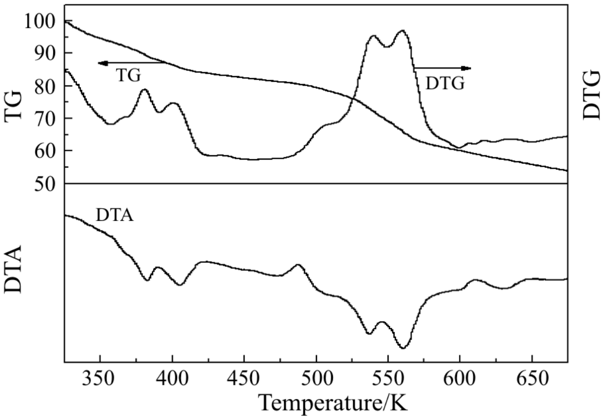

Fig. 2 TG-DTG-DTA curves of $Tb(Tyr)(Gly)_3Cl_3 \cdot 3H_2O$ (s)

From the TG-DTG curves, in the first stage, the complex lost water molecules in two steps. The percentages of mass loss in two steps are 5.04 and 2.54%, respectively, which are in accordance with the calculated percentages of mass loss (4.96 and 2.48%) of two water molecules and one water molecule. It can be suggested that the complex contains two molecules of crystalline water and one molecule of ligand water.

Table 3 Data of thermal decomposition from TG-DTG curve[c]

No.	*T*/K	α	dα/dt /s^{-1}
1	525.15	0.0411	0.06
2	528.15	0,0689	0.09
3	532.15	0.1100	0.13
4	535.15	0.1507	0.16
5	539.15	0.2261	0.22
6	543.15	0.3292	0.22
7	548.15	0.3907	0.20
8	552.15	0.4591	0.20
9	558.15	0.5617	0.22
10	562.15	0.6440	0.24
11	566.15	0.7402	0.29
12	569.15	0.7878	0.20
13	574.15	0.8497	0.12
14	579.15	0.8904	0.07
15	584.15	0.9182	0.05
16	589.15	0.9454	0.04

[c] α was the fraction of the reacted material, and dα/d*t* was the rate of thermal decomposition.

Additionally, it can be deduced that in the second mass loss stage, the loss of three carboxy groups should result from the glycine ligands [15–18].

In the present study, the non-isothermal kinetic data in the second stage of thermal decomposition were analyzed by means of differential and integral methods. The differential equation used was proposed by Achar *et al*. [19, 20]. The integral equation was Coats–Redfern equation [21].

Achar equation: $\ln[(\mathrm{d}\alpha/\mathrm{d}t)/F(\alpha)]=\ln A-E/RT$ (1)

Coats–Redfern equation:

$$\ln[G(\alpha)/T^2]=\ln(AR/\beta E)-E/RT \tag{2}$$

where α is the fraction of the reacted material, T the absolute temperature, R the gas constant and β the linear heating rate. E and A are the apparent activation energy and pre-exponential factor, respectively. $F(\alpha)$ and $G(\alpha)$ are differential and integral mechanism functions, respectively. $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of thermal decomposition.

Table 4 Common mechanism functions of solid-state thermal decomposition reactions[d]

No.	Mechanism	$F(\alpha)$	$G(\alpha)$
1	One-dimensional diffusion, 1D	$1/2\alpha$	α^2
2	Valensi equation, two-dimensional diffusion, 2D	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
3	Ginstling–Brounshtei equation, three-dimensional diffusion, 3D	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2/3\alpha)-(1-\alpha)^{2/3}$
4	Jander equation, three-dimensional diffusion, 3D	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
5	Avrami–Erofeev equation, *n*=1, first-order decay	$(1-\alpha)$	$-\ln(1-\alpha)$
6	Avrami–Erofeev equation, *n*=1.5	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
7	Avrami–Erofeev equation, *n*=2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
8	Avrami–Erofeev equation, *n*=3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev equation, *n*=4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
10	Contracting area	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
11	Contracting volume	$3(1-\alpha)]^{2/3}$	$1-(1-\alpha)]^{1/3}$
12	Mampel–Power law	1	α
13	Mample–Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
14	Second-order decay	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
15	1.5 order decay	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$

[d] $F(\alpha)$ was differential mechanism function, and $G(\alpha)$ was integral mechanism function.

Table 5 The kinetic data of thermal decomposition of $Tb(Tyr)(Gly)_3Cl_3\cdot 3H_2O$[e]

No.	Achar method			Coats–Redfern method		
	E/kJ mol^{-1}	A/s^{-1}	r	E/kJ mol^{-1}	A/s^{-1}	r
1	97.05	$1.34\cdot 10^{8}$	0.6359	223.89	$1.40\cdot 10^{20}$	0.9299
2	142.30	$1.90\cdot 10^{12}$	0.7946	247.64	$1.71\cdot 10^{22}$	0.9453
3	162.41	$3.96\cdot 10^{13}$	0.8442	258.00	$4.14\cdot 10^{22}$	0.9515
4	200.02	$1.95\cdot 10^{19}$	0.9061	279.37	$5.65\cdot 10^{24}$	0.9624
5	93.33	$2.32\cdot 10^{18}$	0.8914	152.58	$7.84\cdot 10^{13}$	0.9742
6	39.40	1.56	0.7216	98.64	$5.12\cdot 10^{8}$	0.9725
7	12.43	3.708	0.3481	71.67	$1.18\cdot 10^{6}$	0.9707
8	–14.54	$7.85\cdot 10^{-3}$	0.4399	44.71	$2.34\cdot 10^{3}$	0.9665
9	–28.02	$3.32\cdot 10^{-4}$	0.7067	31.22	92.01	0.9613
10	36.91	$3.36\cdot 10^{2}$	0.5170	127.26	$1.07\cdot 10^{11}$	0.9516
11	55.72	$1.57\cdot 10^{4}$	0.7026	135.07	$4.41\cdot 10^{11}$	0.9598
12	19.51	$1.95\cdot 10^{-3}$	0.2498	107.33	$1.95\cdot 10^{9}$	0.9242
13	77.79	$5.00\cdot 10^{-9}$	0.8129	49.05	$4.80\cdot 10^{3}$	0.9108
14	206.18	$2.74\cdot 10^{19}$	0.9909	220.17	$4.74\cdot 10^{20}$	0.9962
15	149.76	$3.99\cdot 10^{13}$	0.9728	47.19	$8.57\cdot 10^{3}$	0.9490

[e] E was apparent activation energy, A was pre-exponential factor and r was correlation coefficient.

The original data of the thermal decomposition of the complex in the second stage obtained from the TG and DTG curves (Fig. 2) were listed in Table 3. Using the 15 possible mechanism functions of $F(\alpha)$ and $G(\alpha)$ from Table 4 [22, 23], the data in Table 3 were analyzed by use of the Eqs (1) and (2). The kinetic analysis were performed by the linear least square method. The results of the kinetic parameters E, A and correlation coefficients r are shown in Table 5. Comparing the results obtained from the differential and integral methods, we found that the values of E and A were approximately the same, and the linear correlation coefficients were also better when the possible mechanism functions were $F(\alpha)=(1-\alpha)^2$, $G(\alpha)=(1-\alpha)^{-1}-1$. So we deduced that the possible mechanism of the second step of thermal decomposition of the complex was a second order chemical reaction. The corresponding non-isothermal kinetic equation was $d\alpha/dt=A\exp(-E/RT)(1-\alpha)^2$. The average values of the apparent activation energy E and pre-exponential factor A were 213.18 kJ mol^{-1}, $2.51·10^{20}$ s^{-1}, respectively.

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