

Standard Molar Enthalpy of Formation of $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$ (Hsal = Salicylate $\text{C}_7\text{H}_5\text{O}_3^-$, tch = Thioprolinate $\text{C}_4\text{H}_6\text{NO}_2\text{S}^-$)[†]

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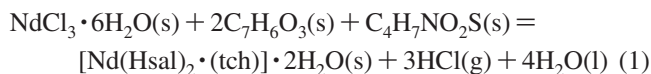
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The product from the reaction of neodymium chloride hexahydrate with salicylic acid and thioprolone, $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$, was synthesized and characterized by IR, elemental analysis, molar conductance, thermogravimetric analysis, and chemical analysis. The standard molar enthalpies of solution of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$, $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ in a mixed solvent of absolute ethyl alcohol, dimethyl sulfoxide (DMSO), and 3 mol·L⁻¹ HCl were determined by calorimetry to be $\Delta_{\text{s}}H_{\text{m}}^{\ominus}[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(51.94 \pm 0.14) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_{\text{s}}H_{\text{m}}^{\ominus}[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = (52.96 \pm 0.48) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_{\text{s}}H_{\text{m}}^{\ominus}[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s}), 298.15 \text{ K}] = (23.50 \pm 0.23) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\text{s}}H_{\text{m}}^{\ominus}\{[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}\} = -(41.76 \pm 0.50) \text{ kJ} \cdot \text{mol}^{-1}$. The enthalpy change of the reaction $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}) + 2\text{C}_7\text{H}_6\text{O}_3(\text{s}) + \text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s}) = [\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}) + 3\text{HCl}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ was determined to be $\Delta_{\text{r}}H_{\text{m}}^{\ominus} = (172.57 \pm 0.75) \text{ kJ} \cdot \text{mol}^{-1}$. From data in the literature, through Hess' law, the standard molar enthalpy of formation of $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ was estimated to be $\Delta_{\text{f}}H_{\text{m}}^{\ominus}\{[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}\} = -(2867.1 \pm 8.6) \text{ kJ} \cdot \text{mol}^{-1}$.

Introduction

It is known that rare earth ions and salicylic acid are antibacterial.^{1–6} Thioprolone possesses some special functions such as prolonging body life, controlling drug toxicity, and catalyzing plant growth and, in particular, functions as anticancer drugs, which can make cancer cells revert to normal cells.⁷ The synthesis and characterization of the rare earth complexes with thioprolone 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 *Escherichia coli* was more significant than that of their ligands, thioprolone, and salicylic acid. Obviously, it is very important to carry out research on the rare earth complex of thioprolone 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 $[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})]$, $[\text{C}_7\text{H}_6\text{O}_3(\text{s})]$, $[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s})]$, and $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ in a mixed solvent of absolute ethyl alcohol, dimethyl sulfoxide (DMSO), and 3 mol·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 $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ were obtained.

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[†] Part of the "Gerhard M. Schneider Festschrift".

Experimental Section

Chemicals and Instruments. The chemicals $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ (>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-Thioprolone ($\text{C}_4\text{H}_7\text{NO}_2\text{S}$, s) (>99.5%) was from Wuhan University Hoyo Co., Ltd.

$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ was dried in a desiccator containing sulfuric acid (60%)¹ 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 purity greater than 99.99% was dried in a vacuum oven for 6 h at 135 °C.

An elemental analyzer (Perkin-Elmer 2400 CHN, USA), an FT-IR spectrometer (Avatar 360, with KBr pellets, USA), a thermogravimetric analyzer (Perkin-Elmer TG6, at a heating rate of 10 °C·min⁻¹ flowing in N_2 , USA), an Abbe refractometer (WAY, Shanghai, China), an ultraviolet–visible spectrometer (U-3010, Hitachi, Japan), a solution-reaction isoperibol calorimeter (SRC 100, constructed by the thermochemical laboratory of Wuhan University, China), and a conductometer (DDS-12A, Shanghai, China) were used.

Synthesis and Characterization of $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$. 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 cm³ 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 thioprolone was dissolved in 50 cm³ 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 $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 cm³ 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 down at pH 5.0 to 6.0 over 12 h. Finally, the white

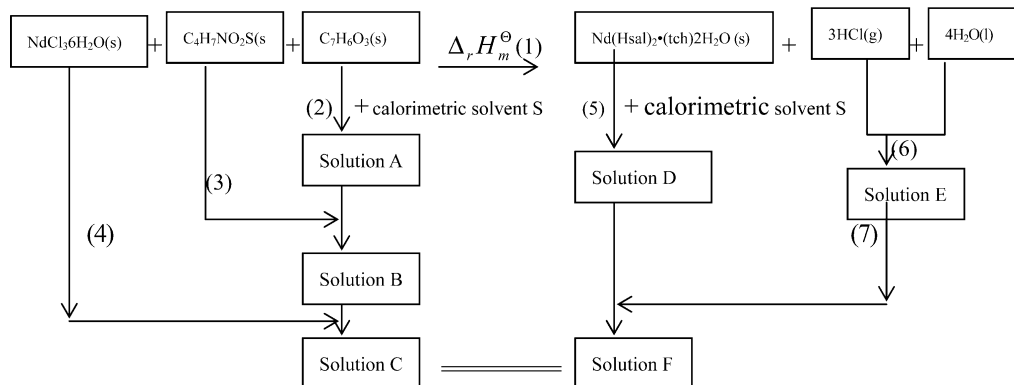


Figure 1. Thermochemical cycle of reaction 1.

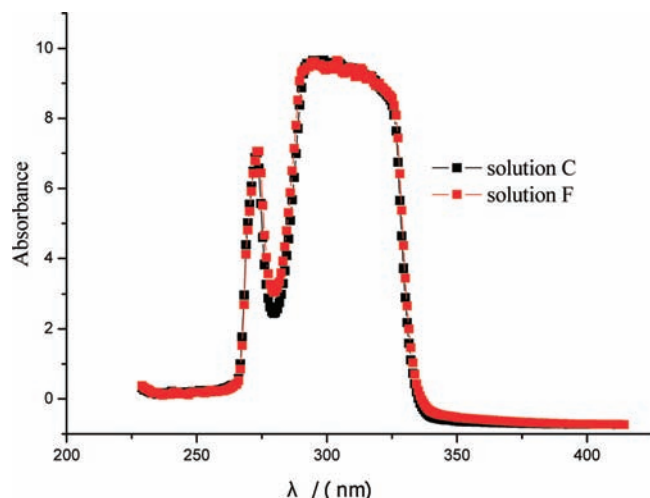


Figure 2. UV spectrum of the final dissolution state of the reactants and products.

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 determined by elemental analysis for C, H, and N, by EDTA titration for Nd^{3+} ,⁹ by mercury salt titration for Cl^- , and by difference and TG-DTG curves for H_2O . The analysis results proved that the composition of the complex was $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$, and its purity was >99.1 %.

Solution-Reaction Isoperibol Calorimetry and Calibration. The solution-reaction isoperibol calorimeter (SRC 100) has been detailed elsewhere.¹⁰ A Dewar vessel with an internal volume of 100 mL, equipped with a twin-blade stirrer, was submerged in the water thermostat. The precisions of temperature control and temperature measurement were ± 0.001 K and ± 0.0001 K, respectively.

The calibration of the calorimeter was carried out by measuring the dissolution enthalpies of 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 $(-29\,776 \pm 16) \text{ J} \cdot \text{mol}^{-1}$ for THAM and $(17\,597 \pm 17) \text{ J} \cdot \text{mol}^{-1}$ for KCl, which agree with published data $[(-29\,766 \pm 31.5) \text{ J} \cdot \text{mol}^{-1}$ for THAM¹¹ and $(17\,536 \pm 9) \text{ J} \cdot \text{mol}^{-1}$ for KCl¹²].

Table 1. Dissolution Enthalpies of $[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s})]$, $[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})]$, and $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s})]$ in the Calorimetric Solvent S at 298.15 K^{a,b}

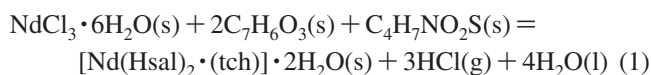
system	no.	<i>m</i> (g)	<i>t</i> (s)	$\Delta_s H_m^\ominus$ (kJ·mol ⁻¹)
$\text{C}_4\text{H}_7\text{NSO}_2(\text{s})$ in S	1	0.0335	40.74	23.4359
	2	0.0334	64.89	23.7289
	3	0.0334	67.44	23.7473
	4	0.0334	63.21	23.3491
	5	0.0333	56.16	23.2407
$\Delta_s H_m^\ominus[\text{C}_4\text{H}_7\text{NSO}_2(\text{s}), 298.15 \text{ K}] = (23.50 \pm 0.23) \text{ kJ} \cdot \text{mol}^{-1c}$				
$2\text{C}_7\text{H}_6\text{O}_3(\text{s})$ in the solution A	1	0.0692	91.46	53.3653
	2	0.0692	81.32	52.2209
	3	0.0691	97.58	53.0947
	4	0.0688	73.79	53.3445
	5	0.0692	77.18	52.7597
$\Delta_s H_m^\ominus(3) = \Delta_s H_m^\ominus[2\text{C}_7\text{H}_6\text{O}_3(\text{s}), 298.15 \text{ K}] = (52.96 \pm 0.48) \text{ kJ} \cdot \text{mol}^{-1}$				
$\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ in the solution B	1	0.0897	60.66	-51.7751
	2	0.0894	62.46	-51.9785
	3	0.0897	51.49	-52.1542
	4	0.0897	54.27	-51.9229
	5	0.0898	64.23	-51.8520
$\Delta_s H_m^\ominus(4) = \Delta_s H_m^\ominus[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = (21.79 \pm 0.35) \text{ kJ} \cdot \text{mol}^{-1}$				
$[\text{La}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ in S	1	0.1458	25.54	-42.1987
	2	0.1457	51.62	-41.8552
	3	0.1460	62.46	-41.3876
	4	0.1458	56.91	-42.2587
	5	0.1460	56.74	-41.1067
$\Delta_s H_m^\ominus(5) = \Delta_s H_m^\ominus[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] =$ $-(41.76 \pm 0.50) \text{ kJ} \cdot \text{mol}^{-1}$				
solution D + solution E	1	0.0451	83.17	-66.3927
	2	0.0453	83.17	-66.1676
	3	0.0441	83.44	-66.4431
	4	0.0451	71.01	-66.5198
	5	0.0455	85.24	-66.3346
$\Delta_s H_m^\ominus(7) = -(66.37 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$				

^a *n*: molar number of sample. ^b *t*: heating period of electrical calibration. ^c Uncertainty was estimated as twice the standard deviation of the mean of the results.

Table 2. Analytical Results of the Complex $[\text{Nd}(\text{C}_7\text{H}_5\text{O}_3)_2 \cdot (\text{C}_4\text{H}_6\text{NO}_2\text{S})] \cdot 2\text{H}_2\text{O}$ (%)

complex	C	H	S	N	Nd
$[\text{Nd}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_4\text{H}_6\text{NO}_2\text{S})] \cdot 2\text{H}_2\text{O}$					
theoretical values	36.85	3.44	5.47	2.39	24.59
experimental data	36.71	3.30	5.88	2.52	24.37

Determination of Dissolution Enthalpies. $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ can be regarded as the product of the reaction 1



and the thermochemical cycle was designed as shown in Figure 1.

Table 3. IR Absorption of Ligands and Complex (cm^{-1})

compound	$\nu_{\text{O-H}}$	$\nu_{\text{C-O}}$	$\nu_{\text{N-H}}$	$\nu_{\text{as}}^{\text{COO}^-}$	$\nu_{\text{s}}^{\text{COO}^-}$	$\delta_{\text{N-H}}$	$\delta_{\text{O-H}}$
$\text{C}_7\text{H}_6\text{O}_3$	2598	1663					1475
$\text{C}_4\text{H}_7\text{NO}_2\text{S}$			3058	1556	1434	1632	
$[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}]$	3398	2922	1560 (1596)	1461 (1389)	1623		

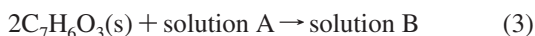
The UV spectrum and refractive indices of the final solution of the reactants and the final solution of the products can be used to determine if they have the same thermodynamic state. In the present experiments, we determined the spectrum and refractive indices of solution C and solution F and found for both of them the same UV spectrum (Figure 2) and equal refractive indices ($\eta_{25^\circ\text{C}} = 1.4102$), 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 dimethyl sulfoxide (DMSO) and absolute ethyl alcohol and 3 mol·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 (0.033 g) was placed into a sample cell in a calorimeter. The calorimetric solvent (100 cm³) 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 were performed.



where S is the calorimetric solvent (100 cm³). The solution A above was kept in the reaction vessel. Powdered salicylic acid $\text{C}_7\text{H}_6\text{O}_3(\text{s})$ (0.069 g) was put into the sample cell. A series of five experiments was performed.

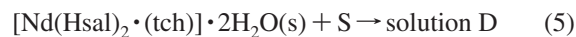


The solution B above was kept in the reaction vessel. Powdered $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ (0.090 g) was put into the sample cell. A series of five experiments were performed.

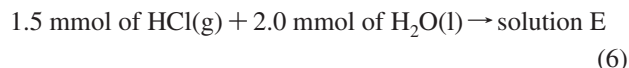


Powdered $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch}) \cdot 2\text{H}_2\text{O}(\text{s})]$ (0.147 g) was put into the sample cell in the calorimeter, and the calorimeter solvent

(100 cm³) 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 were performed.



where S is the calorimetric solvent (100 cm³). A mass of 1.5 mmol of HCl(g) was mixed into 2.0 mmol of H₂O(l)



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



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

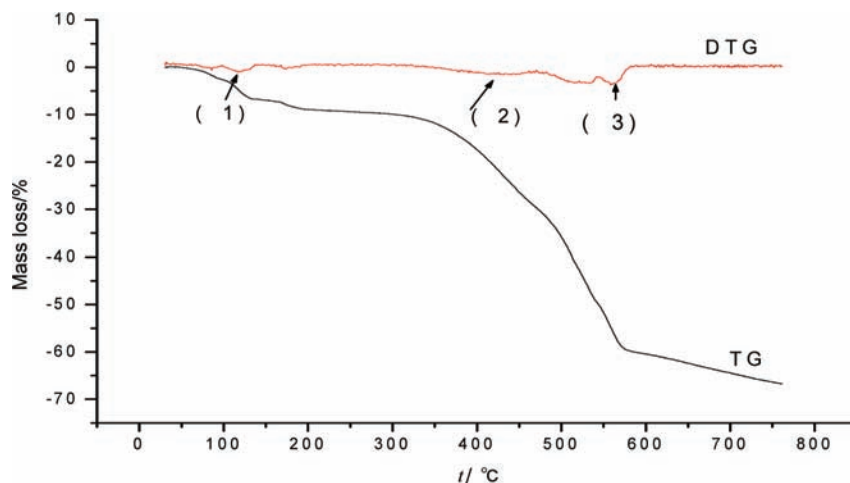
Results and Discussion

Elemental Analyses and Infrared 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.

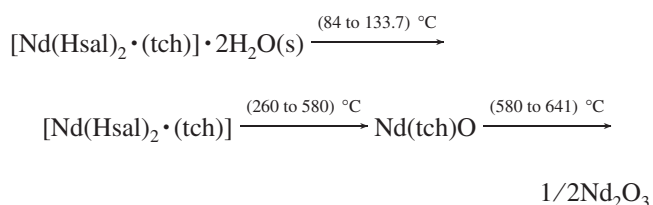
There are five characteristic bands observed for salicylic acid: ¹³ $\nu_{\text{OH}}^{\text{COOH}}$ (hydrogen bond intramolecular, 3237 cm^{-1} , s), $\nu_{\text{OH}}^{\text{COOH}}$ (hydrogen bond intermolecular, 2857 cm^{-1} , s), $\nu_{\text{O-H}}$ (COOH, 2598 cm^{-1} , s), $\nu_{\text{C-O}}$ (COOH, 1663 cm^{-1} , vs) and $\delta_{\text{O-H}}$ (phenol, 1475 cm^{-1} , s). All these bands disappeared after complex formation except 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 $\nu_{\text{s}}^{\text{COO}^-}$ (1387 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} , sh),

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

$\nu_{\text{as}}^{\text{COO}^-}$ (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 $\nu_{\text{s}}^{\text{COO}^-}$ (1462 cm^{-1} , s) and both $\delta_{\text{N-H}}$ and $\nu_{\text{as}}^{\text{COO}^-}$ shift toward lower frequencies $\delta_{\text{N-H}}$ (1622 cm^{-1}) and $\nu_{\text{as}}^{\text{COO}^-}$ (1548 cm^{-1}). According to these results, it can be concluded that the neodymium ion is coordinated with the N atom of the imine group and one O atom of the carboxylate group in thioproline, as an antisymmetric bidentate group.

Thermal Decomposition of the Complex. The TG and DTG curves of $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$, at a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$ in flowing N_2 , are shown in Figure 3. The thermal decomposition process of $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ can be divided into four stages. The first stage is from (84 to 134) $^\circ\text{C}$. The TG curve shows that the mass loss corresponding to this temperature range is 6.22 %, which roughly coincides with the value of 6.14 %, calculated for the loss of 2 mol of H_2O from the complex. The second stage ranges from (260 to 580) $^\circ\text{C}$ with the mass loss of 47.36 %, which corresponds to the loss of 2 mol of Hsal^- . The theoretical mass loss is 46.89 %. The third stage degradation temperature is in the range of (580 to 641) $^\circ\text{C}$ with the mass loss of 42.33 %, which corresponds to the loss of 1 mol of tch^- . The theoretical mass loss is 42.46 %. On the basis of experimental and calculated results, the thermal decomposition of $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ was postulated as follows



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

Estimation of $\Delta_{\text{s}}H_{\text{m}}^\ominus(6)$. According to reaction 6



$$\Delta_{\text{s}}H_{\text{m}}^\ominus(6) = \Delta_{\text{s}}H_{\text{m}}^\ominus(m = 41.7 \text{ mol} \cdot \text{cm}^{-3}) = \Delta_{\text{s}}H_{\text{m}}^\ominus(m = 1.000 \text{ mol} \cdot \text{cm}^{-3}) - \Delta_{\text{d}}H_{\text{m}}^\ominus(41.7 \rightarrow 1.000) = [-74.843 - (-34.923)] \text{ kJ} \cdot \text{mol}^{-1} = -39.92 \text{ kJ} \cdot \text{mol}^{-1}$$

See ref 15.

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

$$\Delta_{\text{r}}H_{\text{m}}^\ominus(1) = \Delta_{\text{s}}H_{\text{m}}^\ominus(2) + \Delta_{\text{s}}H_{\text{m}}^\ominus(3) + \Delta_{\text{s}}H_{\text{m}}^\ominus(4) - \Delta_{\text{s}}H_{\text{m}}^\ominus(5) - \Delta_{\text{s}}H_{\text{m}}^\ominus(6) - \Delta_{\text{s}}H_{\text{m}}^\ominus(7) = (172.57 \pm 0.75) \text{ kJ} \cdot \text{mol}^{-1}$$

Evaluation of $\Delta_{\text{r}}H_{\text{m}}^\ominus([\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}))$. According to Hess' law

$$\Delta_{\text{r}}H_{\text{m}}^\ominus(1) = \Delta_{\text{r}}H_{\text{m}}^\ominus\{[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}\} + 3\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{HCl}(\text{g}), 298.15 \text{ K}] + 4\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{H}_2\text{O}(\text{l}), 298.15 \text{ K}] - \Delta_{\text{f}}H_{\text{m}}^\ominus[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] - 2\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{C}_7\text{H}_6\text{O}_3(\text{s}), 298.15 \text{ K}] - \Delta_{\text{f}}H_{\text{m}}^\ominus[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s}), 298.15 \text{ K}]$$

According to ref 16

$$\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{HCl}(\text{g}), 298.15 \text{ K}] = -(92.31 \pm 0.10) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{H}_2\text{O}(\text{l}), 298.15 \text{ K}] = -(285.830 \pm 0.040) \text{ kJ} \cdot \text{mol}^{-1}$$

According to ref 15

$$\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}] = -(2874.4 \pm 8.0) \text{ kJ} \cdot \text{mol}^{-1}$$

where $\pm 8.0 \text{ kJ} \cdot \text{mol}^{-1}$ was calculated according to the data in refs 16 and 17. According to ref 17

$$\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{C}_7\text{H}_6\text{O}_3(\text{s}), 298.15 \text{ K}] = -(592.1 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$$

According to ref 7

$$\Delta_{\text{f}}H_{\text{m}}^\ominus[\text{C}_4\text{H}_7\text{NO}_2\text{S}(\text{s}), 298.15 \text{ K}] = -(401.33 \pm 1.54) \text{ kJ} \cdot \text{mol}^{-1}$$

and the above-calculated value of

$$\Delta_{\text{r}}H_{\text{m}}^\ominus = (172.57 \pm 0.75) \text{ kJ} \cdot \text{mol}^{-1}$$

so that

$$\Delta_{\text{f}}H_{\text{m}}^\ominus\{[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}\} = [172.57 - 3 \cdot (-92.31) - 4 \cdot (-285.830) + (-2874.4) + 2 \cdot (-592.1) + (-401.33)] \pm \left[\sqrt{0.75^2 + (3 \cdot 0.10)^2 + (4 \cdot 0.040)^2 + (8.0)^2 + (2 \cdot 1.3)^2 + (1.54)^2} \right] = -(2867.1 \pm 8.6) \text{ kJ} \cdot \text{mol}^{-1}$$

Conclusion

In this work, $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}$ was synthesized and characterized by IR, elemental analysis, molar conductance, thermogravimetric analysis, and chemical analysis. The enthalpy change of the reaction (eq 1) was determined to be $\Delta_{\text{r}}H_{\text{m}}^\ominus = (172.57 \pm 0.75) \text{ kJ} \cdot \text{mol}^{-1}$. The standard molar enthalpy of formation of $[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s})$ was estimated to be $\Delta_{\text{f}}H_{\text{m}}^\ominus\{[\text{Nd}(\text{Hsal})_2 \cdot (\text{tch})] \cdot 2\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}\} = -(2867.1 \pm 8.6) \text{ kJ} \cdot \text{mol}^{-1}$.

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