

Solution-reaction Calorimetric Study of Coordination Compounds of Rare Earth Perchlorates with Alanine and Imidazole

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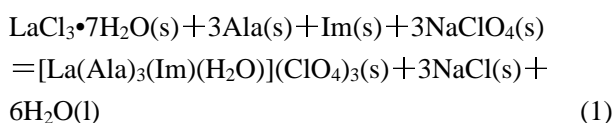
Two coordination compounds of rare earth perchlorates with alanine and imidazole, [RE(Ala)_n(Im)(H₂O)](ClO₄)₃(s) (RE=La, *n*=3; RE=Nd, *n*=2), have been prepared and characterized. The standard molar enthalpies of reaction for the following two reactions, LaCl₃•7H₂O(s)+3Ala(s)+Im(s)+3NaClO₄(s)=[La(Ala)₃(Im)(H₂O)](ClO₄)₃(s)+3NaCl(s)+6H₂O(l) (1) and NdCl₃•6H₂O(s)+2Ala(s)+Im(s)+3NaClO₄(s)=[Nd(Ala)₂(Im)(H₂O)](ClO₄)₃(s)+3NaCl(s)+5H₂O(l) (2), were determined by solution-reaction calorimetry, at *T*=298.15 K, as 36.168±0.642 kJ•mol⁻¹ and 48.590±0.934 kJ•mol⁻¹ respectively. From the results and other auxiliary quantities, the standard molar enthalpies of formation of [La(Ala)₃(Im)(H₂O)](ClO₄)₃(s) and [Nd(Ala)₂(Im)(H₂O)](ClO₄)₃(s) were derived, Δ_f*H*_m[⊖] {[La(Ala)₃(Im)(H₂O)](ClO₄)₃, s}=(−2984.8±1.0) kJ•mol⁻¹ and Δ_f*H*_m[⊖] {[Nd(Ala)₂(Im)(H₂O)](ClO₄)₃, s}=(−2387.8±0.8) kJ•mol⁻¹, respectively.

Keywords solution-reaction calorimetry, standard enthalpy of formation, coordination compound of rare earth, alanine, imidazole

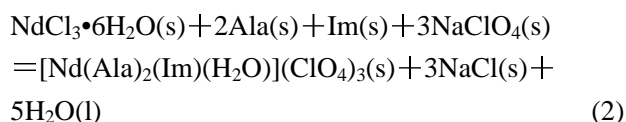
Introduction

Since Anghileri firstly reported that complex of LaCl₃ with glycine had the antitumor function in 1975,¹ coordination compounds of rare earth with amino acid have attracted increasing attention.²⁻⁴ People have found that some compounds of rare earth with amino acids possess disinfection, elimination of inflammation, decrease of the level of blood sugar and anti-cruor functions. Imidazole is a wreath compound, and presents unique biological activities. Ternary coordination compounds of rare earth with amino acid and imidazole have been synthesized.⁵ However, little has been done for the determination of the energies involved in the complex formation. In order to make a deep research into the complexes and provide a theory support for their bioactivity mechanisms, it is necessary to study their basic thermodynamics properties.

In the present study, we designed thermochemical cycles according to Hess' Law to determine the enthalpies of reaction for the two following reactions,



and



and derived the standard molar enthalpies of formation of [RE(Ala)_n(Im)(H₂O)](ClO₄)₃ [RE=La, *n*=3; RE=Nd, *n*=2], respectively.

Experimental

Chemicals

KCl, with a purity more than 99.99%, was purchased from Shanghai No. 1 Reagent Factory, Shanghai, P.R. China. It was dried in a vacuum oven at 500 K for 6 h prior to use. The chemicals, RE₂O₃ (with purities higher than 99.9%), LaCl₃•7H₂O, NdCl₃•6H₂O, HClO₄, alanine (abbreviated as Ala), and imidazole (abbreviated as Im) used were of A.R. grade and obtained from Shanghai Chemical Reagent Co., Shanghai, P.R. China. Doubly distilled water was used to prepare all of the solutions.

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Received May 6, 2003; revised July 1, 2004; accepted August 20, 2004.

Project supported by the Teaching and Research Award Program for Outstanding Young Professors in High Education Institute, Ministry of Education, China.

Sample preparation

RE₂O₃ was dissolved into HClO₄ with the molar ratio 1 : 6 at room temperature. Then the solutions were filtered, and the concentrations of rare earths in the filtrates were titrated by EDTA. The synthesis and purification of the complexes were carried out as described in literature.⁶ RE(ClO₄)₃, Ala and Im reacted in water according to the molar ratio in a water bath at $T=360$ K for 7–8 h. The mixtures were concentrated by evaporation, and subsequently cooled and filtered. The colatures were placed into a desiccator with 98% sulfuric acid until crystalline products appeared from the solutions. The crystals were filtered out and washed with absolute alcohol for three times. Finally, the products were recrystallized from methanol, and the collected crystals were desiccated in a desiccator with P₄O₁₀ until their masses became constant.

The FT-IR spectra in the range of 4000–400 cm⁻¹ of the two crystals were obtained from KBr pellets using FT-IR spectrophotometer (Model Avatar 360, Thermo Nicolet, USA). The infrared data for ligands and the complexes were listed in Table 1. The contents of rare earths in the two coordination compounds were determined by EDTA titration. The purities of the two compounds were checked by an elemental analyzer (Model 1106, Carlo Erba Strumentazione, Italy). The elemental analysis data are presented in Table 2. The TG-DTA test was performed in a thermal analyzer (Model DT-20B) in a nitrogen atmosphere with a heating rate of 4 K•min⁻¹. Satisfactory results of thermal analysis were obtained. The complexes are determined to [RE(Ala)_n(Im)(H₂O)](ClO₄)₃(s) [RE=La, $n=3$; RE=Nd, $n=2$; Ala=alanine; Im=imidazole], respectively.

Solution-reaction calorimetry

The solution-reaction isoperibol calorimeter used for this study was constructed in the laboratory and was

adapted to determine the enthalpies of solid-liquid and liquid-liquid interactions. The volume of the reaction vessel was 100 mL. The water thermostat was maintained at $T=(298.150\pm 0.001)$ K, and the resolution of temperature measurement was ± 0.0001 K. More comprehensive descriptions and detailed procedure of the calorimeter can be found in details.⁷

In order to verify the reliability of the calorimeter, the molar enthalpy of solution of KCl (Standard Reference Material 1655, the National Institute of Standards and Technology) in doubly distilled water was measured. The molar enthalpy of solution of KCl in doubly distilled water was (17560 ± 21) J•mol⁻¹ at $T=298.15$ K, which was in good agreement with the published values in literatures.^{8,9} The uncertainty and the inaccuracy of the experimental results were within $\pm 0.3\%$ compared with the recommended reference data.

Design of thermochemical cycles of reaction

According to Hess's Law, thermochemical cycles were designed as shown in Figure 1 and Figure 2.

Determination of the enthalpies of dissolution

The chosen solvents can dissolve the samples in the sample cell of the calorimeter completely and rapidly. All the samples' mass are listed in Table 3. The calorimetric results are listed in Table 4 and 5, respectively.

Results and discussion

The complex assignment

The IR spectrum of the two complexes shows that characteristic absorption peaks of amino and carboxyl groups in these complexes have a smaller shift than those in the ligand. Table 1 shows that $-\text{NH}_3^+$ of alanine has a positive shift of the antisymmetric stretching mode vibrations, $-\text{COO}^-$ of alanine has a

Table 1 Infrared data for Ala, Im, [La(Ala)₃(Im)(H₂O)](ClO₄)₃ and [Nd(Ala)₂(Im)(H₂O)](ClO₄)₃ (cm⁻¹)

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{as}}(\text{NH}_3^+)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{NH}_3^+)$
Ala	1594	3100	1407	1625
[La(Ala) ₃ (Im)(H ₂ O)](ClO ₄) ₃	1600	3110	1423	1618
[Nd(Ala) ₂ (Im)(H ₂ O)](ClO ₄) ₃	1610	3115	1425	1615
	$\nu(-\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C}-)$	$\nu(\text{HO}-)$
Im	3115	1670	1550	
[La(Ala) ₃ (Im)(H ₂ O)](ClO ₄) ₃	3130	1620	1700–1540	3410
[Nd(Ala) ₂ (Im)(H ₂ O)](ClO ₄) ₃	3120	1640	1700–1540	3410

Table 2 Experimental (exp.) and calculated (calcd.) values of elemental analysis for the two coordination compounds of rare earth perchlorates with alanine and imidazole

Sample	RE (%)		C (%)		N (%)		H (%)	
	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.
[La(Ala) ₃ (Im)(H ₂ O)](ClO ₄) ₃	17.46	17.57	18.68	18.21	8.79	8.85	3.48	3.41
[Nd(Ala) ₂ (Im)(H ₂ O)](ClO ₄) ₃	20.27	20.41	15.65	15.28	7.84	7.92	3.12	2.83

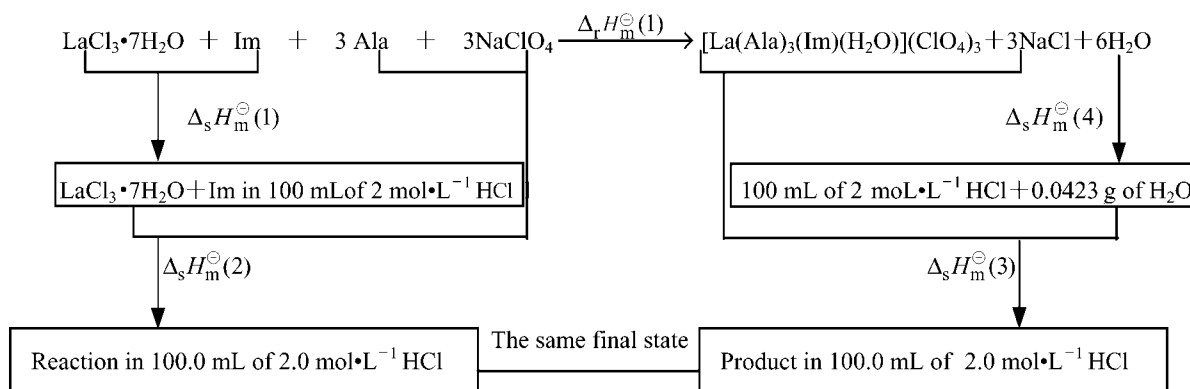


Figure 1 Thermochemical cycle for measuring the enthalpy of reaction for reaction (1).

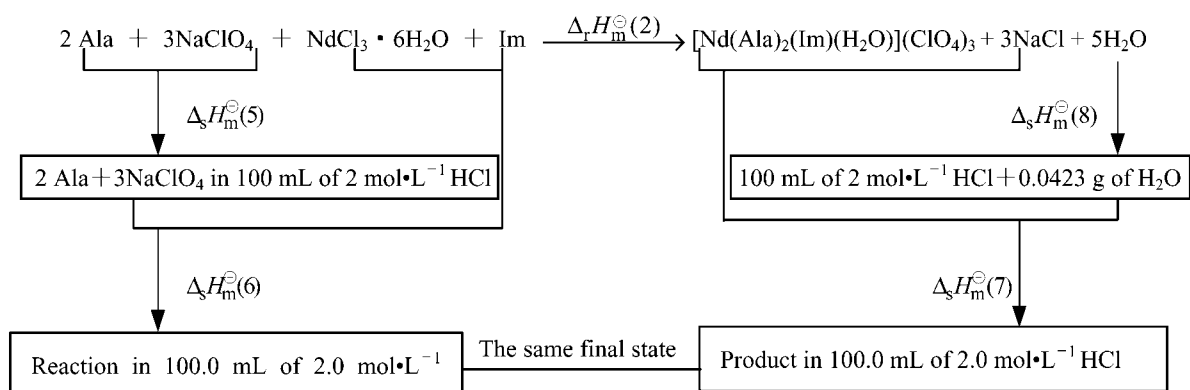


Figure 2 Thermochemical cycle for measuring the enthalpy of reaction for reaction (2).

Table 3 Masses of samples weighted and put into the sample cell of the calorimeter (± 0.0001 g)

Sample	Mass/g	Sample	Mass/g
NaClO ₄	0.1858	NaClO ₄	0.2079
Im	0.0344	Im	0.0385
Ala	0.1352	Ala	0.1008
LaCl ₃ ·7H ₂ O	0.1878	NdCl ₃ ·6H ₂ O	0.2029
NaCl	0.0887	NaCl	0.0992
[La(Ala) ₃ (Im)(H ₂ O)](ClO ₄) ₃	0.4000	[Nd(Ala) ₂ (Im)(H ₂ O)](ClO ₄) ₃	0.4000

Table 4 Enthalpies of dissolution of reactants and products of reaction (1) in 2.0 mol·L⁻¹ HCl at $T=298.15$ K^a

System	Solvent	No.	Q_s/J	$\Delta_s H_m^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$
LaCl ₃ ·7H ₂ O (s) + Im (s)	A	1	-26.332	-52.113
		2	-27.375	-54.175
		3	-26.923	-53.282
		4	-26.667	-52.774
		5	-26.815	-53.068
$\Delta_s H_m^\ominus [\text{LaCl}_3 \cdot 7\text{H}_2\text{O}(\text{s}) + \text{Im}(\text{s})] = (-53.083 \pm 0.753) \text{ kJ} \cdot \text{mol}^{-1}$				
LaCl ₃ ·7H ₂ O(s) + Im(s) + 3NaClO ₄ (s) + 3Ala(s)	B	1	32.002	63.258
		2	32.765	64.765
		3	32.031	63.316
		4	32.629	64.498
		5	32.049	63.351
$\Delta_s H_m^\ominus [3\text{NaClO}_4(\text{s}) + 3\text{Ala}(\text{s})] = (63.838 \pm 0.732) \text{ kJ} \cdot \text{mol}^{-1}$				

Continued

System	Solvent	No.	Q_s/J	$\Delta_s H_m^\ominus /(\text{kJ}\cdot\text{mol}^{-1})$
[La(Ala) ₃ (Im)(H ₂ O)](ClO ₄) ₃ (s) + 3NaCl(s)	C	1	-13.081	-25.862
		2	-12.590	-24.892
		3	-12.732	-25.172
		4	-12.911	-25.526
		5	-12.841	-25.388

$$\Delta_s H_m^\ominus \text{ [[La(Ala)}_3\text{(Im)(H}_2\text{O)](ClO}_4\text{)}_3\text{(s) + 3NaCl(s)]} = (-25.368 \pm 0.366) \text{ kJ}\cdot\text{mol}^{-1}$$

^a Q_s is the heat of dissolution, $\Delta_s H_m^\ominus$ is the standard molar enthalpy of dissolution and the uncertainty quoted for $\Delta_s H_m^\ominus$ corresponds to the standard deviation. Solvent A is 100.0 mL of 2.0 mol·L⁻¹ HCl (aq), B is [100.0 mL of 2.0 mol·L⁻¹ HCl (aq) + 0.506 mmol of LaCl₃·7H₂O + 0.506 mmol of Im], and C is [100.0 mL of 2.0 mol·L⁻¹ HCl (aq) + 3.036 mmol of H₂O], respectively.

Table 5 Enthalpies of dissolution of reactants and products of reaction (2) in 2 mol·L⁻¹ HCl (aq) at $T=298.15 \text{ K}^a$

System	Solvent	No.	Q_s/J	$\Delta_s H_m^\ominus /(\text{kJ}\cdot\text{mol}^{-1})$
3NaClO ₄ (s) + 2Ala(s)	A	1	32.489	57.400
		2	33.604	59.372
		3	33.573	59.316
		4	32.688	57.753
		5	33.320	58.870

$$\Delta_s H_m^\ominus \text{ [3NaClO}_4\text{(s) + 2Ala(s)]} = (58.542 \pm 0.911) \text{ kJ}\cdot\text{mol}^{-1}$$

3NaClO ₄ (s) + 2Ala(s) + NdCl ₃ ·6H ₂ O(s) + Im(s)	D	1	-26.715	-47.199
		2	-27.494	-48.576
		3	-26.626	-47.043
		4	-27.995	-49.461
		5	-27.530	-48.640

$$\Delta_s H_m^\ominus \text{ [NdCl}_3\cdot\text{6H}_2\text{O(s) + Im(s)]} = (-48.184 \pm 1.033) \text{ kJ}\cdot\text{mol}^{-1}$$

[Nd(Ala) ₂ (Im)(H ₂ O)](ClO ₄) ₃ (s) + 3NaCl(s)	E	1	-21.756	-38.439
		2	-22.141	-39.600
		3	-21.183	-37.425
		4	-21.379	-37.773
		5	-21.465	-37.924

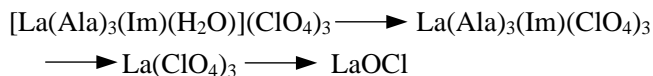
$$\Delta_s H_m^\ominus \text{ [[Nd(Ala)}_2\text{(Im)(H}_2\text{O)](ClO}_4\text{)}_3\text{(s) + 3NaCl(s)]} = (-38.232 \pm 0.847) \text{ kJ}\cdot\text{mol}^{-1}$$

^a Q_s , $\Delta_s H_m^\ominus$, the uncertainty quoted for $\Delta_s H_m^\ominus$ and solvent A are the same as those noticed in Table 1, D is [100.0 mL of 2.0 mol·L⁻¹ HCl(aq) + 1.698 mmol of NaClO₄(s) + 1.132 mmol of Ala], and E is [100.0 mL of 2.0 mol·L⁻¹ HCl(aq) + 2.829 mmol of H₂O], respectively.

positive shift of the symmetric and antisymmetric stretching mode vibrations, and in comparison to the free ligands, $\nu_s(\text{COO}^-)(\text{complex}) > \nu_s(\text{COO}^-)$ (free ligand), and changes to have great capacity in the 15 cm⁻¹. It indicates that nitrogen and oxygen atoms in the complex coordinate to RE³⁺ in a bidentate fashion. In addition, characteristic absorption peak of imidazolyl group in the complex has a great shift, which shows that nitrogen atom in the imidazolyl group coordinates to RE³⁺ as well. Band 3410 cm⁻¹ in the IR spectrum for the complex was assigned to hydroxyl absorption of water, and the existence of water molecule was believed in the complex.

The thermal decomposition process of [La(Ala)₃(Im)(H₂O)](ClO₄)₃ can be divided into three stages. The first stage mass loss is 2.2% between 119 and 160 °C, which coincides with the calculated value 2.28% of losing 1 mol of H₂O from the complex. In the second stage, [La(Ala)₃(Im)(H₂O)](ClO₄)₃ is decomposed at 160—315 °C with the mass loss of 42.06%. The theoretical mass loss is 42.41%, corresponding to the loss of 3 mol of Ala and 1 mol of Im, and the formation of La(ClO₄)₃. The third stage begins at 315—520 °C accompanied with 31.1% mass loss. It is in agreement with the theoretical value of the mass loss of 31.24%, corresponding to the decomposition of ClO₄ and the formation of

LaOCl.⁵ On the basis of experimental and calculated results, the thermal decomposition mechanism was postulated to be as follows:



Determination of the standard molar enthalpies of reaction

The enthalpy of dilution when putting "6H₂O" (or "5H₂O") into the solution of 2.0 mol·L⁻¹ HCl is small and can be neglected

$$\Delta_{\text{s}}H_{\text{m}}^{\ominus}(4) \approx 0 \text{ and } \Delta_{\text{s}}H_{\text{m}}^{\ominus}(8) \approx 0.$$

$$\Delta_{\text{r}}H_{\text{m}}^{\ominus}(1) = \Delta_{\text{s}}H_{\text{m}}^{\ominus}(1) + \Delta_{\text{s}}H_{\text{m}}^{\ominus}(2) - \Delta_{\text{s}}H_{\text{m}}^{\ominus}(3) \\ = -53.083 + 63.838 - (-25.368) \\ = (36.168 \pm 0.642) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{r}}H_{\text{m}}^{\ominus}(2) = \Delta_{\text{s}}H_{\text{m}}^{\ominus}(5) + \Delta_{\text{s}}H_{\text{m}}^{\ominus}(6) - \Delta_{\text{s}}H_{\text{m}}^{\ominus}(7) \\ = 58.542 + (-48.184) - (-38.232) \\ = (48.590 \pm 0.934) \text{ kJ}\cdot\text{mol}^{-1}$$

Evaluation of the standard molar enthalpy of formation

From the standard molar enthalpies of reaction and other auxiliary quantities in Table 6.¹⁰⁻¹²

Table 6 Ancillary data^a

Compound	$\Delta_{\text{f}}H_{\text{m}}^{\ominus}/(\text{kJ}\cdot\text{mol}^{-1})$	Reference
H ₂ O(l)	-285.830 ± 0.042	10, 11
LaCl ₃ ·7H ₂ O(s)	-3178.6	10
NdCl ₃ ·6H ₂ O(s)	-2871.7	10, 11
Alanine(s)	-563.58 ± 0.6	12
Imidazole(s)	49.8 ± 0.6	11
NaClO ₄ (s)	-382.93	11
NaCl(s)	-410.76	11

^a $\Delta_{\text{f}}H_{\text{m}}^{\ominus}$ and the uncertainty quoted for $\Delta_{\text{f}}H_{\text{m}}^{\ominus}$ are the same as those noticed in Table 1.

$$\Delta_{\text{f}}H_{\text{m}}^{\ominus}\{[\text{La}(\text{Ala})_3(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3, \text{s}\} \\ = \Delta_{\text{r}}H_{\text{m}}^{\ominus}(1) + \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{LaCl}_3\cdot 7\text{H}_2\text{O}, \text{s}) \\ + 3\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Ala}, \text{s}) + \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Im}, \text{s}) \\ + 3\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NaClO}_4, \text{s}) - 3\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NaCl}, \text{s}) \\ - 6\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{H}_2\text{O}, \text{l}) \\ = 36.168 + (-3178.6) + 3(-563.58) + 49.8 \\ + 3(-382.93) - 3(-410.76) - 6(-285.830) \\ = (-2984.8 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H_{\text{m}}^{\ominus}\{[\text{Nd}(\text{Ala})_2(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3, \text{s}\} \\ = \Delta_{\text{r}}H_{\text{m}}^{\ominus}(2) + \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NdCl}_3\cdot 6\text{H}_2\text{O}, \text{s}) \\ + 2\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Ala}, \text{s}) + \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Im}, \text{s}) \\ + 3\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NaClO}_4, \text{s}) - 3\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NaCl}, \text{s}) \\ - 5\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{H}_2\text{O}, \text{l}) \\ = 48.590 + (-2871.7) + 2(-563.58) + 49.8 \\ + 3(-382.93) - 3(-410.76) - 5(-285.830) \\ = (-2387.8 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$$

Determination of the final states

UV-Vis spectra and refractive indexes of dissolution products of LaCl₃·7H₂O(s) + 3Ala(s) + Im(s) + 3NaClO₄(s) and [La(Ala)₃(Im)(H₂O)](ClO₄)₃(s) + 3NaCl(s) + 6H₂O(l) (or NdCl₃·6H₂O(s) + 2Ala(s) + Im(s) + 3NaClO₄(s) and [Nd(Ala)₂(Im)(H₂O)](ClO₄)₃(s) + 3NaCl(s) + 5H₂O(l)) in 2.0 mol·L⁻¹ HCl were determined with UV-vis spectrophotometer and refractometer. The duplicate UV-Vis spectra and equal refractive index ($\eta_{25}^{\text{c}} = 1.3492$) were obtained. Thus, it was believed that the values of $\Delta_{\text{f}}H_{\text{m}}^{\ominus}$ determined by solution-reaction calorimetry were reliable.

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(E0305061 ZHAO, X. J.)