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Preparation and Thermochemical Properties of Ternary Complexes of Rare Earth Chlorides with Nicotinic Acid and 8-Hydroxylquinoline

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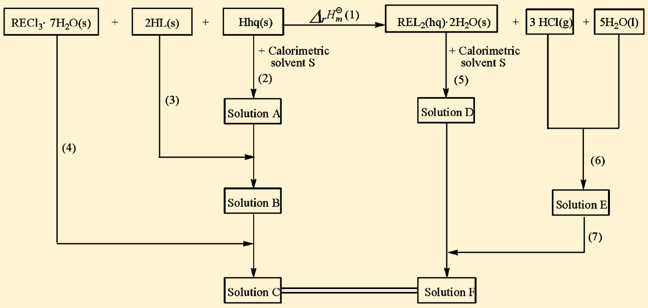
ABSTRACT: Two solid ternary complexes were synthesized by using three raw materials: rare earth chlorides, nicotinic acid ($C_6H_5NO_2$, HL), and 8-hydroxylquinoline (C_9H_7NO, Hhq) in a water bath (333.15 K). During the process of coordination, HL was bidentate-coordinated with rare earth ions (RE^{3+}) through an acidic group which was formed by removing the proton; the hydroxyl oxygen atom and heterocyclic nitrogen atom of hq^- formed a chelate ring with RE^{3+} for coordination. At a constant temperature of 298.15 K, the dissolution enthalpies of the reactants and the products of the designed thermochemical cycle in the calorimetric solvent ($V_{HCl}/V_{DMF}/V_{EtOH} = 3:1:1$) were determined by a solution-reaction isoperibol calorimeter, respectively. At the same time, the rational design of the thermochemical cycle was verified by UV spectra and refractive indexes. Finally, supported by the thermodynamic data from literature, the standard molar enthalpies of formation of the two complexes were estimated to be: $\Delta_f H_m^\ominus$ [$LaL_2 \cdot hq \cdot 2H_2O(s)$, 298.15 K] = $-(2181.1 \pm 2.4)$ kJ·mol^{-1}; $\Delta_f H_m^\ominus$ [$CeL_2 \cdot hq \cdot 2H_2O(s)$, 298.15 K] = $-(2102.7 \pm 2.4)$ kJ·mol^{-1}.



■ INTRODUCTION

Rare earth ions (RE^{3+}) have unique physiological and biochemical characteristics and excellent luminescent properties.[1,2] Furthermore, they have antisepsis, anti-inflammation, and anticancer functions.[3] Hhq, with its good coordination property, is widely used in the separation and analysis of metal ions. Also, because of their strong stiffness and large absorption coefficients, 8-hydroxylquinoline derivatives are extensively applied to the preparation of luminescent organic rare earth complexes.[4] Commonly known as vitamin PP, nicotinic acid is an alkaloid and has obvious effects on dilating vessels, decreasing blood lipids, inhibiting the synthesis of cholesterol, dissolving fibrin, and restraining the formation of thrombus, and so forth.[5] Thermochemical studies on complexes of above-mentioned substances have particular significance and practical value, because the studies showed reaction heat and thermodynamic functions of chemical reactions, revealed the close connection of their chemical structures, and illuminated the close relationship between stability of complexes and atomic numbers.

In recent years, research on the synthesis and characterization of complexes of rare earth chlorides coordinating with amino acids and heterocyclic compounds is quite active. However, using vitamin PP as a ligand to prepare rare earth complexes has been rarely conducted, especially in the situation that the thermodynamics database of rare earth−vitamin complexes is still blank. In this work, two ternary complexes of rare earth chlorides with nicotinic acid and 8-hydroxylquinoline have been synthesized, and their thermodynamic properties have also been investigated by using an advanced microcalorimeter[6] which extremely improved the accuracy of the dissolution enthalpies of samples, with the value of accuracy being 99.5 %. Obviously, this value is indispensable for strict modern experimental technology.

■ EXPERIMENTAL SECTION

Reagents and Instruments. The chemicals used in this work are listed in Table 1.

The instruments used were as follows: a Fourier IR spectrometer (model: Avatar360, Nicolet USA, with a KBr pellet); UV−visible spectrophotometer (model: U-3010, Hitachi, Japan); digital Abbe refractometer (model: WAY-IS, Shanghai Precision & Scientific Instrument Co., Ltd., China); elemental analyzer (model: Perkin-Elmer 2400 CHN, USA). The dissolution enthalpies were measured by an isoperibol calorimeter (model: SRC-100, constructed by the Thermochemical Laboratory of Wuhan University, China),[6] and the precisions of the control temperature and test temperature are ± 0.001 K and ± 0.0001 K, respectively. The calibration of the calorimeter was carried out by measuring the dissolution enthalpies of KCl (calorimetric primary standard) in triple-distilled water and trihydroxymethyl aminomethane (THAM, NBS 742a, USA)

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Table 1. Chemical Samples

chemical name	source	initial mass fraction purity	purification method	final mole fraction purity	analysis method
$CeCl_3{\cdot}7H_2O$	Chengdu Fei Tian Co., Ltd.	0.985	recrystallization	0.995	complexometric titration
$LaCl_3{\cdot}7H_2O$	Chengdu Fei Tian Co., Ltd.	0.985	recrystallization	0.995	complexometric titration
nicotinic acid (HL)	Shanghai Reagent Company	0.960	recrystallization	0.990	neutral titration
8-hydroxylquinoline (Hhq)	Tianjin Guangfu Fine Chemical Research Institute	0.980	recrystallization	0.995	HPLC
dimethylformamide (DMF)	Nanjing Kezheng Chemical Co., Ltd.	0.999			
ethanol (EtOH)	Shanghai Guanghua Technology Co., Ltd.	0.995.			

Table 2. Elemental Analytical Results of the Complexes[a]

complexes	RE/%	C/%	H/%	N/%
$[LaL_2{\cdot}hq]{\cdot}2H_2O(s)$	24.76 (24.66)	44.65 (44.74)	3.14 (3.22)	7.41 (7.46)
$[CeL_2{\cdot}hq]{\cdot}2H_2O(s)$	25.16 (24.82)	44.47 (44.68)	3.22 (3.21)	7.25 (7.44)

[a] The results in parentheses are theoretical values.

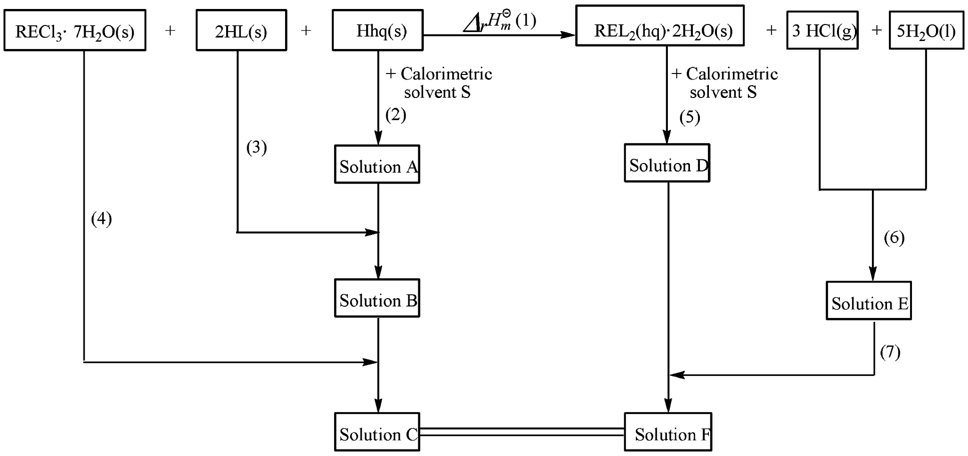

Figure 1. Thermochemical cycle of the coordination reactions.

in 0.0001 mol·cm^{-3} HCl at 298.15 K. The mean dissolution enthalpies were (17597 ± 17) J·mol^{-1} for KCl and −(29776 ± 16) J·mol^{-1} for THAM which agreed with published data [(17536 ± 9) J·mol^{-1} for KCl[6] and −(29766 ± 31.5) J·mol^{-1} for THAM[7]]. The eventual errors were within ± 0.5 %, which suggested the calorimeter was practicable.

Synthesis of Complexes. Quantitative NaOH/ethanol solution was added into HL/ethanol solution under the condition of slight heating. Then the sodium salt solution (formed in the former procedure) and Hhq/ethanol solution were mixed. At a constant temperature of 333.15 K, rare earth chloride/ethanol solution was added dropwise to the mixture. Then, the reaction solution was stirred for 6 h (the value of pH was adjusted to 6.5 to 7.0). After overnight deposition and air pump filtration, a solid complex was acquired. A more detailed description was available in the ref 8. The product was washed alternatively with ethanol and water at the temperature of 353.15 K until it was detected that there was no Cl$^-$ existing in the filtrate. After that, the product was dried at 333.15 K until its mass remained constant. Subsequently, the contents of C, H, and N were determined by elemental analysis individually. The content of RE^{3+} was determined by the ethylenediaminetetraacetic acid titration after the complex was decomposed by heating together with concentrated hydrochloric acid, and the content of crystal water was proved by thermogravimetry/differential thermal analysis (TG-DTA). Elemental analytical results for the complexes are given in Table 2. The results showed that the general molecular formula of the two complexes was $[REL_2{\cdot}hq]{\cdot}2H_2O$ (RE = La, Ce).

Thermochemical Cycle of the Coordination Reactions. As the thermal effect of solid state coordination reaction was difficult to be determined, it was feasible to deduce the enthalpies of formation from the dissolution enthalpies measured when the samples were dissolved. Thermochemical studies were carried out by an isoperibol calorimeter (model: SRC-100, constructed by the Thermochemical Laboratory of Wuhan University, China). In the process, the temperature was 298.15 K, the current was 11.760 mA, and the resistance of heater was 1251.5 Ω. A convincing thermochemical cycle based on Hess's law was designed and shown in Figure 1.

In Figure 1, HL denotes nicotinic acid, Hhq stands for 8-hydroxylquinoline, and RE stands for La or Ce. The equations of the two coordination reactions are as follows:

$$\begin{aligned}&LaCl_3{\cdot}7H_2O(s) + 2HL(s) + Hhq(s)\\&\quad \rightarrow [LaL_2{\cdot}hq]{\cdot}2H_2O(s) + 3HCl(g) + 5H_2O(1) \qquad (1a)\end{aligned}$$

Table 3. Dissolution Enthalpies of 2HL(s), Hhq(s), $LaCl_3 \cdot 7H_2O(s)$, $[LaL_2 \cdot hq] \cdot 2H_2O(s)$, and Solution E in the Calorimetric Solvent S at 298.15 K

	$\Delta_s H_m^\ominus$ ($kJ \cdot mol^{-1}$)				
sample	2HL(s)	Hhq(s)	$LaCl_3 \cdot 7H_2O(s)$	$[LaL_2 \cdot hq] \cdot 2H_2O(s)$	solution E
1	34.409	−3.483	−88.049	−65.575	−10.669
2	34.103	−3.347	−88.370	−65.241	−10.846
3	33.909	−3.380	−87.961	−65.510	−10.660
4	34.324	−3.326	−88.331	−65.408	−10.813
5	34.197	−3.443	−88.235	−65.417	−10.831
avg	34.188 ± 0.195	−3.396 ± 0.066	−88.189 ± 0.178	−65.430 ± 0.126	−10.764 ± 0.091

Table 4. Dissolution Enthalpies of 2HL(s), Hhq(s), $CeCl_3 \cdot 7H_2O(s)$, $[CeL_2 \cdot hq] \cdot 2H_2O(s)$, and Solution E in the Calorimetric Solvent S at 298.15 K

	$\Delta_s H_m^\ominus$ ($kJ \cdot mol^{-1}$)				
sample	2HL(s)	Hhq(s)	$CeCl_3 \cdot 7H_2O(s)$	$[CeL_2 \cdot hq] \cdot 2H_2O(s)$	solution E
1	34.443	−3.345	−31.361	−77.517	−10.856
2	34.133	−3.366	−31.612	−78.035	−10.868
3	33.954	−3.463	−31.526	−77.985	−10.634
4	34.237	−3.413	−31.464	−77.652	−10.909
5	34.326	−3.432	−31.653	−77.778	−10.765
avg	34.219 ± 0.187	−3.404 ± 0.048	−31.523 ± 0.117	−77.794 ± 0.219	−10.806 ± 0.110

Table 5. IR Data of Ligands and Complexes (cm^{-1})

samples	ν_{O-H}	δ_{O-H}	$\nu_{C=O}$	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	$\nu_{N=C+C=N}$	ν_{RE-O}
HL(s)	2200−2700	951	1715	1596	1417		
Hhq(s)	3136	1223				1576	
$[LaL_2 \cdot hq] \cdot 2H_2O(s)$				1599	1403	1570	422
$[CeL_2 \cdot hq] \cdot 2H_2O(s)$				1596	1404	1569	422

$$CeCl_3 \cdot 7H_2O(s) + 2HL(s) + Hhq(s) \rightarrow [CeL_2 \cdot hq] \cdot 2H_2O(s) + 3HCl(g) + 5H_2O(1) \quad (1b)$$

Then we detected the properties of the solutions of the reactant C and the product F. The results revealed that both of them have the similar UV spectrum curves and equal refractive indexes, which demonstrated that they have the same thermodynamics state and the thermochemical cycle of the coordination reactions designed was reliable.

Selection of Solvent. It is very important to choose a solvent which could dissolve all of the reactants and products rapidly and completely. Research indicated that the relevant substances in the coordination reactions are highly soluble in the mixed solvent of 2 $mol \cdot L^{-1}$ HCl, DMF, and EtOH. By mixing those three solvents uniformly at different ratios and testing the solubility of samples continually, the best solubility appeared when the volume ratio of the three solvents was $V_{HCl}/V_{DMF}/V_{EtOH} = 3:1:1$. Consequently, it was chosen as the calorimetric solvent S.

Determination of Dissolution Enthalpies of Reactants and Products. Thoroughly dried samples were ground completely in an agate mortar, then 0.25 mmol of samples were placed exactly into the sample container of the calorimeter. The calorimetric solvent S (100.00 mL) was added into the reaction vessel in advance. When the calorimeter was adjusted to a constant temperature of (298.150 ± 0.001) K, added the samples into the reaction vessel, and then measured their dissolution enthalpies. The results are listed in Tables 3 and 4 after five parallel measurements.

■ RESULTS AND DISCUSSION

IR Spectra of Complexes. Between 4000 to 400 cm^{-1}, the IR spectra of HL, Hhq, and the complexes were determined by a Fourier IR spectrometer with a KBr pellet. The similarity of IR spectra of the two complexes and the obvious differences between complexes and ligands suggested that the bonding structures of the two complexes were similar. Further being compared with the IR spectra of similar complexes (like rare earth/salicylic acid/8-hydroxylquinoline complexes, rare earth/salicylic acid/thioproline complexes, and rare earth/thioproline/8-hydroxylquinoline complexes), the characteristic absorption bands of the two synthetic complexes and ligands are listed in Table 5.

There are five characteristic absorption bands in free HL: the symmetric stretching vibration absorption band (ν_s, 1417 cm^{-1}) of COO^-, the asymmetric stretching vibration absorption band (ν_{as}, 1596 cm^{-1}) of COO^-, and three characteristic absorption bands of carboxylate groups: ν_{O-H} (2200 to 2700 cm^{-1}), $\nu_{C=O}$ (1715 cm^{-1}), and δ_{00p}^{O-H} (951 cm^{-1}). After coordination, three characteristic absorption bands of carboxylate groups vanished, while the symmetric stretching vibration absorption band and asymmetric stretching vibration absorption band of COO^- remained. The fact proved that carboxylic acid which has removed the proton of carboxylic acid and existed in the form of an acidic group was bidentate-coordinated with RE^{3+}.

There are five characteristic bands for free Hhq: ν_{O-H} (3136 cm^{-1}), δ_{O-H} (1223 cm^{-1}, S), and $\nu_{C=N+C=C}$ (1576 cm^{-1}, 1505 cm^{-1}, 1471 cm^{-1}). The ν_{O-H} and δ_{O-H} vanished after the complexes formed, which certified that Hhq was coordinated with RE^{3+} after removing the hydrogen of the hydroxyl group. Besides, the skeleton vibration peak of quinoline ring shifted to a low wavenumber, decreasing by (5 to 7) cm^{-1}, indicating that the hydroxyl oxygen atom and heterocyclic nitrogen atom of hq^- were bidentate-coordinated with RE^{3+} and formed a five-membered chelate ring, which increased the conjugation degree of quinoline ring yet decreased the bond strength of C═N and C═C.

The single IR absorption band at 422 cm^{-1} was assigned to the stretching vibration of the RE-O bond. The characteristic absorption band of ν_{O-H} of H_2O appeared between (3550 and 3000) cm^{-1}. The H−OH bending vibration band presenting at 1622 cm^{-1} further showed the existence of water in the complexes. According to the data from elemental analysis and TG-DTA, there were two water molecules coordinated with RE^{3+} in the complexes.[8]

Calorimetric Determination of Enthalpies of Formation of the Complexes. Evaluation of $\Delta_s H_m^\Theta(6)$. According to reaction 6

$$3HCl(g) + 5H_2O(l) \rightarrow \text{solution E} \qquad (6)$$

The molality of solution E is 33.33 $mol \cdot kg^{-1}$.

According to ref 9,

$$\Delta_d H^\Theta_{(33.33\rightarrow 1.000)} = \Delta_d H^\Theta_{(33.33\rightarrow 0)} - \Delta_d H^\Theta_{m\,(1.000\rightarrow 0)}$$

So that, the evaluation of $\Delta_s H_m^\Theta(6)$ is:

$$\begin{aligned}\Delta_s H_m^\Theta(6) &= \Delta_s H_m^\Theta(m = 33.33\ mol\cdot kg^{-1}) \\ &= \Delta_s H_m^\Theta(m = 1.000\ mol\cdot kg^{-1}) \\ &\quad - \Delta_d H^\Theta_{m\,(33.33\rightarrow 1.000)}\end{aligned}$$

The relevant data in the above equation are given in Table 6. Putting these data into the above equation, then we can obtain the value of $\Delta_s H_m^\Theta(6)$ which is also listed in Table 6.

Table 6. Relevant Data of Evaluation of $\Delta_s H_m^\Theta(6)$ and the Standard Molar Enthalpies of the Coordination Reactions

	enthalpies	
items	$kJ\cdot mol^{-1}$	refs
$\Delta_d H^\Theta_{33.33\rightarrow 0}$	−31.210	9
$\Delta_s H_m^\Theta(HCl(g))$	−74.843	10
$\Delta_d H^\Theta_{m1.000\rightarrow 0}$	−1.695	10
$\Delta_s H_m^\Theta(6)$	−45.328	calculated result
$\Delta_r H_m^\Theta(1a)$	64.13 ± 0.31	calculated result
$\Delta_r H_m^\Theta(1b)$	133.22 ± 0.33	calculated result

Standard Molar Reaction Enthalpies of the Coordination Reactions. According to Hess's law, the standard molar reaction enthalpy of the coordination reaction is as follows:

$$\begin{aligned}\Delta_r H_m^\Theta &= \Delta_s H_m^\Theta(2) + \Delta_s H_m^\Theta(3) + \Delta_s H_m^\Theta(4) \\ &\quad - \Delta_s H_m^\Theta(5) - \Delta_s H_m^\Theta(6) - \Delta_s H_m^\Theta(7) \\ &= \Delta_s H_m^\Theta[Hhq(s)] + \Delta_s H_m^\Theta[2HL(s)] \\ &\quad + \Delta_s H_m^\Theta[RECl_3\cdot 7H_2O(s)] \\ &\quad - \Delta_s H_m^\Theta[REL_2\cdot hq\cdot 2H_2O(s)] - \Delta_s H_m^\Theta(6) \\ &\quad - \Delta_s H_m^\Theta(\text{solution E})\end{aligned}$$

The relevant dissolution enthalpies ($\Delta_s H_m^\Theta$) in the equation above are given in Tables 3, 4, and 6. Putting the corresponding data into the above equation, then we can get the final calculated results $\Delta_r H_m^\Theta(1a)$ and $\Delta_r H_m^\Theta(1b)$ (listed in Table 6).

Standard Molar Enthalpies of Formation of the Complexes. According to Hess's law and the principles of thermodynamics

$$\begin{aligned}\Delta_r H_m^\Theta &= \Delta_f H_m^\Theta[REL_2\cdot hq\cdot 2H_2O(s),\ 298.15\ K] \\ &\quad + 3\Delta_f H_m^\Theta[HCl(g),\ 298.15\ K] \\ &\quad + 5\Delta_f H_m^\Theta[H_2O(l),\ 298.15\ K] \\ &\quad - 2\Delta_f H_m^\Theta[HL(s),\ 298.15\ K] \\ &\quad - \Delta_f H_m^\Theta[Hhq(s),\ 298.15\ K] \\ &\quad - \Delta_f H_m^\Theta[RECl_3\cdot 7H_2O(s),\ 298.15\ K]\end{aligned}$$

So, the standard molar enthalpies of formation of the complexes can be calculated by the following equation:

$$\begin{aligned}&\Delta_f H_m^\Theta[REL_2\cdot hq\cdot 2H_2O(s),\ 298.15\ K] \\ &\quad = \Delta_r H_m^\Theta + 2\Delta_f H_m^\Theta[HL(s),\ 298.15\ K] \\ &\quad + \Delta_f H_m^\Theta[Hhq(s),\ 298.15\ K] \\ &\quad + \Delta_f H_m^\Theta[RECl_3\cdot 7H_2O(s),\ 298.15\ K] \\ &\quad - 3\Delta_f H_m^\Theta[HCl(g),\ 298.15\ K] \\ &\quad - 5\Delta_f H_m^\Theta[H_2O(l),\ 298.15\ K]\end{aligned}$$

The relevant standard molar enthalpies of formation ($\Delta_f H_m^\Theta$) and standard molar enthalpies of the coordination reactions ($\Delta_r H_m^\Theta$) in the equation above are given in Tables 6 and 7.

Therefore, we can get the standard molar enthalpies of formation of the two synthetic complexes $[LaL_2\cdot hq]\cdot 2H_2O(s)$ and $[CeL_2\cdot hq]\cdot 2H_2O(s)$. The results are summarized in Table 7.

Table 7. Standard Molar Enthalpies of the Chemicals in the Coordination Reactions

	enthalpies	
items	$kJ\cdot mol^{-1}$	refs
$\Delta_f H_m^\Theta(HCl(g))$	−92.31 ± 0.10	11
$\Delta_f H_m^\Theta(H_2O(l))$	−285.83 ± 0.04	11
$\Delta_f H_m^\Theta(HL(s))$	−344.81 ± 0.92	12
$\Delta_f H_m^\Theta(Hhq(s))$	−83.0 ± 1.5	13
$\Delta_f H_m^\Theta(LaCl_3\cdot 7H_2O(s))$	−3178.6	14
$\Delta_f H_m^\Theta(CeCl_3\cdot 7H_2O(s))$	−3169.4	14
$\Delta_f H_m^\Theta(LaL_2\cdot hq\cdot 2H_2O(s))$	−2181.1 ± 2.4	calculated result
$\Delta_f H_m^\Theta(CeL_2\cdot hq\cdot 2H_2O(s))$	−2102.7 ± 2.4	calculated result

Experimental Discussion. The ideas, methods, and procedures of the experiment were completely rigorous. Moreover, the calorimetric experiment results were very reliable because the precisions of the control temperature and test temperature were ± 0.001 K and ± 0.0001 K, respectively. In the calculation of standard molar enthalpies of the coordination reactions, the distinction between experimental atmosphere and normal atmosphere was neglected during the determination of $\Delta_r H_m^\Theta$, so was the influence of a very small amount of HCl(g) volatilization. Nevertheless, these errors had little effect on the experiment considering the results of calorimetry.[15]

CONCLUSIONS

Two solid ternary complexes were synthesized by using rare earth chlorides, Hhq, and HL. Their compositions and structures were characterized by elemental analysis, IR spectra, UV spectra, and thermogravimetry−differential thermal analysis (TG-DTA). A reasonable thermochemical cycle based on Hess's law was designed. At a constant temperature of 298.15 K, the dissolution enthalpies were measured when relevant substances were dissolved. The standard molar enthalpies of the coordination reactions were determined based on the experimental data to be $\Delta_r H_m^\ominus(1a) = (64.13 \pm 0.31)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_r H_m^\ominus(1b) = (133.22 \pm 0.33)\ \mathrm{kJ \cdot mol^{-1}}$, and the standard molar enthalpies of formation of the synthetic coordination complexes were calculated to be $\Delta_f H_m^\ominus\ [\mathrm{LaL_2 \cdot hq \cdot 2H_2O(s)}, 298.15\ \mathrm{K}] = -(2181.1 \pm 2.4)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_f H_m^\ominus\ [\mathrm{CeL_2 \cdot hq \cdot 2H_2O(s)}, 298.15\ \mathrm{K}] = -(2102.7 \pm 2.4)\ \mathrm{kJ \cdot mol^{-1}}$.

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REFERENCES

(1) Wang, M.; Xu, Z. D.; Feng, D. Z. Synthesis, Spectroscopic Property and Fluorescence of Ternary Complex of Eu(III) with Nicotinic Acid and Phenanthroline. *Spectrosc. Spect. Anal.* **1999**, *19*, 484−486.

(2) Xiao, S. X.; Zhang, J. J.; Li, X.; Ye, L. J.; Gu, H. W.; Ren, N. Synthesis and Thermochemical Properties of the Ternary Complex $[\mathrm{Sm}(m\text{-NBA})_3\mathrm{phen}]_2 \cdot 2\mathrm{H_2O}$. *J. Chem. Eng. Data* **2010**, *55*, 1688−1692.

(3) Xiao, S. X.; Li, Q. G.; Li, X.; Hu, J. L.; Yang, D. J.; Xiao, F. B. Thermochemical and thermokinetic studies on complex of praseodymium. *Sci. Sin. Chim.* **2010**, *40*, 1422−1429.

(4) Li, Q. G.; Huang, Y.; Li, X.; Ye, L. J.; Xiao, S. X.; Yang, D. J.; Liu, Y. Synthesis, characterization and standard molar enthalpy of formation of $\mathrm{Nd(C_7H_5O_3)_2 \cdot (C_9H_6NO)}$. *J. Therm. Anal. Calorim.* **2008**, *91*, 615−620.

(5) Di, Y. Y.; Kong, Y. X.; Zhang, S.; Yang, W. W.; Wu, E. S.; Shi, Q.; Tan, Z. C. Synthesis, Characterization and Thermochemistry of the Hydrated Barium Nicotinate. *Acta Phys.-Chim. Sin.* **2008**, *24*, 1884−1890.

(6) Yu, H. G.; Liu, Y.; Tan, Z. C.; Dong, J. X.; Zou, T. J.; Huang, X. M.; Qu, S. S. A Solution-Reaction Isoperibol Calorimeter and Standard-Molar Enthalpies of Formation of $\mathrm{Ln(hq)_2Ac}$ (Ln = La, Pr). *Thermochim. Acta* **2003**, *401*, 217−224.

(7) Rychly, R.; Pekarek, V. The Use of Potassium Chloride and Tris(hydroxymethyl) aminomethane as Standard Substances for Solution Calorimetry. *J. Chem. Thermodyn.* **1977**, *9*, 391−396.

(8) Wu, H. X.; Wang, Z. M.; Yang, H. F.; Yu, X. B. Synthesis and Characterization of Solid Ternary Complexes of Rare Earths with Nicotinic Acid and 8-Hydroxyquinoline. *J. Rare Earth Met.* **2002**, *20*, 289−292.

(9) Li, X.; Yang, D. J.; Li, Q. G.; Li, A. T.; Ye, L. J.; Jiang, J. H.; Liu, Y. Thermochemical study of $[\mathrm{Sm(C_7H_5O_3)_2(C_4H_6NO_2S)}] \cdot 2\mathrm{H_2O}$. *J. Therm. Anal. Calorim.* **2009**, *5*, 579−584.

(10) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 84th ed.; CRC Press Inc.: Boca Raton, FL, 2003/2004; pp 5−102.

(11) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1984; p 1.

(12) Sato-Toshima, T.; Kamagughi, A.; Nishiyama, K.; Sakiyama, M.; Seki, S. Enthalpies of combustion of organic compounds. IV. Acetaneilide and nicotinic acid. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 51−54.

(13) Ribeiro Da Silva, M. A. V.; Monte, M. J. S.; Matos, M. A. R. Enthalpies of combustion, vapour pressures, and enthalpies of sublimation of 8-hydroxyquinoline, 5-nitro-8-hydroxyquinoline, and 2-methyl-8-hydroxyquinoline. *J. Chem. Thermodyn.* **1989**, *21*, 159−166.

(14) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 69th ed.; CRC Press Inc.: Boca Raton, FL, 1988/1989; pp D−71.

(15) Xiao, S. X.; Gu, H. W.; Li, X.; Zhang, J. J.; Ren, N. Thermochemical Study on Ternary Complexes of Dysprosium with Aromatic Acid and Phenanthroline. *J. Chem. Eng. Data* **2010**, *55*, 3520−3524.