

Thermochemical Study of $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$

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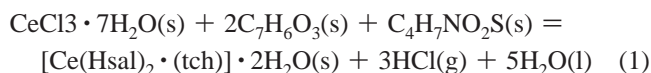
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The reaction of cerium chloride heptahydrate with salicylic acid and thioproline produced $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$ [Hsal = salicylate ($\text{C}_7\text{H}_5\text{O}_3^-$), tch = thioproline ($\text{C}_4\text{H}_6\text{NO}_2\text{S}^-$)], which was isolated and characterized by IR, elemental, chemical, and thermogravimetric analysis. The standard molar enthalpies of solution of $[\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s})]$, $[\text{C}_7\text{H}_6\text{O}_3(\text{s})]$, $[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s})]$, and $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s})]$ in a mixed solvent of absolute ethyl alcohol, dimethyl sulfoxide (DMSO), and $3 \text{ mol} \cdot \text{L}^{-1}$ HCl were determined by calorimetry to be $\Delta_s H_m^\ominus[\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(42.22 \pm 0.37) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_s H_m^\ominus[\text{C}_7\text{H}_6\text{O}_3(\text{s}), 298.15 \text{ K}] = (45.54 \pm 0.37) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_s H_m^\ominus[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s}), 298.15 \text{ K}] = (21.91 \pm 0.60) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_s H_m^\ominus[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(30.87 \pm 0.39) \text{ kJ} \cdot \text{mol}^{-1}$. The enthalpy change of the reaction $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{C}_7\text{H}_6\text{O}_3(\text{s}) + \text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s}) = [\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}) + 3\text{HCl}(\text{g}) + 5\text{H}_2\text{O}(\text{l})$ was determined to be $\Delta_r H_m^\ominus = (263.12 \pm 0.95) \text{ kJ} \cdot \text{mol}^{-1}$. From data in the literature, through Hess's law, the standard molar enthalpy of formation of $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ was estimated to be $\Delta_f H_m^\ominus[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(2785.7 \pm 3.2) \text{ kJ} \cdot \text{mol}^{-1}$.

Introduction

It is known that rare earth ions and salicylic acid are antibacterial.^{1–6} Thioproline possesses some special functions such as prolonging body life, controlling drug toxicity, and catalyzing plant growth and, in particular, participates in anticancer drugs, which can make cancer cells reverse to normal cells.⁷ The synthesis and characterization of rare earth complexes with thioproline and salicylic acid have been reported, and their research applications in experiments were carried out on *Escherichia coli*,⁸ indicating that the catalysis of the ternary complexes of rare earth ions against *E. coli* was more significant than that of the ligands, thioproline and salicylic acid. Obviously, it is very important to carry out research on the rare earth complex of thioproline and salicylic acid. The standard molar enthalpy of formation of the complex has not yet been reported. As commonly known, it is necessary to obtain basic thermodynamic properties as the basis for theoretical research and industrial design when they are synthesized and developed industrially.

In this paper, the standard molar enthalpies of solution of $[\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s})]$, $[\text{C}_7\text{H}_6\text{O}_3(\text{s})]$, $[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s})]$, and $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s})]$ in a mixed solvent of absolute ethyl alcohol, dimethyl sulfoxide (DMSO), and $3 \text{ mol} \cdot \text{L}^{-1}$ HCl at 298.15 K are reported. By a thermochemical cycle, the molar enthalpy of the reaction:



and the standard molar enthalpy of formation of $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ were obtained.

Experimental Section

Chemicals and Instruments. The chemicals $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s})$ (> 99 %), salicylic acid $\text{C}_7\text{H}_6\text{O}_3(\text{s})$ (> 99.5 %), and KCl (> 99.99 %)

%) were obtained from the Shanghai Reagent Company. L-Thioproline ($\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s})$; > 99.5 %) was from the Wuhan University Hoyo Co., Ltd.

$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s})$ was dried in a desiccator containing sulfuric acid (60 %) at room temperature, and $\text{C}_7\text{H}_6\text{O}_3(\text{s})$ and $\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s})$ were dried in a vacuum desiccator containing P_4O_{10} to constant mass. KCl (calorimetric primary standard) of a purity greater than 99.99 % was dried in a vacuum oven for 6 h at 408.15 K.

An elemental analyzer (Perkin-Elmer 2400 CHN), a Fourier transform infrared (FT-IR) spectrometer (Avatar 360, with KBr pellet), a thermogravimetry analyzer (HCT-1, at a heating rate of $283.15 \text{ K} \cdot \text{min}^{-1}$ in flowing Ar, Beijing, China), an Abbe refractometer (WAY, Shanghai, China), an ultraviolet–visible spectrophotometer (U-3010, Hitachi, Japan), and a solution-reaction isoperibol calorimeter (SRC 100, constructed by the thermochemical laboratory of Wuhan University, China) were used.

Synthesis and Characterization of $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$. A mass of 0.04 mol of powdered salicylic acid $[\text{C}_7\text{H}_6\text{O}_3(\text{s})]$ was dissolved in 30 cm^3 of absolute ethyl alcohol (solution I). Sodium salicylate solution was formed when an aqueous solution of 10 % NaOH (0.04 mol of NaOH) was added into solution I (solution II). A mass of 0.02 mol of powdered thioproline was dissolved in 50 cm^3 of distilled water (solution III) at 333.15 K in a water bath. A solution mixture was obtained when solution II was added into solution III (solution IV). A mass of 0.02 mol of powdered $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was dissolved in 40 cm^3 of distilled water (solution V). White crystals were separated out when solution IV was added slowly into solution V at 333.15 K in a water bath after 11 h of magnetic stirring. The solution was left to settle at pH 5.0 to 6.0 over 12 h. Finally, the white solid complex was obtained by filtration in a vacuum and washed with absolute ethyl alcohol three times and several portions of hot distilled water many times at 343.15 K. The product was put into a desiccator in a vacuum at 333.15 K for 24 h and kept until the mass of the crystals became constant. The chemical composition of the synthetic sample was deter-

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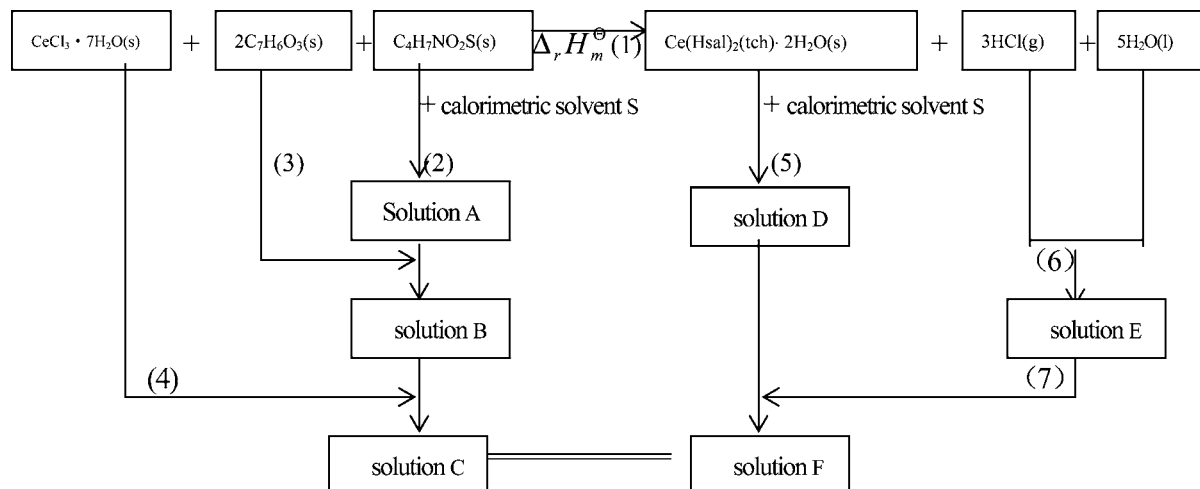


Figure 1. Thermochemical cycle of reaction 1.

mined by elemental analysis for C, H, and N, by ethylenediaminetetraacetic acid (EDTA) titration for Ce^{3+} ,⁹ by mercury salt titration for Cl^- and by difference and thermogravimetric/differential thermogravimetric (TG–DTG) curves for H_2O . The analysis results proved that the composition of the complex was $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s})]$, and its purity was > 99.0 %.

Solution-Reaction Isoperibol Calorimeter and Calibration. The solution-reaction isoperibol calorimeter (SRC 100) has been described elsewhere.¹⁰ A Dewar vessel with an internal volume of 100 cm^3 , equipped with a twin-blade stirrer, was submerged in the water thermostat. The precision values of temperature control and temperature measurement were ± 0.001 and $\pm 0.0001 \text{ K}$, respectively.

The calibration of the calorimeter was carried out by measuring the dissolution enthalpies of tris(hydroxymethyl)aminomethane (THAM; NBS 742a, USA) in $0.0001 \text{ mol} \cdot \text{cm}^{-3}$ HCl and KCl (calorimetric primary standard) in water at 298.15 K . The mean dissolution enthalpies were $[-(29776 \pm 16)] \text{ J} \cdot \text{mol}^{-1}$ for THAM and $(17597 \pm 17) \text{ J} \cdot \text{mol}^{-1}$ for KCl which agree with published data, $[-(29766 \pm 31.5)] \text{ J} \cdot \text{mol}^{-1}$ for THAM¹¹ and $(17536 \pm 9) \text{ J} \cdot \text{mol}^{-1}$ for KCl.¹²

Determination of Dissolution Enthalpies. $[\text{Ce}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_4\text{H}_6\text{NO}_2\text{S})] \cdot 2\text{H}_2\text{O}(\text{s})$ can be regarded as the product of reaction 1, and the thermochemical cycle was designed as shown in Figure 1.

The UV spectrum and refractive indices of the final solution of the reactants and the final solution of the products can be used to determine if they have the same thermodynamic state. In the present experiments, we determined the spectrum and refractive indices of solution C and solution F and found for both of them the same UV spectrum (Figure 2) and equal refractive indices ($n_{25} = 1.4098$), which proves that both have the same thermodynamic state and that the thermochemical cycle of reaction 1 is reliable.

The chosen calorimetric solvent must dissolve the chemicals in the sample cell completely and very rapidly. The calorimetric solvent (S) of DMSO, absolute ethyl alcohol, and $3 \text{ mol} \cdot \text{L}^{-1}$ HCl ($V_{\text{DMSO}}/V_{\text{EtOH}}/V_{\text{HCl}} = 1:1:1$) is the most appropriate solvent for this experiment. Rigorous control of the stoichiometry was maintained through each series of experiments to ensure that the final solutions resulting from the dissolution of the reactants were of the same composition as those from the dissolution of the products.

The thioproline $\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s})$ was ground in an agate mortar, and a sample (0.066 g) was placed into a sample cell in a

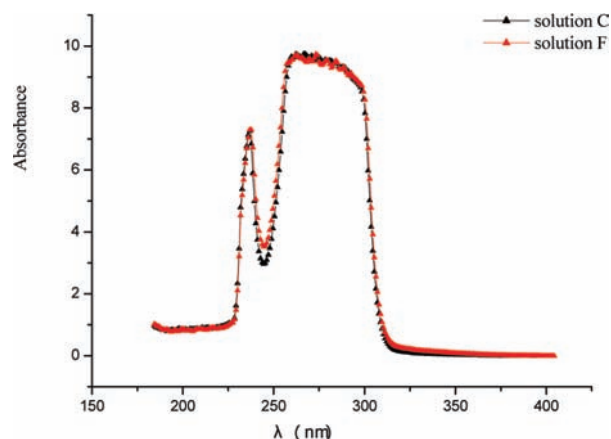


Figure 2. UV–vis spectrum of solution C and solution F obtained from the dissolution of the reactants and products in the supposed reaction 1 in 100 cm^3 of a mixed solvent of absolute ethyl alcohol, DMSO, and $3 \text{ mol} \cdot \text{L}^{-1}$ HCl (diluted into a 1:20 ratio).

calorimeter. The calorimetric solvent (100 cm^3) was added into the reaction vessel. The calorimeter was adjusted to a constant temperature of 298.15 K , and the dissolution enthalpy was determined. A series of five experiments was performed.



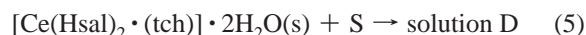
where S is the calorimetric solvent (100 cm^3). The solution A above was kept in the reaction vessel. Powdered salicylic acid $\text{C}_7\text{H}_6\text{O}_3(\text{s})$ (0.138 g) was put into the sample cell. A series of five experiments was performed.



The solution B above was kept in the reaction vessel. Powdered $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s})$ (0.186 g) was put into the sample cell. A series of five experiments was performed.



Powdered $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ (0.291 g) was put into the sample cell in the calorimeter, and the calorimeter solvent (100 cm^3) was added into the reaction vessel. The calorimeter was adjusted to a constant temperature of 298.15 K , and the dissolution enthalpy was determined. A series of five experiments was performed.

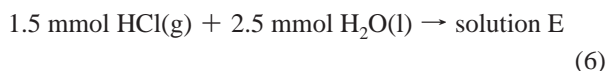


where S is the calorimetric solvent (100 cm^3). A mass of 1.5 mmol of HCl(g) was mixed into 2.5 mmol of $\text{H}_2\text{O}(\text{l})$.

Table 1. Dissolution Enthalpies of [C₄H₇NO₂S(s)], [2C₇H₆O₃(s)], [CeCl₃·7H₂O(s)], and [Ce(Hsal)₂·(tch)·2H₂O(s)] in the Calorimetric Solvent S at 298.15 K^{a,b}

system	no.	m g	t s	$\Delta_s H_m^\ominus$ kJ·mol ⁻¹
C ₄ H ₇ NSO ₂ (s) in S	1	0.0666	47.97	21.8128
	2	0.0667	45.07	21.8463
	3	0.0672	49.02	21.0269
	4	0.0663	49.42	22.6403
	5	0.0666	50.17	22.2397
$\Delta_s H_m^\ominus[\text{C}_4\text{H}_7\text{NSO}_2(\text{s}), 298.15 \text{ K}] = (21.91 \pm 0.60) \text{ kJ}\cdot\text{mol}^{-1c}$				
2C ₇ H ₆ O ₃ (s) in A	1	0.1387	135.43	45.7400
	2	0.1385	130.81	45.5989
	3	0.1383	124.86	45.0466
	4	0.1391	121.47	45.9875
	5	0.1387	121.77	45.3222
$\Delta_s H_m^\ominus[2\text{C}_7\text{H}_6\text{O}_3(\text{s}), 298.15 \text{ K}] = (45.54 \pm 0.37) \text{ kJ}\cdot\text{mol}^{-1}$				
CeCl ₃ ·7H ₂ O(s) in B	1	0.1862	112.30	-42.3827
	2	0.1859	112.83	-41.9846
	3	0.1864	114.15	-42.0902
	4	0.1862	112.83	-41.8615
	5	0.1866	113.09	-42.7822
$\Delta_s H_m^\ominus[\text{CeCl}_3\cdot 7\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(42.22 \pm 0.37) \text{ kJ}\cdot\text{mol}^{-1}$				
[Ce(C ₇ H ₅ O ₃) ₂ (C ₄ H ₆ NO ₂ S)]·2H ₂ O (s) in S	1	0.2919	108.51	-30.4140
	2	0.2918	108.99	-30.9414
	3	0.2913	107.76	-30.6400
	4	0.2911	108.29	-31.4484
	5	0.2909	108.11	-30.9154
$\Delta_s H_m^\ominus[\text{Ce}(\text{Hsal})_2\cdot(\text{tch})\cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(30.87 \pm 0.39)$				
solution D + solution E	1	0.0991	197.62	-71.4995
	2	0.1012	198.56	-71.0552
	3	0.0987	197.48	-71.1836
	4	0.1033	194.73	-70.7774
	5	0.0978	193.97	-70.6261
$\Delta_s H_m^\ominus(7) = -(71.03 \pm 0.34) \text{ kJ}\cdot\text{mol}^{-1}$				

^a m : mass of the sample. ^b t : heating period of electrical calibration. ^c Uncertainty was estimated as twice the standard deviation of the mean of the results.



The solution D above was kept in the reaction vessel. Solution E was put into the sample cell. A series of five experiments was performed.



The calorimetric results of reactions 2 to 5 and 7 are listed in Table 1.

Results and Discussion

Elemental Analyses and IR Spectra. Analytical results for the complex and proposed formula are given in Table 2. The determined results coincide with the theoretical ones very well.

Frequencies of characteristic absorption bands in the IR spectra (cm⁻¹) for the ligands and complex are given in Table 3.

Table 2. Analytical Results of the Complex [Ce(Hsal)₂·(tch)·2H₂O (%)

[Ce(Hsal) ₂ ·(tch)]· 2H ₂ O	C	H	S	N	Ce
theoretical values	37.11	3.46	5.50	2.40	24.05
experimental data	37.21	3.48	5.55	2.42	24.24

Table 3. IR Absorption for Ligands and Complex (cm⁻¹)

compounds	$\nu_{\text{O-H}}$	$\nu_{\text{C-O}}$	$\nu_{\text{N-H}}$	$\nu_{\text{as}}^{\text{COO}^-}$	$\nu_{\text{s}}^{\text{COO}^-}$	$\delta_{\text{N-H}}$	$\delta_{\text{O-H}}$
C ₇ H ₆ O ₃	3237	1663					1475
C ₄ H ₇ NO ₂ S			3058	1556	1434	1632	
[Ce(Hsal) ₂ (tch)]·2H ₂ O	3323		2960	1594 (1561)	1384 (1463)	1623	1482

There are five characteristic bands observed for salicylic acid:¹³ $\nu_{\text{OH}}^{\text{COOH}}$ (hydrogen bond intramolecular, 3237 cm⁻¹, s), $\nu_{\text{OH}}^{\text{COOH}}$ (hydrogen bond intermolecular, 2857 cm⁻¹, s), $\nu_{\text{O-H}}$ (COOH, 2598 cm⁻¹, s), $\nu_{\text{C-O}}$ (COOH, 1663 cm⁻¹, vs), and $\delta_{\text{O-H}}$ (phenol, 1475 cm⁻¹, s). All of these bands disappeared after complex formation except for the band due to the angular deformation of the OH group. At the same time, two new absorption bands due to the carboxylate groups, $\nu_{\text{as}}^{\text{COO}^-}$ (1594 cm⁻¹, s) and $\nu_{\text{s}}^{\text{COO}^-}$ (1384 cm⁻¹, s), appeared, indicating that the oxygen atoms of the carboxylate group are coordinated to the metal ion. These observed frequencies in the complex shifted to higher values when compared with the frequencies observed for the sodium salicylate salt, but $\Delta\nu(\nu_{\text{as}} - \nu_{\text{s}})$ stayed the same (207 cm⁻¹). According to these results, it can be concluded that the carboxylate group is coordinated to the metal ion through the two oxygen atoms, as a symmetrical bidentate group.

There are four characteristic absorption bands observed for thioproline:¹⁴ $\nu_{\text{N-H}}$ (3058 cm⁻¹, s, sh), $\delta_{\text{N-H}}$ (1632 cm⁻¹, sb), $\nu_{\text{as}}^{\text{COO}^-}$ (1556 cm⁻¹, s), and $\nu_{\text{s}}^{\text{COO}^-}$ (1434 cm⁻¹, s). After complex formation, both $\nu_{\text{N-H}}$ and $\nu_{\text{s}}^{\text{COO}^-}$ shift toward higher frequencies, $\nu_{\text{N-H}}$ (3066 cm⁻¹, m) and $\nu_{\text{s}}^{\text{COO}^-}$ (1463 cm⁻¹, s), and both $\delta_{\text{N-H}}$ and $\nu_{\text{as}}^{\text{COO}^-}$ shift toward lower frequencies, $\delta_{\text{N-H}}$ (1623 cm⁻¹) and $\nu_{\text{as}}^{\text{COO}^-}$ (1561 cm⁻¹). According to these results, it can be concluded that the cerium ion is in coordination with the N-atom of the imine group and one

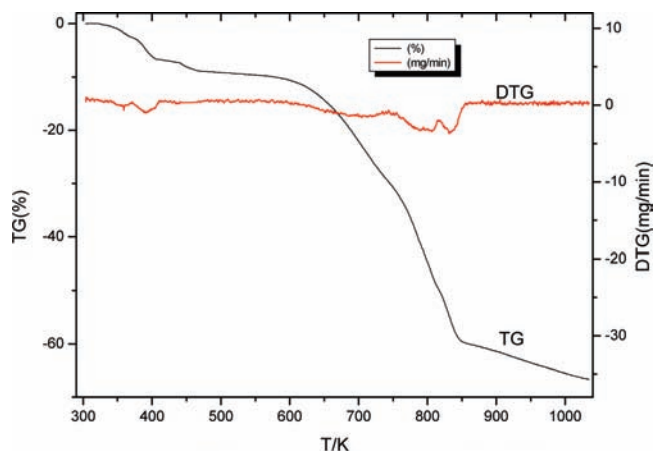
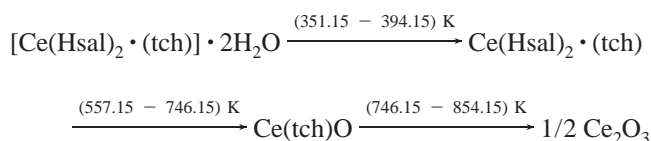
Figure 3. TG-DTG curves of $[\text{Ce}(\text{Hsal})_2(\text{tch})] \cdot 2\text{H}_2\text{O}$

Figure 3. TG-DTG curves of $[\text{Ce}(\text{Hsal})_2(\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$.

O-atom of the carboxylate group in thioproline, as an asymmetric bidentate group.

Thermal Decomposition of the Complex. The TG and DTG curves of $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$, at a heating rate of $283.15 \text{ K} \cdot \text{min}^{-1}$ in flowing Ar, are shown in Figure 3. The thermal decomposition process of $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$ can be divided into four stages. The first stage is from (351.15 to 394.15) K. The TG curve shows that the mass loss corresponding to this temperature range is 6.36 %, which roughly coincides with the value of 6.19 %, calculated for the loss of 2 mol of H_2O from the complex. The second stage ranges from (557.15 to 746.15) K with the mass loss of 47.18 %, which corresponds to the loss of 2 mol of Hsal^- . The theoretical mass loss is 47 %. The third stage degradation temperature is in the range of (746.15 to 854.15) K with the mass loss of 28.22 %, which corresponds to the loss of 1 mol of tch^- . The theoretical mass loss is 28.17 %. On the basis of experimental and calculated results, the thermal decomposition of $[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$ was postulated as follows:



Results of the Calorimetric Experiment. The results of the calorimetric measurements are given in Table 1.

Estimation of $\Delta_s H_m^\ominus(6)$. According to reaction 6



$$\begin{aligned} \Delta_s H_m^\ominus(6) &= \Delta_s H_m^\ominus(m = 33.33 \text{ mol} \cdot \text{cm}^{-3}) \\ &= \Delta_s H_m^\ominus(m = 1.000 \text{ mol} \cdot \text{cm}^{-3}) - \\ &\quad \Delta_d H_m^\ominus(33.33 \rightarrow 1.000) \\ &= [-74.84 - (-29.51)] \text{ kJ} \cdot \text{mol}^{-1} = \\ &\quad - 45.33 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

See ref 15.

Molar Enthalpy of Reaction 1. According to Hess's law, the standard molar reaction enthalpy of reaction 1 was obtained:

$$\begin{aligned} \Delta_r H_m^\ominus(1) &= \Delta_s H_m^\ominus(2) + \Delta_s H_m^\ominus(3) + \Delta_s H_m^\ominus(4) - \\ &\quad \Delta_s H_m^\ominus(5) - \Delta_s H_m^\ominus(6) - \Delta_s H_m^\ominus(7) \\ &= [21.91 + 45.54 - 42.22 + 30.87 + 45.33 \cdot 3 + \\ &\quad 71.03] \pm [\sqrt{0.60^2 + 0.37^2 + 0.37^2 + 0.39^2 + 0.34^2}] \\ &= (263.12 \pm 0.95) \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Evaluation of $\Delta_r H_m^\ominus[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s})]$. According to Hess's law

$$\begin{aligned} \Delta_r H_m^\ominus(1) &= \\ &\quad \Delta_r H_m^\ominus[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] + \\ &\quad 3\Delta_r H_m^\ominus[\text{HCl}(\text{g}), 298.15 \text{ K}] + \\ &\quad 5\Delta_r H_m^\ominus[\text{H}_2\text{O}(\text{l}), 298.15 \text{ K}] - \\ &\quad \Delta_r H_m^\ominus[\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] - \\ &\quad 2\Delta_r H_m^\ominus[\text{C}_7\text{H}_6\text{O}_3(\text{s}), 298.15 \text{ K}] - \\ &\quad \Delta_r H_m^\ominus[(\text{C}_4\text{H}_7\text{NO}_2\text{S})(\text{s}), 298.15 \text{ K}] \end{aligned}$$

According to ref 16

$$\begin{aligned} \Delta_r H_m^\ominus[\text{HCl}(\text{g}), 298.15 \text{ K}] &= -(92.31 \pm 0.10) \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta_r H_m^\ominus[\text{H}_2\text{O}(\text{l}), 298.15 \text{ K}] &= -(285.830 \pm 0.040) \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

According to ref 15

$$\begin{aligned} \Delta_r H_m^\ominus[\text{CeCl}_3 \cdot 7\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] &= \\ &\quad -(3178.6 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

where $\pm 2.5 \text{ kJ} \cdot \text{mol}^{-1}$ was calculated according to the data in refs 16 and 17.

According to ref 17

$$\begin{aligned} \Delta_r H_m^\ominus[\text{C}_7\text{H}_6\text{O}_3(\text{s}), 298.15 \text{ K}] &= -(592.1 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

According to ref 18

$$\begin{aligned} \Delta_r H_m^\ominus[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s}), 298.15 \text{ K}] &= \\ &\quad -(401.33 \pm 1.54) \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

and the above-calculated values of

$$\Delta_r H_m^\ominus = (263.12 \pm 0.95) \text{ kJ} \cdot \text{mol}^{-1}$$

so that

$$\begin{aligned} \Delta_r H_m^\ominus[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] &= \\ &\quad [263.12 - 3(-92.31) - 5(-285.83) + (-3169.4) + \\ &\quad 2(-592.1) + (-401.33)] \pm \\ &\quad [\sqrt{0.95^2 + (30.10)^2 + (5 \cdot 0.04)^2 + (2 \cdot 1.3)^2 + (1.54)^2}] = \\ &\quad -(2785.7 \pm 3.2) \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Conclusions

In this work, $\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}$ was synthesized and characterized by IR, elemental, thermogravimetric, and chemical analysis. The enthalpy change of the reaction (eq 1) was determined to be $\Delta_r H_m^\ominus = (263.12 \pm 0.95) \text{ kJ} \cdot \text{mol}^{-1}$. The standard molar enthalpy of formation of $\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s})$ was estimated to be $\Delta_r H_m^\ominus[\text{Ce}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(2785.7 \pm 3.2) \text{ kJ} \cdot \text{mol}^{-1}$.

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