

Thermokinetics on the Reaction of Formation of the Ternary Complex $\text{Nd}[(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$

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The title ternary complex $\text{Nd}[(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$ has been synthesized in absolute ethanol by the reaction of $\text{NdCl}_3 \cdot 3.74\text{H}_2\text{O}$ with ammonium pyrrolidinyldithiocarboxylate (APDC) and 1,10-phenanthroline (phen $\cdot\text{H}_2\text{O}$) at air atmosphere without any cautions against moisture. The bonding characteristics of the complex were characterized by IR, showing that Nd^{3+} is bonded with sulfur atom in the APDC and coordinated with nitrogen atom in the phen. TG-DTG investigation indicates that the title complex was decomposed into Nd_2S_3 and deposited carbon in one step where Nd_2S_3 predominated in the final products. The enthalpy change of formation of the reaction on the title complex in liquid-phase has been determined by a microcalorimeter. Thermodynamic parameters (the activation enthalpy, the activation entropy and the activation free energy) and kinetics parameters (the rate constant, the apparent activation energy, the pre-exponential constant and the reaction order) of the title reaction have been calculated. The enthalpy change of the solid-phase reaction has been obtained by a thermochemistry cycle.

Keywords hydrous neodymium chloride, ammonium pyrrolidinyldithiocarboxylate (APDC), 1,10-phenanthroline (phen), characterization, thermochemistry

Introduction

The chemistry of the complexes containing lanthanide-sulfur bond has been of substantial interest because of high performance in biological properties¹ and friction properties.² In addition, they have been largely used because of their chemical and physical properties, e.g. as vulcanization accelerator.^{2,3} The vast investigations have been reported on preparations, characterizations and structures of these compounds,⁵⁻¹⁷ which are of great importance for illuminating the bonding characterization of lanthanide series and enriching the application of these compounds. Common to the preparation of the class of the complexes is observed that the experiments must be performed using anhydrous salts in dry inert gas just because of difficulty of preparation and stability of the complexes towards moisture.¹³ There was a report on the preparation of the ternary complexes involving the variable-valence transitional elements, that 2,2'-bipyridyl or 1,10-phenanthroline with π donor and dithiocarbamates were selected as ligands, which overcame the drawbacks of the preparation on the dual-ity complexes.¹⁸ In Ref. 18, the complexes of rare earth

metal with the mixed ligands of NaEt_2dtc and phen were characterized. $\text{Eu}(\text{Et}_2\text{dtc})_3(\text{phen})$ was structurally determined.¹⁹ The complexes of rare earth metal with the ligands of NaEt_2dtc and bipy were reported and the crystal structure of $\text{Er}(\text{Et}_2\text{dtc})_3(\text{bipy})$ was described.^{20,21} However, little investigation has been extended on these complexes.

Calorimetry is recognized as an experimentally simple method for the determination of both the thermodynamic and kinetic parameters associated with chemical reaction systems. The developed procedures for maximal utility enable direct calculation of the required parameters (n , k , ΔH , ΔS , ΔG and E), which would greatly improve the interpretation of the reaction system.

In this paper, we describe the synthesis of ternary complex of $\text{Nd}[(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$, which can be prepared and investigated using hydrated lanthanide salts at air atmosphere without any cautions against moisture. The title complex was characterized by XRD, IR and TD-DTG. Moreover, Thermodynamics on the reaction of formation of $\text{Nd}[(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$ was reported.

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Experimental

Reagents

Neodymium chloride hydrate, $\text{NdCl}_3 \cdot 3.74\text{H}_2\text{O}$ was prepared. Ammonium pyrrolidinyldithiocarbonylate (APDC), 1,10-phenanthroline ($\text{phen} \cdot \text{H}_2\text{O}$), absolute ethanol and dichloromethane are of A.R. grade from Xi'an chemical reagent company.

Analysis method and equipment

Nd^{3+} was determined with EDTA by complexometric titration. C, H, N and S analyses were carried out by an instrument of Vario EL III CHNOS of German. TG-DTG analyses for the title compound were conducted on a P. E 2100 company thermal analyzer in a $60 \text{ mL} \cdot \text{min}^{-1}$ N_2 atmosphere (99.99%), at the heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The weight of the sample was about 1 mg. IR analysis was conducted on a BEQ, UZNDX-550 spectrometer (KBr discs). An X-ray powder diffractometer typed in D/max-III with $\text{Cu K}\alpha$ radiation was used. ICP-AES experiment was carried out on a T. E. IRIS advantage inductively coupled plasma atomic emission spectrophotometer.

Experimental conditions of calorimetric method

The calorimetric experiment was performed using an RD496-III type microcalorimeter.²² The calorimetric constants at 292.15, 295.15, 298.15 and 301.15 K were determined by the Joule effect before experiment, which are (63.691 ± 0.035) , (63.799 ± 0.042) , (63.901 ± 0.030) and $(64.000 \pm 0.026) \mu\text{V} \cdot \text{mW}^{-1}$. The enthalpy of solution in deionized water of KCl (spectral purity) was measured to be $(17.238 \pm 0.048) \text{ kJ} \cdot \text{mol}^{-1}$, which is in good agreement with the value of $(17.241 \pm 0.018) \text{ kJ} \cdot \text{mol}^{-1}$ in Ref. 23. The accuracy is 0.02% and the precision is 0.3%, indicating that the calorimetric system is accurate and reliable. The reaction solution/solvent and the diluents were put into the stainless steel sample cell with the container of 15 mL^{24} (Figure 1), respectively. After equilibrium, the containers of sample and reference were pushed down simultaneously. As a result, the two liquids were mixed and the power-time curve was recorded.

Synthesis of the complex

$\text{NdCl}_3 \cdot 3.74\text{H}_2\text{O}$, $\text{phen} \cdot \text{H}_2\text{O}$ and APDC were dissolved in a minimal amount of anhydrous ethanol, re-

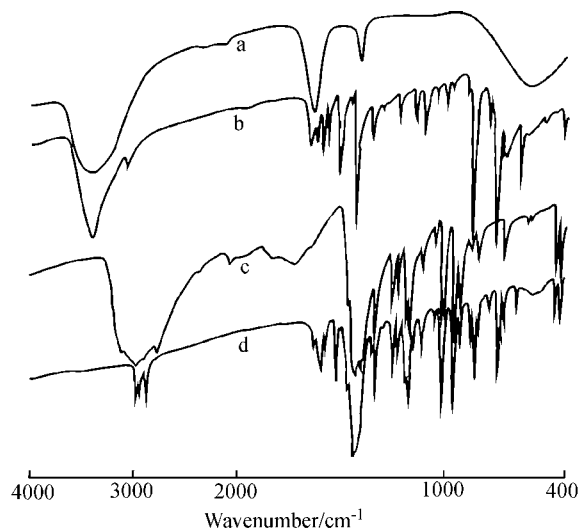


Figure 1 The IR spectra of salt (a), $\text{phen} \cdot \text{H}_2\text{O}$ (b), APDC (c) and the title complex (d).

spectively, and the alcoholic salt solution was poured into a three-necked round bottle. To the alcoholic salt solution, the ligands of phen and APDC mixed in molar ratio of 1 : 3 was dropwise added when keeping electromagnetic stirring. After the addition, the mixture was allowed to stand overnight and the precipitate was collected by suction filter, then the crude product was purified with dichloromethane. The fine crystal was obtained and followed by a small amount of absolute ethanol washing three times and kept in vacuum over P_4O_{10} to dryness, which was ready for being used.

Result and discussion

Composition and XRD analysis of the complex

The elemental analysis results of the title complex are as follows: $w\%$ (Calcd): Nd 18.33, C 42.79, H 4.26, N 9.24, S 25.39; $w\%$ (Found): Nd 18.10, C 42.60, H 4.20, N 9.17, S 25.30, which was identified as the formula of $\text{Nd}[(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$. The main XRD data of ligands and the complex are shown in Table 1. Clearly, the main XRD data of the complex are very different from those of hydrous neodymium chloride (L.C.D.D.card) and ligands, indicating that the complex is of a new phase.

Table 1 Main XRD data of the title complex and ligands

Compound	Main X-ray powder diffraction data								
APDC	I/I_0	40	100	12	26	62	10	20	13
	d/nm	0.1099	0.5507	0.4736	0.4107	0.3675	0.2877	0.2641	0.2206
$\text{phen} \cdot \text{H}_2\text{O}$	I/I_0	46	26	54	99	72	34	25	33
	d/nm	0.8909	0.6189	0.5169	0.4454	0.3959	0.3847	0.3149	0.2817
complex	I/I_0	100	71	66	54	85	69	71	42
	d/nm	0.9036	0.8170	0.7894	0.7202	0.4682	0.4467	0.3911	0.3351

IR spectrum of the complex

Comparison of IR spectra of salts, ligands and the complex is depicted in Figure 1. Compared with the spectra of salt and the ligands, the characteristic absorption of hydroxyl group is absent in the complex, showing that the complex does not consist of water. As for those in the ligand of phen, the peaks of 1624, 1589, 1578 and 1515 cm^{-1} are assigned as the skeleton vibration of benzene ring and the bands of 844 and 728 cm^{-1} are assigned to the bending vibration of C—H in the complex, which displays certain shifts in contrast with those of (1617, 1587, 1561, 1504 cm^{-1}) and (854, 739 cm^{-1}) in the ligand. It is thus assumed that two nitrogen atoms in the ligand of phen are coordinated to Nd^{3+} . Corresponding to the peak of 938 cm^{-1} ascribable to the characteristic absorption of —CSS in the ligand of APDC, it is split into two peaks of 1007 and 947 cm^{-1} in the complex, indicating that —CSS group in the ligand of APDC is bonded with Nd^{3+} .^{9,25} Consulting Ref. 19, the structure of the title complex is presumed as that in Figure 2.

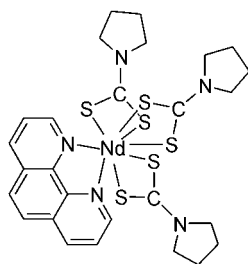


Figure 2 Presumed structure of the title complex.

Thermostability of the title complex

TG-DTG curve of the complex is presented in Figure 3. The complex is decomposed into the finals in one step, which begins at 250 °C and completes at 454 °C, with the mass loss of 71.34%. In order to explore the decomposition process of the title complex, the finals determined by XPS are compounds of Nd_2S_3 and deposited carbon where Nd_2S_3 predominates in the final products, which coincides with the result in Ref. 26. Based on the above analyses, the decomposition process is postulated as follows (288 °C is the peak value in

DTG curve and 71.65% is the calculated value of mass loss). Clearly, the experimental result is in good agreement with the calculated one.

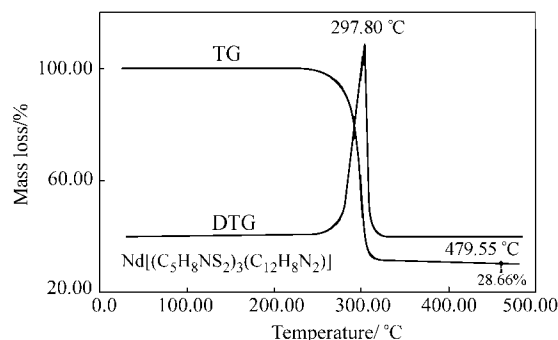
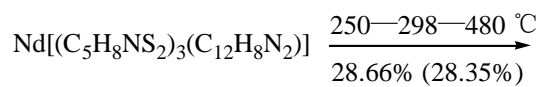


Figure 3 TG-DTG curve of the title complex ($\beta=10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$).

Calculation of the enthalpy change of formation of the title solid-phase reaction

The molar enthalpies of solution $\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{1})$, $\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{2})$ and $\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{3})$ of $\text{NdCl}_3\cdot 3.74\text{H}_2\text{O}$, ADTC and phen $\cdot\text{H}_2\text{O}$ in absolute alcohol at 298.15 K are given in Table 2, respectively. They can be considered as alcoholic compound. The mixture enthalpy of the alcoholic solutions of two ligands $\Delta_{\text{mix}}H_{\text{m}}^\ominus$ and the enthalpy changes of the liquid-phase reaction $\Delta_{\text{r}}H_{\text{m}}^\ominus(\mathbf{l})$ at 298.15 K are listed in Table 3.

Therefore, the enthalpy change of the title solid-phase reaction at 298.15 K can be calculated following a thermochemistry cycle (Scheme 1).

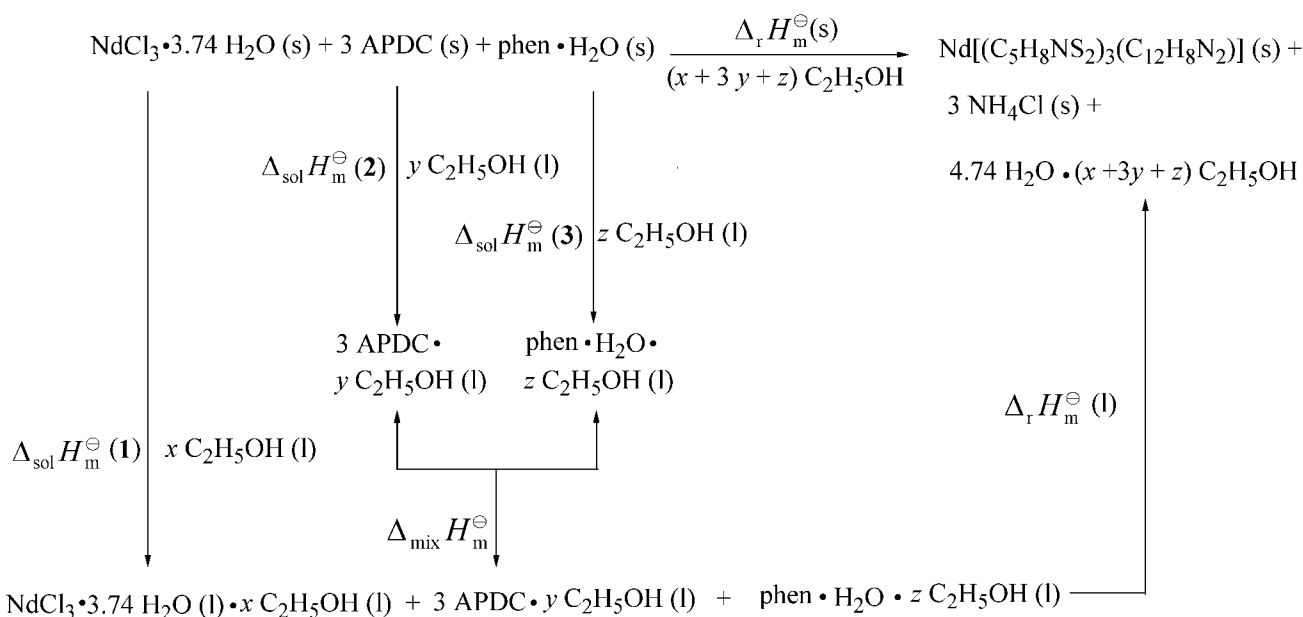
Certain work has been done to prove the reasonability of the thermochemistry cycle. The crude products from liquid-phase reaction were collected and separated by centrifugal effect. The solid crude product was purified and identified as the general formula of $\text{Nd}[(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$ by chemical and elemental analyses. The concentration of Nd^{3+} left in the centrifugal liquid

Table 2 The experimental data of $\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{1})$, $\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{2})$ and $\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{3})$ at 298.15 K

No	<i>m</i> /mg	<i>Q</i> /mJ	$\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{1}) /$ (kJ·mol ⁻¹)	<i>m</i> /mg	<i>Q</i> /mJ	$\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{2}) /$ (kJ·mol ⁻¹)	<i>m</i> /mg	<i>Q</i> /mJ	$\Delta_{\text{sol}}H_{\text{m}}^\ominus(\mathbf{3}) /$ (kJ·mol ⁻¹)
1	86.14	-7589.956	-28.346	26.29	3099.238	19.368	31.71	3351.540	20.950
2	85.12	-7452.084	-27.838	26.25	3121.801	19.539	31.77	3393.602	21.173
3	85.10	-7592.446	-28.369	26.27	3171.104	19.832	31.76	3343.271	20.866
4	85.15	-7503.716	-28.021	26.24	3082.010	19.297	31.73	3356.008	20.965
5	85.13	-7524.978	-28.107	26.33	3157.941	19.705	31.68	3315.208	20.746
6	85.09	-7515.560	-28.085	26.28	3117.297	19.488	31.73	3379.615	21.123
mean			-28.128±0.090			19.538±0.090			20.970±0.071

Table 3 The experimental data of $\Delta_{\text{mix}}H_{\text{m}}^{\ominus}$ and $\Delta_{\text{r}}H_{\text{m}}^{\ominus}(\text{l})$ at 298.15 K

No	Q_1/mJ	$\Delta_{\text{mix}}H_{\text{m}}^{\ominus}/(\text{kJ}\cdot\text{mol}^{-1})$	Q_2/mJ	$\Delta_{\text{r}}H_{\text{m}}^{\ominus}/(\text{kJ}\cdot\text{mol}^{-1})$
1	84.809	10.601	-183.383	-22.923
2	86.293	10.787	-182.564	-22.820
3	84.231	10.529	-180.956	-22.620
4	86.064	10.508	-185.069	-22.509
5	83.987	10.498	-183.448	-22.931
6	85.006	10.626	-182.781	-22.848
mean	85.065 ± 0.421	10.592 ± 0.049	-183.035 ± 0.600	-22.775 ± 0.077

Scheme 1

was determined as $6 \times 10^{-3} \mu\text{g}\cdot\text{mL}^{-1}$ by the ICP-AES experiment, indicating the starting reactants have been transformed fully to the title product, that is, the liquid-phase reaction proceeds in 100% yield. All of these suggested that the final thermodynamic states of the title solid reaction and those of liquid-phase reaction are the same and the designed thermochemistry cycle is correct. Therefore,

$$\begin{aligned}
 \Delta_{\text{r}}H_{\text{m}}^{\ominus}(\text{s}) &= \Delta_{\text{sol}}H_{\text{m}}^{\ominus}(\mathbf{1}) + 3 \Delta_{\text{sol}}H_{\text{m}}^{\ominus}(\mathbf{2}) + \Delta_{\text{sol}}H_{\text{m}}^{\ominus}(\mathbf{3}) \\
 &\quad + \Delta_{\text{mix}}H_{\text{m}}^{\ominus} + \Delta_{\text{r}}H_{\text{m}}^{\ominus}(\mathbf{l}) \\
 &= [(-28.128 \pm 0.090) + 3(19.538 \pm 0.090) + (20.970 \pm \\
 &\quad 0.071) + (10.592 \pm 0.049) + (-22.775 \pm 0.077)] \\
 &\quad \text{kJ}\cdot\text{mol}^{-1} \\
 &= (39.273 \pm 0.377) \text{kJ}\cdot\text{mol}^{-1} .
 \end{aligned}$$

Calculation of the thermokinetic parameters of liquid-phase reaction

The results of complex synthesis and the thermo-

chemistry cycle indicate that the liquid-phase reaction is an irreversible one. The typical heat flow-time (T/K) curve at 298.15 K is depicted in Figure 4, to which the curves in shape at other different temperatures are similar and the reaction is an exothermic one. The experimental data from the curves are shown in Table 4. The energy change of the reaction system depends on the reaction progression. Based on the thermodynamic equations,²⁷ the thermodynamic parameters and kinetic parameters of the liquid phase reaction are obtained and shown in Table 5.

$$\ln \left(\frac{1}{H_0} \frac{dH_i}{dt} \right) = \ln k + n \ln \left(1 - \frac{H_i}{H_0} \right) \quad (1)$$

$$\ln k = \ln A - \frac{E}{RT} \quad (2)$$

$$\Delta G_{\ddagger}^{\ominus} = RT \ln \frac{RT}{Nhk} \quad (3)$$

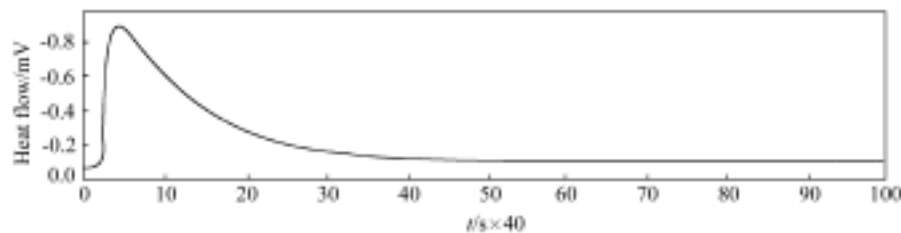


Figure 4 Heat flow-time curve of the liquid-phase reaction at 298.15 K.

Table 4 Thermokinetical data of liquid-phase reaction

295.15 K			295.15 K			298.15 K			301.15 K		
<i>t/s</i>	H_t/H_0	$dH_t/dt/$ ($10^{-4} \text{ J}\cdot\text{s}^{-1}$)	<i>t/s</i>	H_t/H_0	$dH_t/dt/$ ($10^{-4} \text{ J}\cdot\text{s}^{-1}$)	<i>t/s</i>	H_t/H_0	$dH_t/dt/$ ($10^{-4} \text{ J}\cdot\text{s}^{-1}$)	<i>t/s</i>	H_t/H_0	$dH_t/dt/$ ($10^{-4} \text{ J}\cdot\text{s}^{-1}$)
160	0.3531	6.2332	180	0.3600	7.3355	180	0.4643	7.5938	140	0.3245	7.5938
170	0.3783	6.0919	190	0.3809	7.1945	190	0.4933	7.4063	150	0.3541	7.4063
180	0.4028	5.9349	200	0.4059	7.0221	200	0.5216	7.1875	160	0.3830	7.1875
190	0.4271	5.8093	210	0.4280	6.8340	210	0.5489	7.0000	170	0.4112	7.0000
200	0.4502	5.6523	220	0.4497	6.6772	220	0.5754	6.8125	180	0.4386	6.8125
210	0.4729	5.5110	230	0.4708	6.5205	230	0.6010	6.6250	190	0.4653	6.6250
220	0.4951	5.3854	240	0.4914	6.3794	240	0.6255	6.4219	200	0.4913	6.4219
230	0.5167	5.2284	250	0.5114	6.2227	250	0.6491	6.2188	210	0.5164	6.2188
240	0.5377	5.0871	260	0.5309	6.0659	260	0.6716	6.0625	220	0.5408	6.0625
250	0.5581	4.9615	270	0.5498	5.9092	270	0.6930	5.8750	230	0.5642	5.8750

$H_0=0.2440 \text{ J}$ (292.15 K), 0.2164 J (295.15 K), 0.1834 J (298.15 K) and 0.1154 J (301.15 K).

Table 5 Kinetic and thermokinetic parameters of liquid-phase reaction

<i>T/K</i>	Eq. (1)			Eq. (2)			Eq. (3)	Eq. (4)		
	<i>k/</i> ($10^{-3}/\text{s}^{-1}$)	<i>n</i>	<i>r^a</i>	<i>E/</i> ($\text{kJ}\cdot\text{mol}^{-1}$)	$\ln A/$ s^{-1}	<i>r^a</i>	$\Delta G_{\ddagger}^{\ominus} /$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta H_{\ddagger}^{\ominus} /$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta S_{\ddagger}^{\ominus} /$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	<i>r^a</i>
292.15	3.323	0.6019	0.9995	74.29	24.871	0.9995	85.39	71.83	-46.40	0.9995
295.15	4.459	0.6138					85.52			
298.15	6.063	0.6234					85.66			
301.15	8.283	0.5872					85.80			

^aLinear correlation coefficient.

$$\ln \frac{k}{T} = -\frac{\Delta H_{\ddagger}^{\ominus}}{RT} + \frac{\Delta S_{\ddagger}^{\ominus}}{R} + \ln \frac{k_B}{h} \quad (4)$$

where H_0 is the total heat of reaction (corresponding to the area under the heat flow-time curve), H_t the reaction heat at some time t (corresponding to the area under the curve at time t), dH_t/dt the rate of heat production at time t , k rate constant, n reaction order, A pre-exponent, E apparent activation energy, R gas constant, T absolute temperature, N Avogadro constant, h Planck constant, $\Delta G_{\ddagger}^{\ominus}$ activation Gibbs energy, $\Delta H_{\ddagger}^{\ominus}$ activation enthalpy, $\Delta S_{\ddagger}^{\ominus}$ activation entropy, k_B Boltzmann constant.

Conclusions

1. The title ternary complex $\text{Nd}[(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$ has been synthesized in absolute ethanol by $\text{NdCl}_3\cdot 3.74\text{H}_2\text{O}$ reacting with the mixed ligands of APDC and phen at air atmosphere without any cautions against moisture.

2. TG-DTG investigation indicates that the title complex is decomposed into Nd_2S_3 and deposited carbon in one step, which provides a probe for the preparation of nanocrystalline of rare earth sulfide.

3. The enthalpy change of formation of the reaction on the title complex in liquid-phase has been determined by a microcalorimeter. Thermodynamic parameters and

kinetic parameters of the title reaction have been calculated, and the enthalpy change of the solid-phase reaction has been obtained by the thermochemistry cycle.

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