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Synthesis and Thermochemical Properties of the Ternary Complex $[Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O$

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The coordination complex $[Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O$, synthesized via the reaction of samarium chloride hexahydrate ($SmCl_3 \cdot 6H_2O$, CAS No. 13465-55-9) with *m*-nitrobenzoic acid (*m*-HNBA, $C_7H_5NO_4$, CAS No. 121-92-6) and 1,10-phenanthroline (phen, $C_{12}H_8N_2$, CAS No. 66-71-7), was characterized by IR and elemental analysis, molar conductance, and thermogravimetric analysis. The dissolution enthalpies of [*m*-HNBA(s)], $[phen \cdot H_2O(s)]$, $[SmCl_3 \cdot 6H_2O(s)]$, and $[Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O$ in the calorimetric solvent were determined by the solution-reaction isoperibol calorimeter at 298.15 K to be $\Delta_s H_m^\theta[6m\text{-HNBA(s)}, 298.15\ K] = (97.72 \pm 1.05)\ kJ \cdot mol^{-1}$, $\Delta_s H_m^\theta[2phen \cdot H_2O(s), 298.15\ K] = -(11.40 \pm 0.08)\ kJ \cdot mol^{-1}$, $\Delta_s H_m^\theta[2SmCl_3 \cdot 6H_2O(s), 298.15\ K] = -(94.80 \pm 0.34)\ kJ \cdot mol^{-1}$, and $\Delta_s H_m^\theta[[Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O(s), 298.15\ K] = -(11.70 \pm 0.25)\ kJ \cdot mol^{-1}$, respectively. The enthalpy change was determined to be $\Delta_r H_m^\theta = (214.49 \pm 1.47)\ kJ \cdot mol^{-1}$ for the reaction. According to the above results and the data given in the literature, the standard molar enthalpy of formation of $[Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O(s)$ was estimated to be $\Delta_f H_m^\theta[[Sm(m\text{-}NBA)_3\ phen]_2 \cdot 2H_2O(s), 298.15\ K] = -(4808.8 \pm 6.6)\ kJ \cdot mol^{-1}$ through Hess's law.

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1. Introduction

Rare earth resources are abundant in China and can be used as ion probes to investigate the interaction between biomacromolecules and metallic ions such as Ca^{2+}.[1,2] The coordination complexes of rare earth metals with carboxylic acids have special structures and potential applications in extraction, separation, catalysis, and luminescence.[3−5] So, it is important to accelerate the research on the rare earth complexes of carboxylic acids.[6] From the viewpoint of basic research, it is necessary to study their thermochemical properties. Now the synthesis and characterization of the complex of samarium chloride hexahydrate with *m*-nitrobenzoic acid (*m*-HNBA) and 1,10-phenanthroline (phen) are reported.

Dissolution calorimetry is a classic calorimetric method and is a good experimental method to measure the standard enthalpy of formation of compounds. The selection of an appropriate calorimetric solvent is important in designing a thermochemical cycle that ensures that the reactants and products have the same final state when they are dissolved in the solvent. Generally, we can obtain a series of reliable data of the standard enthalpy of formation by a thermochemical cycle. The molar enthalpy of the following reaction

$$2SmCl_3 \cdot 6H_2O(s) + 2phen \cdot H_2O(s) + 6m\text{-}HNBA(s) = [Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O(s) + 6HCl(g) + 12H_2O(l) \quad (1)$$

and the standard molar enthalpy change of formation of $[Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O(s)$ were estimated.

2. Experiment

2.1. Reagents and Instruments. Sm_2O_3 (> 99.9 %, produced by the Chengdu Fei Tian Co., Ltd.), $SmCl_3 \cdot 6H_2O$ (prepared from Sm_2O_3 by dissolution in hydrochloric acid followed by drying), *m*-HNBA (> 99.5 %, A.R.); *o*-phenanthroline monohydrate ($phen \cdot H_2O$, > 99.5 %, A.R., recrystallized with anhydrous ethanol), cyclohexanone (CYC, A.R.), *N*,*N*-dimethylformamide (DMF, A.R.), NaOH (A.R.), HCl (A.R.), and KCl (calorimetric primary standard) of purity greater than 99.99 % were dried in a vacuum for 6 h at 135 °C.

The instrumentation used included the following: an elemental analyzer (PE-2400, USA), Fourier IR spectrometer (Avatar360, Nicolet), thermogravimetric analyzer (PE-TGA7, USA), UV−visible spectrophotometer (U-3010, HITACHI, Japan), digital Abbe refractometer (WAY-IS, Shanghai, China), and an isoperibol calorimeter (SRC100, constructed by the thermochemical laboratory of Wuhan University, China).[7] The volume of the reaction vessel was 100 cm^3, and the precision of the test temperature and control temperature are ± 0.001 K and ± 0.0001 K, respectively.

2.2. Synthesis of the Complex $[Sm(m\text{-}NBA)_3phen]_2 \cdot 2H_2O(s)$. $SmCl_3 \cdot 6H_2O$, *m*-HNBA, and $phen \cdot H_2O$ were dissolved in 95 % ethanol in a molar ratio of 1:3:1, respectively. Then the two ligand solutions were mixed, and the mixture was adjusted to pH = 6 to 7 using $1.0\ mol \cdot L^{-1}$ NaOH. After that, the solution of $SmCl_3 \cdot 6H_2O$ was added dropwise with plenty of white precipitate formed immediately. The mixture was stirred for (2 to 3) hours and then allowed to settle overnight. Subsequently, the precipitate was filtrated and washed with 95 % ethanol. The product was dried under vacuum at 333.15 K until the weight of the crystals was constant, with a yield of 85 %. The chemical composition of the synthetic complex was determined by elemental analysis for C, H, and N and by ethylenediaminetetraacetic acid (EDTA) titration for the Sm^{3+}

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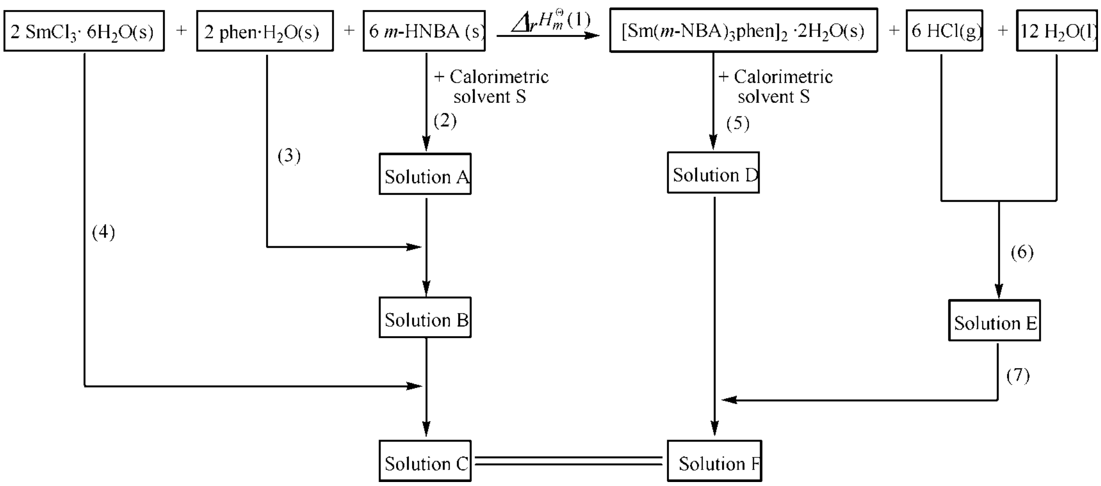

Figure 1. Thermochemical cycle of reaction 1.

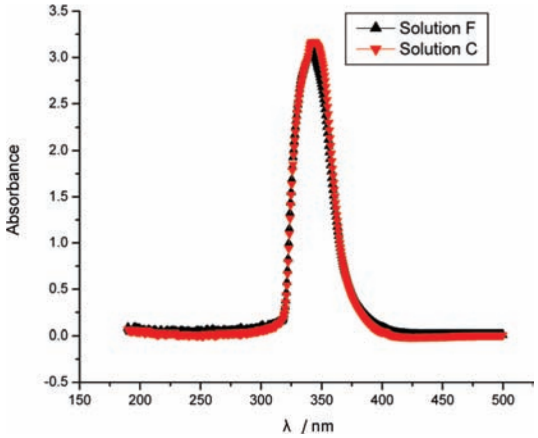

Figure 2. UV spectrum of the final dissolution state of the reactants and products.

ion. The analytical results proved that the composition of the complex was $[Sm(m\text{-}NBA)_3\ phen]_2 \cdot 2H_2O$, and its purity was greater than 99.0 %.

2.3. Solution-Reaction Isoperibol Calorimeter and Calibration. The solution-reaction isoperibol calorimeter with a constant temperature environment was constructed and calibrated according to the literature.[7] The solution-reaction isoperibol calorimeter was calibrated by means of six para-experiments carried out at 298.15 K using a solution of KCl in H_2O with a molar ratio of 1:1110 as a standard substance. The dissolution enthalpy of the six tests, $\Delta_s H_m^\theta[\mathrm{KCl(s)}, 298.15\ \mathrm{K}] = (17597 \pm 17)\ \mathrm{J{\cdot}mol^{-1}}$, is similar to the reported value of $(17536 \pm 9)\ \mathrm{J{\cdot}mol^{-1}}$. The error is less than 0.5 %.

2.4. Determination of Dissolution Enthalpies. 2.4.1. Thermochemical Cycle of the Synthetic Reaction 1. According to Hess's law, the thermochemical cycle was designed as Figure 1.

The UV spectra and refractive indexes of the final solution of the reactants and the products can be used to determine if they have the same thermodynamic state. In this experiment, the UV spectrum and refractive indexes of solution C and solution F were determined according to Figure 1; the experimental results suggested that both have similar UV spectrum curves (Figure 2) and equal refractive indexes ($\eta_{25°\mathrm{C}} = 1.4101$). It proves that they have the same thermodynamic state and the thermochemical cycle of the designed reaction is reliable.

2.4.2. Choice of Solvent. It is very important to choose a calorimetric solvent which should dissolve all of the chemicals in the sample cell rapidly and completely. The optimized calorimetric solvent (S) for this experiment was a mixture of DMF, CYC, and 2 $\mathrm{mol{\cdot}L^{-1}}$ HCl (V_{DMF}:V_{CYC}:V_{HCl} = 2:1:2).

2.4.3. Determination of Dissolution Enthalpies of All of the Chemicals in Synthetic Reaction 1. Both the calorimeter's calibration and the enthalpy of solution of the sample were determined under the same conditions. The experimental temperature was 298.15 K, the current was 11.7600 mA, and the resistance of the heater was 1251.5 Ω.

The sample was ground completely. *m*-HNBA (0.2500 g) was put into the sample cell in the calorimeter. Then the calorimetric solvent S (100 mL) was added into the reaction vessel. The calorimeter was adjusted to a constant temperature of 298.15 K. The dissolution enthalpy of the dissolution reaction 2 was determined by five para-experiments, and the results are listed in Table 1.

$$6m\text{-HNBA(s)} + \text{solvent S} \rightarrow \text{solution A} \tag{2}$$

Solution A was kept in the reaction vessel, and powdery $\mathrm{phen{\cdot}H_2O}$ (0.0990 g) was put into the cell. The calorimeter was then adjusted to a constant temperature of 298.15 K. The dissolution enthalpy of reaction 3 was determined by five para-experiments. The results are listed in Table 1.

$$2\ \text{phen} \cdot \text{H}_2\text{O(s)} + \text{solvent A} \rightarrow \text{solution B} \tag{3}$$

Solution B was kept in the reaction vessel. Powdery $\mathrm{SmCl_3{\cdot}6H_2O}$ (0.1820 g) was put into the sample cell. The calorimeter was adjusted to a constant temperature of 298.15 K. The dissolution enthalpy of reaction 4 was determined by five para-experiments. The results are listed in Table 1.

$$2\ \text{SmCl}_3 \cdot 6\text{H}_2\text{O(s)} + \text{solution B} \rightarrow \text{solution C} \tag{4}$$

$[Sm(m\text{-}NBA)_3phen]_2{\cdot}2H_2O$ (0.4230 g) was put into the sample cell, and the calorimetric solvent S (100 mL) was added. The calorimeter was adjusted to a constant temperature of 298.15 K. The dissolution enthalpy of reaction 5 was determined by five para-experiments. The results are listed in Table 1.

$$[\text{Sm}(m\text{-NBA})_3\text{phen}]_2 \cdot 2\text{H}_2\text{O(s)} + \text{solvent S} \rightarrow \text{solution D} \tag{5}$$

Solution D was kept in the reaction vessel. At the same time, 1.5 mmol of HCl(g) was dissolved into 3.0 mmol of $H_2O(l)$ to give solution E.

$$6HCl(g) + 12H_2O(l) \rightarrow \text{solution E} \qquad (6)$$

Subsequently, solution E was added into the sample cell, and the calorimeter was adjusted to a constant temperature of 298.15 K. Then the enthalpy of this reaction 7 was determined, and the results are listed in Table 1.

$$\text{solution D} + \text{solution E} \rightarrow \text{solution F} \qquad (7)$$

3. Results and Discussion

3.1. Elemental Analysis and General Properties of the Complex. The theoretical value of the elemental analysis for $[Sm(m\text{-NBA})_3phen]_2 \cdot 2H_2O$ is the following: C, 46.80 %; H, 2.62 %; N, 8.27 %; Sm, 17.75 %. Found values are the following: C, 46.59 %; H, 2.52 %; N, 8.14 %; Sm, 17.83 %. The molar conductance of the complex solution in dimethyl sulfoxide (DMSO) was determined to be 24.3 $S \cdot cm^2 \cdot mol^{-1}$, which proves that the complex exists in DMSO in the form of a nonelectrolyte. The complex is a white powder and is very stable in the atmosphere. It can be dissolved by *N*,*N*-dimethylformamide and dimethyl sulfoxide but can not be dissolved in H_2O, chloroform, methanol, ethanol, acetone, petroleum ether, or tetrahydrofuran.

3.2. IR Spectra. The frequencies of the characteristic vibration absorption of $[Sm(m\text{-NBA})_3\ phen]_2 \cdot 2H_2O$ (Figure 3) and dissociative ligands were obviously different. There were three characteristic absorption bands, $\nu_{C=O}$(1692 cm^{-1}), ν_{O-H}(3000 cm^{-1}), and δ_{O-H} (928 cm^{-1}), ascribed to the *m*-NBA ligand (Figure 4). All of these bands disappeared in the IR spectra of the complex, and meanwhile, two new absorption bands assigned to the carboxylate group, $\nu_{as(COO^-)}$ (1598 cm^{-1}) and $\nu_{s(COO^-)}$ (1404 cm^{-1}), appeared. A slight band of flex vibration absorption belonging to Sm—O appeared near 414 cm^{-1}. These results indicated that the carboxylate group was coordinated to the samarium ion via the two oxygen atoms. In addition, the characteristic absorption of $\nu_{as(-NO_2)}$ and $\nu_{s(-NO_2)}$ originating from nitryl did not change obviously on complexation. It was confirmed that nitryl did not participate in the coordination.

Table 1. Dissolution Enthalpies of [6*m*-HNBA(s)], [2phen·H₂O(s)], [2SmCl₃·6H₂O(s)], and [Sm(*m*-NBA)₃phen]₂·2H₂O(s) in the Calorimetric Solvent S at 298.15 K

		m	*t*	$\Delta_s H_m^\Theta$
system	no.	g	s	$kJ \cdot mol^{-1}$
6 *m*-HNBA(s) in solvent S	1	0.2507	135.61	96.7314
	2	0.2506	243.27	98.4396
	3	0.2507	137.90	98.8404
	4	0.2506	137.06	98.1162
	5	0.2504	137.33	96.483
$\Delta_s H_m^\theta$[6*m*-HNBA(s), 298.15 K] = (97.72 ± 1.05) $kJ \cdot mol^{-1}$				
2 phen·H_2O (s) in solvent A	1	0.0989	15.59	−11.3256
	2	0.0992	11.17	−11.3020
	3	0.0992	10.09	−11.4652
	4	0.0992	13.09	−11.4516
	5	0.0991	13.62	−11.4526
$\Delta_s H_m^\theta$[2 phen·H_2O(s), 298.15 K] = −(11.40 ± 0.08) $kJ \cdot mol^{-1}$				
$2SmCl_3 \cdot 6H_2O$(s) in solvent B	1	0.1820	150.55	−94.7294
	2	0.1822	150.24	−95.3992
	3	0.1826	144.73	−94.6448
	4	0.1826	150.24	−94.5420
	5	0.1822	150.11	−94.7084
$\Delta_s H_m^\theta$[$2SmCl_3 \cdot 6H_2O$(s), 298.15 K] = −(94.80 ± 0.34) $kJ \cdot mol^{-1}$				
$[Sm(m\text{-NBA})_3\ phen]_2 \cdot 2H_2O$(s) in solvent S	1	0.4238	15.64	−11.4823
	2	0.4236	15.37	−11.9847
	3	0.4242	15.86	−11.7431
	4	0.4232	15.55	−11.8811
	5	0.4240	15.64	−11.3938
$\Delta_s H_m^\theta$[$[Sm(m\text{-NBA})_3phen]_2 \cdot 2H_2O$(s), 298.15 K] = −(11.70 ± 0.25) $kJ \cdot mol^{-1}$				
solution D + solution E	1	0.0551	221.63	−159.7962
	2	0.0553	186.73	−160.2002
	3	0.0541	204.53	−161.9748
	4	0.0551	201.01	−161.5684
	5	0.0555	215.24	−161.2750
$\Delta_s H_m^\theta$(7) = −(160.96 ± 0.93) $kJ \cdot mol^{-1}$				

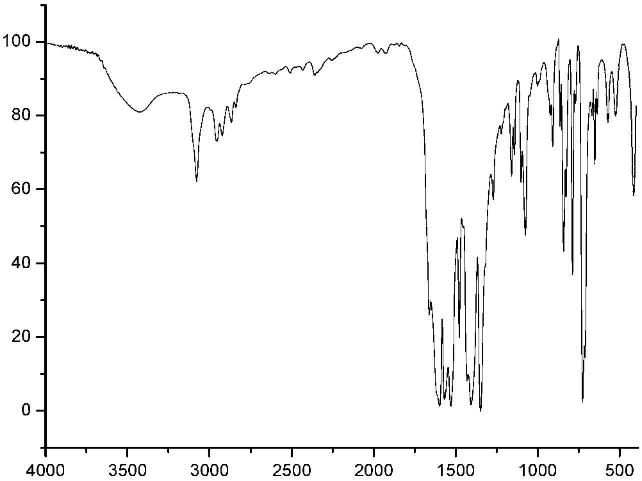

Figure 3. IR spectrum of $[Sm(m\text{-NBA})_3phen]_2 \cdot 2H_2O$(s).

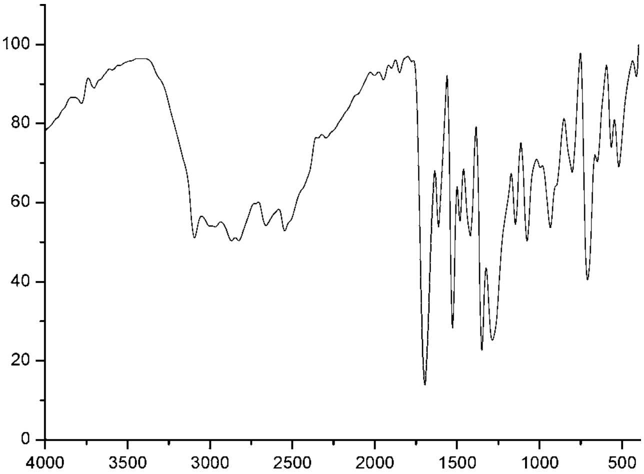

Figure 4. IR spectrum of *m*-HNBA(s).

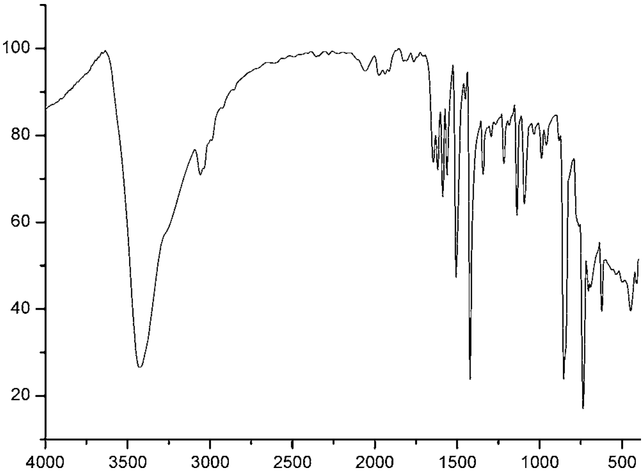

Figure 5. IR spectrum of phen·H_2O(s).

There were four characteristic absorption bands observed for phen (Figure 5): $\nu_{C=N}$ (1645 cm^{-1}), $\nu_{C=C}$ [(1616, 1587, and 1506) cm^{-1}], δ_{C-H} [(853 and 738) cm^{-1}]. After being coordinated, the $\nu_{C=N}$ vanished, and the skeleton vibration peak $\nu_{C=C}$ was retained; the δ_{C-H} [(841 and 725) cm^{-1}] had a red shift. Obviously, the phen·H_2O basic structure did not change, and

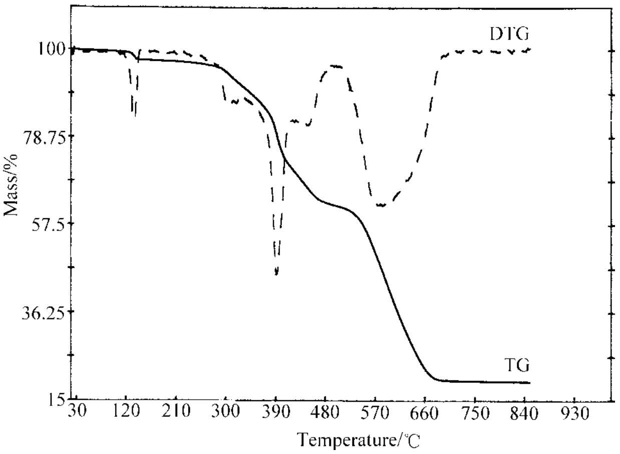

Figure 6. TG−DTG curves of the complex $[Sm(m\text{-}NBA)_3\ phen]_2\cdot 2H_2O$ ($\beta = 5\ °C\cdot min^{-1}$).

the phen was bidentate coordinated to the Sm^{3+} ion via the two nitrogen atoms, as a chelating ring.[8]

3.3. Mechanism of Thermal Decomposition. TG−DTG (thermal gravimetry/differential thermal gravimetry) curves ($\beta = 5\ °C\cdot min^{-1}$, static air atmosphere) of $[Sm(m\text{-}NBA)_3phen]_2\cdot 2H_2O$ are shown in Figure 6. The thermal decomposition process could be divided into three steps. The first decomposition process starts from (107.17 to 155.11) °C with a mass loss of 2.07 % corresponding to the loss of 2 mol H_2O (theoretical loss is 2.12 %), which produces an intermediate substance $[Sm(m\text{-}NBA)_3phen]_2$. The second decomposition process starts from (281.49 to 497.95) °C with a mass loss of 33.61 % corresponding to the loss of 2 mol phen (theoretical loss is 21.74 %), which indicates that part of the *m*-NBA ligands have also been lost. The IR spectra of the residue showed that the absorption band of C═N disappeared at 1644 cm^{-1}. It demonstrated that the phen molecule was lost in the second step. As shown by Figure 6, two successive decomposition processes existed in the third step. The decomposition temperature was in the range from (497.95 to 707.15) °C with a mass loss of 42.84 % corresponding to the loss of residual *m*-NBA, and three oxygen atoms remained. The characteristic absorption of the IR spectra of the residue was similar to the sample of Sm_2O_3. So the complex was decomposed into Sm_2O_3 completely (actual value: 19.84 %, theoretical value: 21.03 %). The high decomposition temperature of the complex suggested that the complex had good thermal stabilization.

3.4. Results of the Calorimetry Experiment. The dissolution enthalpies of $2SmCl_3\cdot 6H_2O$, 6*m*-HNBA, $2phen\cdot H_2O$, and $[Sm(m\text{-}NBA)_3phen]_2\cdot 2H_2O$ in the calorimetric solvent S are listed in Table 1 (298.15 K, $R = 1251.5\ \Omega$, $I = 11.7600$ mA).

3.5. Data Treatment. 3.5.1. Evaluation of $\Delta_d H_m^\theta$ (Reaction 6). According to reaction 6

$$6HCl(g) + 12H_2O(l) \rightarrow \text{solution E} \qquad (6a)$$

the molality of solution E was 27.78 $mol\cdot kg^{-1}$. According to the relationship between the enthalpy of dilution and the dissolution enthalpy

$$\Delta_d H_m^\theta = \Delta_s H_m^\theta(\text{diluted}) - \Delta_s H_m^\theta(\text{concentrated})$$

so that

$$\Delta_d H_m^\theta = \Delta_s H_m^\ominus(m = 1.000\ mol\cdot kg^{-1}) - \Delta_s H_m^\ominus(m = 27.78\ mol\cdot kg^{-1})$$

According to ref 9, the enthalpy of extremely diluted HCl(g) is:

$$\Delta_s H_m^\ominus(HCl(g),\ 298.15\ K) = -74.843\ kJ\cdot mol^{-1}$$

According to the relationship between the apparent molar enthalpy and the integration enthalpy of the extremely diluted solution: $\Delta_d H_{c\to 0}^\theta = -\Phi_{L2}$.

According to the data in ref 9,

$$\Delta_d H_{(1.000\to 0)}^\theta = -\Phi_{L(1.000\to 0)} = -1.695\ kJ\cdot mol^{-1}$$

$$\Delta_d H_{(27.78\to 0)}^\theta = -\Phi_{L(27.78\to 0)} = -26.230\ kJ\cdot mol^{-1}$$

so that

$$\Delta_d H_{(27.78\to 1.000)}^\theta = \Delta_d H_{(27.78\to 0)}^\theta - \Delta_d H_{L(27.78\to 0)}^\theta = -\Phi_{L(27.78\to 0)} + \Phi_{L(1.000\to 0)} = -26.230 + 1.695 = -24.535\ kJ\cdot mol^{-1}$$

and

$$\begin{aligned}\Delta_s H_m^\theta(6) &= \Delta_s H_m^\theta(m = 27.78\ mol\cdot kg^{-1})\\ &= \Delta_s H_m^\theta(m = 1.000\ mol\cdot kg^{-1}) - \Delta_d H_m^\theta(27.78 \rightarrow 1.000)\\ &= [-74.843 - (-24.535)]\ kJ\cdot mol^{-1}\\ &= -50.31\ kJ\cdot mol^{-1}\end{aligned}$$

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

$$\begin{aligned}\Delta_r H_m^\theta(1) &= \Delta_s H_m^\theta(2) + \Delta_s H_m^\theta(3) + \Delta_s H_m^\theta(4) - \Delta_s H_m^\theta(5) - \Delta_s H_m^\theta(6) - \Delta_s H_m^\theta(7) =\\ &(97.72 - 11.40 - 94.80 + 11.70 + 50.31 + 160.96) \pm (\sqrt{1.05^2 + 0.08^2 + 0.34^2 + 0.93^2 + 0.25^2}) =\\ &(214.49 \pm 1.47)\ kJ\cdot mol^{-1}\end{aligned}$$

3.5.3. Estimation of $\Delta_f H_m^\theta[[Sm(m\text{-}NBA)_3\ phen]_2\cdot 2H_2O(s),\ 298.15\ K]$. According to Hess's law,

$$\begin{aligned}\Delta_r H_m^\theta(1) = {}&\Delta_f H_m^\theta[[Sm(m\text{-}NBA)_3phen]_2\cdot 2H_2O(s),\ 298.15\ K] +\\ &6\Delta_f H_m^\theta[HCl(g),\ 298.15\ K] + 12\Delta_f H_m^\theta[H_2O(l),\ 298.15\ K] -\\ &2\Delta_f H_m^\theta[SmCl_3\cdot 6H_2O(s),\ 298.15\ K] -\\ &6\Delta_f H_m^\theta[m\text{-}HNBA(s),\ 298.15\ K] -\\ &2\Delta_f H_m^\theta[phen\cdot H_2O(s),\ 298.15\ K]\end{aligned}$$

According to refs 9 to 12,

$$\Delta_f H_m^\theta[HCl(g),\ 298.15\ K] = -(92.31 \pm 0.10)\ kJ\cdot mol^{-1}$$

$$\Delta_f H_m^\theta[H_2O(l),\ 298.15\ K] = -(285.830 \pm 0.040)\ kJ\cdot mol^{-1}$$

$$\Delta_f H_m^\theta[SmCl_3\cdot 6H_2O(s),\ 298.15\ K] = -2870.2\ kJ\cdot mol^{-1}$$

$$\Delta_f H_m^\theta[m\text{-}HNBA(s),\ 298.15\ K] = -(414.0 \pm 0.4)\ kJ\cdot mol^{-1}$$

$$[phen\cdot H_2O(s),\ 298.15\ K] = -(391.34 \pm 2.98)\ kJ\cdot mol^{-1}$$

and from reaction 1

$$\Delta_r H_m^\theta(1) = (214.49 \pm 1.47)\ \mathrm{kJ \cdot mol^{-1}}$$

so that

$$\begin{aligned}
&\Delta_f H_m^\theta[[\mathrm{Sm}(m\text{-NBA})_3\mathrm{phen}]_2 \cdot 2H_2O(s),\ 298.15\ \mathrm{K}] = \\
&\quad [214.49 - 6(-92.31) - 12(-285.830) + \\
&\quad 2(-2870.2) + 6(-414.0) + 2(-391.34)] \pm \\
&\quad [\sqrt{1.47^2 + (6 \cdot 0.10)^2 + (12 \cdot 0.040)^2 + (6 \cdot 0.4)^2 + (2 \cdot 2.98)^2}] = \\
&\quad -(4808.8 \pm 6.6)\ \mathrm{kJ \cdot mol^{-1}}
\end{aligned}$$

4. Conclusion

The thermostable ternary solid complex $[\mathrm{Sm}(m\text{-NBA})_3\text{-}\mathrm{phen}]_2 \cdot 2H_2O$ was synthesized and characterized by elemental analysis, IR spectroscopy, molar conductance, and thermogravimetric analysis. As shown by the IR spectra, *m*-NBA was bonded to rare earth ion through carboxylate groups, and phen was bonded through two nitrogen atoms.

The dissolution enthalpy of the relevant substances was determined by calorimetry at 298.15 K. The calculated results based on experimental data indicated that the standard molar enthalpy of reaction of the synthesis of the complex was (214.49 ± 1.47) $\mathrm{kJ \cdot mol^{-1}}$ and the standard molar enthalpy of formation of $[\mathrm{Sm}(m\text{-NBA})_3\mathrm{phen}]_2 \cdot 2H_2O$ was $-(4808.8 \pm 6.6)\ \mathrm{kJ \cdot mol^{-1}}$.

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