

Thermochemistry of the Ternary Complex $\text{Nd}(\text{Et}_2\text{dtc})_3(\text{phen})$

FAN, Xue-Zhong^{a,b}(樊学忠) CHEN, San-Ping^a(陈三平) GAO, Sheng-Li^{*a}(高胜利)
 JIAO, Bao-Juan^a(焦宝娟) HU, Rong-Zu^{a,b}(胡荣祖) SHI, Qi-Zhen^a(史启祯)

^a Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069, China

^b Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, China

The ternary solid complex has been synthesized with sodium diethyldithiocarbamate ($\text{NaEt}_2\text{dtc}\cdot 3\text{H}_2\text{O}$), 1,10-phenanthroline ($o\text{-phen}\cdot\text{H}_2\text{O}$) and hydrated neodymium chloride in absolute ethanol. The title complex was identified as the general formula of $\text{Nd}(\text{Et}_2\text{dtc})_3(\text{phen})$ by chemical and elemental analyses. IR spectrum of the complex showed that the Nd^{3+} coordinated with six sulfur atoms of three NaEt_2dtc and two nitrogen atoms of $o\text{-phen}$. It was assumed that the coordination number of Nd^{3+} is eight. The enthalpy change of liquid-phase reaction of formation, $\Delta_f H_m^\ominus$ (l), was determined as $(-12.274 \pm 0.050) \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K by a microcalorimeter, the enthalpy change of the solid-phase reaction of formation, $\Delta_f H_m^\ominus$ (s), was calculated as $(149.069 \pm 0.314) \text{ kJ}\cdot\text{mol}^{-1}$ on the basis of a thermochemical cycle. The thermodynamics of reaction of formation was studied by changing the temperature of liquid-phase reaction. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as $(-18674.22 \pm 8.33) \text{ kJ}\cdot\text{mol}^{-1}$ by a precise rotating-bomb calorimeter at 298.15 K. Its standard enthalpy of combustion, $\Delta_c H_m^\ominus$, and standard enthalpy of formation, $\Delta_f H_m^\ominus$, were calculated as $(-18693.43 \pm 8.33) \text{ kJ}\cdot\text{mol}^{-1}$ and $(-47.03 \pm 9.17) \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

Keywords $\text{Nd}(\text{Et}_2\text{dtc})_3(\text{phen})$, microcalorimeter, thermodynamic, constant-volume combustion energy, standard molar enthalpy of formation

Introduction

A series of lanthanide sulfide complexes have been largely used for ceramics and thin film materials¹ and these complexes could be prepared from the precursors which are the compounds containing lanthanide-sulfur bonds.²⁻⁴ For instance, the compounds synthesized with $[(\text{alkyl})_2\text{dtc}]^-$, $\text{phen}\cdot\text{H}_2\text{O}$ and lanthanide salts were used as the volatile precursors for preparing lanthanide sulfide, its friction properties in lubricant was investigated in literature⁵ and the preparation and properties of these compounds were also reported in literature.⁶ In addition, the crystal structure and spectroscopy properties of $\text{Eu}(\text{Et}_2\text{dtc})_3(\text{phen})$ were reported.⁷ To the best of our knowledge, little investigation was made concerning the thermochemistry of these complexes previously.

Calorimetry is recognized as an experimentally simple method for the determination of both thermodynamic and kinetic parameters associated with chemical reaction systems. The developed procedures for maximum 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, the ternary solid complex $\text{Nd}(\text{Et}_2\text{dtc})_3(\text{phen})$ was synthesized from the direct reaction of neodymium chloride hydrate with sodium diethyldithiocarbamate (NaEt_2dtc) and 1,10-phenanthroline ($o\text{-phen}$) in absolute ethanol. The composition of the complex was determined by chemical and elemental analyses, the bonding characterization of which was studied by IR. The enthalpy change of the liquid-phase reaction $\Delta_f H_m^\ominus$ (l) at 298.15 K was measured by a microcalorimeter and that of solid-phase $\Delta_f H_m^\ominus$ (s) was calculated according to a thermochemical cycle. The thermokinetics of the liquid-phase reaction at different temperatures were also investigated. Fundamental parameters for the title reaction, the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H_\ddagger^\ominus$), the activation entropy ($\Delta S_\ddagger^\ominus$) and the activation free energy ($\Delta G_\ddagger^\ominus$), were obtained on the basis of reaction thermodynamic and kinetic equations. The constant-volume combustion energy $\Delta_c U$ of the complex was measured by a precise rotating-bomb calorimeter at 298.15 K. Its standard enthalpy of combustion, $\Delta_c H_m^\ominus$, and standard enthalpy of formation, $\Delta_f H_m^\ominus$, were calculated. Clearly, the present work will assist in going deep into the formation reaction of the complexes containing "RE—S" bonds, and the re-

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* E-mail: gaoshli@nwu.edu.cn

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lated thermochemistry study would provide thermodynamic basis for the syntheses and applications of these complexes.

Experimental

Reagents

Neodymium chloride hydrate, $\text{NdCl}_3 \cdot 3.74\text{H}_2\text{O}$ was prepared according to Ref. 8; sodium diethyldithiocarbamate ($\text{NaEt}_2\text{dtc} \cdot 3\text{H}_2\text{O}$) was of A.R. grade from Shanghai reagent company; 1,10-phenanthroline (*o*-phen $\cdot\text{H}_2\text{O}$), absolute ethanol and CHCl_3 were of A.R. grade from Xi'an chemical reagent company.

Equipment

The IR analysis was conducted on a BEQ, UZNDX-550 FTIR instrument (KBr discs). The calorimetric experiment was performed using an RD496-III type microcalorimeter.⁹ The constant-volume combustion energy of the compound was determined by a precise rotating-bomb calorimeter (RBC-type II)¹⁰. ICP-AES experiment was carried out on a T.E. IRIS advantage inductively coupled plasma atomic emission spectrophotometer.

Analysis method

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.

Experimental conditions of calorimetric method

All the enthalpies of solutions and that of reaction were measured in an RD496-III micro-calorimeter. The detailed description about the structure and the technical parameters of this calorimeter has been given.⁹ The sensibility of the calorimeter was measured through electrical calibration at 292.15, 295.15, 298.15 and 301.15, K, respectively. The Joule cell, which has 1000 Ω electrical resistance was given 100 mW electric power for 100 s at 298.15 K. The corresponding calorimetric constants are (63.691 ± 0.035) , (63.799 ± 0.042) , (63.901 ± 0.030) and (64.000 ± 0.026) $\mu\text{V} \cdot \text{mW}^{-1}$. The accuracy and precision were determined through chemical calibration at 298.15 K. The enthalpy of solution in deionized water of KCl (spectral purity) was measured as (17.581 ± 0.039) $\text{kJ} \cdot \text{mol}^{-1}$, and comparison with the literature value (17.584 ± 0.0066) $\text{kJ} \cdot \text{mol}^{-1}$ ¹¹ shows that the accuracy is 0.02% and the precision is 0.2%, indicating that the calorimetric system is accurate and reliable.

The constant-volume combustion energy of the compound was determined by a precise rotating-bomb calorimeter (RBC-type II).¹⁰ The main experimental procedures were described previously.¹⁰ The initial temperature was regulated to (25.0000 ± 0.0005) $^\circ\text{C}$, and the initial oxygen pressure was 2.5 MPa. The correct value of the heat exchange was calculated according to Linio-Pyfungdelel-Wsava formula.¹¹ The calorimeter was calibrated with benzoic acid of 99.999% purity. Its

isothermal heat of combustion at 25 $^\circ\text{C}$ was (-26434 ± 3) J/g. The energy equivalent of calorimeter was calibrated as (17775.09 ± 7.43) $\text{J} \cdot \text{K}^{-1}$. The analytical methods of final products (gas, liquid and solid) were the same as those in Ref. 10. The analytical results of the final products showed that the combustion reactions were complete.

Synthesis of the complex

$\text{NdCl}_3 \cdot 3.74\text{H}_2\text{O}$, NaEt_2dtc and *o*-phen $\cdot\text{H}_2\text{O}$ were dissolved in a minimal amount of anhydrous ethanol with the molar ratio of 1 : 3 : 1, respectively. Then alcoholic solutions of phen and NaEt_2dtc were mixed together and the alcoholic salt solution was dropwise added into the resulting mixture when keeping electromagnetic stirring. After the addition, the mixture was allowed to stand for 30 min and the crude product was washed three times with a small amount of absolute ethanol, then purified by recrystallization with CHCl_3 . The fine crystal was obtained and kept in vacuum over P_4O_{10} to dryness for being used.

Result and discussion

Composition of the complex

The elemental analysis result of the title complex is as follows: *w* (Calcd): Nd 18.75%, C 42.16%, H 4.98%, N 9.10%, S 25.01%; *w* (Found): Nd 18.59%, C 42.08%, H 4.69%, N 9.01%, S 24.87%, which is identified as the formula of $\text{Nd}(\text{Et}_2\text{dtc})_3(\text{phen})$.

IR spectrum of the complex

Referred to the literatures 12 and 13, IR spectra of salts, ligands and the complex depicted in Figure 1 were assigned as follows: Compared with the spectra of salt (a), $\text{NaEt}_2\text{dtc} \cdot 3\text{H}_2\text{O}$ (b) and phen $\cdot\text{H}_2\text{O}$ (c) (3390, 3366, 3388 cm^{-1} , respectively), the characteristic absorption

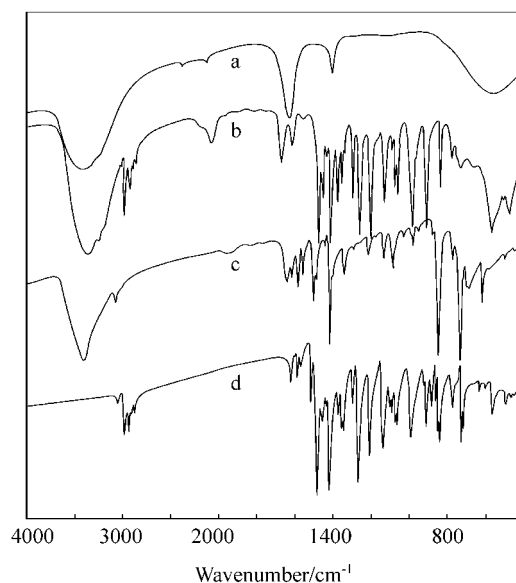
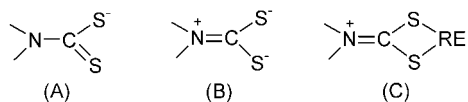


Figure 1 Comparison of IR spectra of $\text{NdCl}_3 \cdot 3.74\text{H}_2\text{O}$ (a), $\text{NaEt}_2\text{dtc} \cdot 3\text{H}_2\text{O}$ (b), phen $\cdot\text{H}_2\text{O}$ (c) and complex (d).

of hydroxyl group is not present in the complex, showing that the complex does not consist of water. As those in the ligand of phen, the peaks of 1624, 1589, 1572, and 1516 cm^{-1} are assigned as skeleton vibration of benzene ring and the bands of 851 and 730 cm^{-1} are assigned to the bend vibration of C—H in the complex, which display 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 has been coordinated to Nd^{3+} . As for the ligand $\text{NaEt}_2\text{dtc}\cdot 3\text{H}_2\text{O}$ (b), the ν_{CN} assumes a double-bond character which is reflected in the appearance of a stretching bond shifted to higher frequency. For the complex the bond frequency is higher (1482—1516 cm^{-1}) than that of the respective ligand (1477 cm^{-1}). It can be attributed to that NCS_2^- group has two main shapes of vibration (A) and (B):¹⁴



The (B) enhanced its vibration intensity when the two sulfur atoms of ligand were coordinated to Nd^{3+} to form the new cycle (C), thus the wave number of ν_{CN} moved to the higher one. On the other hand, an increase in ν_{CSS} stretching band was observed. In the complex the wave number has a change of 11 cm^{-1} compared with that of ligand. Obviously, this can be due to the new

formed cycle, the formation of which increased the vibration intensity of CN.¹³ The changes of ν_{CN} and ν_{CSS} indicated that the two sulfur atoms of ligand were coordinated to Nd^{3+} in a bidentate manner.

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

The molar enthalpies of solution $\Delta_{\text{sol}}H_m^\ominus$ (1), $\Delta_{\text{sol}}H_m^\ominus$ (2) and $\Delta_{\text{sol}}H_m^\ominus$ (3) of $\text{NdCl}_3\cdot 3.74\text{H}_2\text{O}$, $\text{NaEt}_2\text{dtc}\cdot 3\text{H}_2\text{O}$ and *o*-phen $\cdot\text{H}_2\text{O}$ in absolute alcohol are given in Table 1, respectively (They can be considered as alcoholic solution). The mixture enthalpy of the alcoholic solutions of two ligands $\Delta_{\text{mix}}H_m^\ominus$ and the enthalpy changes of the liquid-phase reaction $\Delta_rH_m^\ominus$ (1) are listed in Table 2. The other data of $\Delta_rH_m^\ominus$ (1) at different temperature were omitted because of the space, but for each experiment all of them were performed six times and the results were the same. Therefore, the enthalpy change of the title solid-phase reaction at 298.15 K can be calculated according to a thermochemistry cycle.

Some amount of 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 products were purified and identified as the general formula of $\text{Nd}(\text{Et}_2\text{dtc})_3(\text{C}_{12}\text{H}_8\text{N}_2)$ by chemical and elemental analyses. The concentration of Nd^{3+} left in the centrifugal liquid was determined as the numerical value of 6×10^{-3} $\mu\text{g}/\text{mL}$ by the ICP-AES experiment, indicating

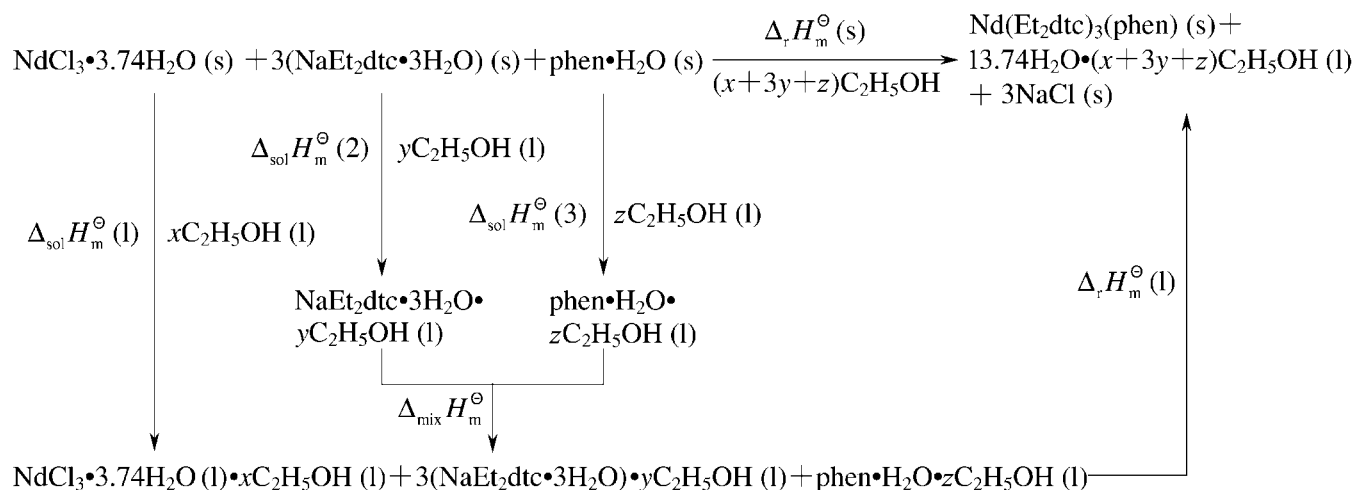


Table 1 The experimental data of $\Delta_{\text{sol}}H_m^\ominus$ (1), $\Delta_{\text{sol}}H_m^\ominus$ (2) and $\Delta_{\text{sol}}H_m^\ominus$ (3) at 298.15 K

No	<i>m</i> /mg	<i>Q</i> /mJ	$\Delta_{\text{sol}}H_m^\ominus$ (1)/(kJ $\cdot\text{mol}^{-1}$)	<i>m</i> /mg	<i>Q</i> /mJ	$\Delta_{\text{sol}}H_m^\ominus$ (2)/(kJ $\cdot\text{mol}^{-1}$)	<i>m</i> /mg	<i>Q</i> /mJ	$\Delta_{\text{sol}}H_m^\ominus$ (3)/(kJ $\cdot\text{mol}^{-1}$)
1	76.36	-4366.715	-18.184	36.07	7935.321	49.566	31.71	3351.540	20.950
2	76.36	-4214.647	-17.550	36.02	7916.679	49.518	31.77	3393.602	21.173
3	76.36	-4290.479	-17.866	36.09	8010.432	50.007	31.76	3343.271	20.866
4	76.35	-4330.569	-18.035	36.02	7911.509	49.485	31.73	3356.008	20.965
5	76.35	-4298.969	-17.904	36.05	7968.605	49.801	31.68	3315.208	20.746
6	76.36	-4275.816	-17.805	36.04	7972.883	49.842	31.73	3379.615	21.123
mean			-17.890 ± 0.096			49.703 ± 0.094			20.970 ± 0.071

Table 2 The experimental data of $\Delta_{\text{mix}}H_{\text{m}}^{\ominus}$ and $\Delta_{\text{r}}H_{\text{m}}^{\ominus}$ (1) 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	73.360	9.170	-98.895	-12.362
2	74.266	9.283	-99.370	-12.421
3	72.746	9.093	-96.949	-12.119
4	73.096	9.137	-97.820	-12.228
5	74.097	9.262	-97.568	-12.196
6	71.842	8.980	-98.524	-12.316
mean	72.234 ± 0.401	9.154 ± 0.050	-98.188 ± 0.403	-12.274 ± 0.050

that the starting reactants had been transformed fully to the title products, that is, the liquid-phase reaction proceeded in yield of 100%. All of these suggested that the final thermodynamic states of solid reaction and those of liquid-phase reaction were the same and the designed thermochemistry cycle was correct. Therefore,

$$\Delta_{\text{r}}H_{\text{m}}^{\ominus}(\text{s}) = \Delta_{\text{sol}}H_{\text{m}}^{\ominus}(1) + 3\Delta_{\text{sol}}H_{\text{m}}^{\ominus}(2) + \Delta_{\text{sol}}H_{\text{m}}^{\ominus}(3) + \Delta_{\text{mix}}H_{\text{m}}^{\ominus} + \Delta_{\text{r}}H_{\text{m}}^{\ominus}(1) = [(-17.890 \pm 0.096) + 3 \times (49.703 \pm 0.094) + (20.970 \pm 0.071) + (9.154 \pm 0.050) + (-12.274 \pm 0.050)] \text{ kJ}\cdot\text{mol}^{-1} = (149.069 \pm 0.314) \text{ kJ}\cdot\text{mol}^{-1}.$$

Calculation of the thermodynamic parameters of liquid-phase reaction

The liquid-phase reaction has been proved to be an irreversible one. According to the experiment, the reaction is an exothermic one. The experimental data are shown in Table 3. The energy change of the reaction system depends on the reaction progression. Based on the thermodynamic equations,¹⁵ the thermodynamic parameters and kinetic parameters of the liquid-phase reaction are obtained and shown in Table 4.

Combustion energy of Nd(Et₂dtc)₃(phen)

The determination method of combustion energy for the complex was the same as the calibration of the calorimeter with benzoic acid. The combustion energies of the samples were calculated by the formula

$$\Delta_{\text{c}}U(\text{complex, s}) = \frac{W\Delta T - aG - 5.983b}{m} \quad (1)$$

where $\Delta_{\text{c}}U$ (complex, s) denotes the constant-volume combustion energy of the samples, W the energy equivalent of the RBC-type II calorimeter (in J/K), ΔT the correct value of the temperature rising, a the length of actual Ni-Cr wire consumed (in cm), G the combustion enthalpy of Ni-Cr wire for ignition (0.9 J/cm), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 mL of 0.1000 mol/L solution of

Table 3 Thermokinetic data of liquid-phase of formation reaction

292.15 K			295.15 K			298.15 K			301.15 K		
<i>t/s</i>	H_t/H_0	dH_t/dt (10 ⁴ J/s)	<i>t/s</i>	H_t/H_0	dH_t/dt (10 ⁴ J/s)	<i>t/s</i>	H_t/H_0	dH_t/dt (10 ⁴ J/s)	<i>t/s</i>	H_t/H_0	dH_t/dt (10 ⁴ J/s)
160	0.4110	4.7573	130	0.3812	5.0628	100	0.4331	4.8200	110	0.3672	5.0469
170	0.4410	4.6003	140	0.4182	4.9060	110	0.4771	4.6009	120	0.4070	4.8438
180	0.4702	4.4433	150	0.4540	4.7493	120	0.5188	4.3505	130	0.4456	4.6563
190	0.4985	4.3020	160	0.4886	4.5925	130	0.5583	4.1470	140	0.4827	4.4688
200	0.5285	4.1607	170	0.5220	4.4045	140	0.5956	3.9436	150	0.5183	4.2969
210	0.5522	4.0194	180	0.5541	4.2320	150	0.6308	3.7245	160	0.5523	4.0938
220	0.5776	3.8624	190	0.5847	4.0596	160	0.6641	3.5211	170	0.5839	3.9063
230	0.6020	3.7368	200	0.6141	3.8715	170	0.6956	3.3176	180	0.6157	3.7344
240	0.6256	3.5955	210	0.6421	3.6991	180	0.7252	3.1142	190	0.6450	3.5625
250	0.6482	3.4524	220	0.6688	3.5110	190	0.7529	2.9421	200	0.6729	3.3906
260	0.6699	3.3286	230	0.6940	3.3229	200	0.7789	2.7230	210	0.6992	3.2500

$H_0 = 0.1702$ J (292.15 K), 0.1342 J (295.15 K), 0.0989 J (298.15 K) and 0.0709 J (301.15 K).

Table 4 Kinetic, thermodynamic parameters of liquid-phase reaction

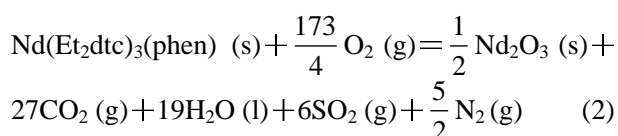
<i>T/K</i>	$k \times 10^3/\text{s}^{-1}$	<i>n</i>	r^a	$E/(\text{kJ}\cdot\text{mol}^{-1})$	$\ln A$	r^a	$\Delta G_{\neq}^{\ominus}/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H_{\neq}^{\ominus}/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S_{\neq}^{\ominus}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	r^a
292.15	3.869	0.6161	0.9999				84.99			
295.15	5.077	0.5971	0.9978				85.22			
298.15	6.859	0.6017	0.9998	71.68	23.94	0.9986	85.37	69.21	-54.12	0.9985
301.15	9.326	0.5958	0.9997				85.48			

^aLinear correlation coefficient.

NaOH (in J/mL), b the volume in mL of consumed 0.1000 mol/L solution of NaOH and m the mass (in g) of the sample. The results of the calculations were given in Table 5. $\Delta_c U$ is $(-18674.22 \pm 8.33) \text{ kJ}\cdot\text{mol}^{-1}$.

Standard combustion enthalpy of Nd(Et₂dtc)₃(phen)

The standard combustion enthalpy of the complex, $\Delta_f H_m^\ominus$ (complex, s, 298.15 K), referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.



The standard combustion enthalpy of the complex was calculated by the following equations:

$$\Delta_c H_m^\ominus (\text{complex, s, 298.15 K}) = \Delta_c U (\text{complex, s, 298.15 K}) + \Delta nRT \quad (3)$$

$$\Delta n = n_g (\text{products}) - n_g (\text{reactants}) \quad (4)$$

where n_g is the total amount in mole of gases present as

products or as reactants, $R=8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $T=298.15 \text{ K}$. The results of the calculations were $(-18693.43 \pm 8.33) \text{ kJ}\cdot\text{mol}^{-1}$.

Standard enthalpy of formation of Nd(Et₂dtc)₃(phen)

The standard enthalpy of formation of the complex, $\Delta_f H_m^\ominus$ (complex, s, 298.15 K), was calculated by Hess's law according to the above thermochemical equation (2).

$$\Delta_f H_m^\ominus [\text{Nd}(\text{Et}_2\text{dtc})_3(\text{phen}), \text{s}] = \left[\frac{1}{2} \Delta_f H_m^\ominus (\text{Nd}_2\text{O}_3, \text{s}) + 27 \Delta_f H_m^\ominus (\text{CO}_2, \text{g}) + 19 \Delta_f H_m^\ominus (\text{H}_2\text{O}, \text{l}) + 6 \Delta_f H_m^\ominus (\text{SO}_2, \text{g}) + \frac{5}{2} \Delta_f H_m^\ominus (\text{N}_2, \text{g}) \right] - \Delta_c H_m^\ominus [\text{Nd}(\text{Et}_2\text{dtc})_3(\text{phen}), \text{s}] \quad (5)$$

When $\Delta_f H_m^\ominus (\text{Nd}_2\text{O}_3, \text{s}) = (-1808.12 \pm 1.00) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus (\text{CO}_2, \text{g}) = (-393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus (\text{H}_2\text{O}, \text{l}) = (-285.830 \pm 0.042) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus (\text{SO}_2, \text{g}) = (-296.81 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$,¹⁶ the results of the calculations were $(-47.03 \pm 9.17) \text{ kJ}\cdot\text{mol}^{-1}$.

Table 5 Experimental results for the combustion energies of the samples

Sample	No.	Mass of sample (m/g)	Calibrated heat of combustion wire (Q_c/J)	Calibrated heat of acid (Q_N/J)	Calibrated $\Delta T/\text{K}$	Combustion energy of sample ($\Delta_c U/\text{J}\cdot\text{g}^{-1}$)
	1	0.75680	12.60	1476.62	1.1167	24260.34
	2	0.76321	12.60	1489.13	1.1274	24289.39
	3	0.74535	12.60	1454.28	1.0997	24257.58
Nd(Et ₂ dtc) ₃ (phen)	4	0.75237	12.60	1467.98	1.1096	24246.93
	5	0.72358	12.60	1411.81	1.0684	24277.20
	6	0.73770	12.60	1439.36	1.0910	24319.73
	mean					24275.20 ± 10.83

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