

Standard Enthalpies of Formation of $[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (Ln = Pr, Nd; Gly = Glycine): A Calorimetric Study

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Crystals of two coordination compounds of rare earth chlorides with glycine, $[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (Ln = Pr, Nd; Gly = glycine), were prepared and characterized. Using a solution-reaction isoperibol calorimeter, the standard molar enthalpies of reaction for the general thermochemical reaction, $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}) + 3\text{Gly}(\text{s}) = [\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{cr}) + 2\text{H}_2\text{O}(\text{l})$ (Ln = Pr, Nd; Gly = glycine), were determined at $T = 298.15$ K, as (19.2 ± 0.4) kJ·mol⁻¹ and (63.4 ± 0.5) kJ·mol⁻¹, respectively. From the above standard molar enthalpies of reaction and other auxiliary thermodynamic quantities, the standard molar enthalpies of formation of $[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (Ln = Pr, Nd; Gly = glycine), at $T = 298.15$ K, have been derived to be $-(3875.7 \pm 1.1)$ kJ·mol⁻¹ and $-(3825.2 \pm 1.1)$ kJ·mol⁻¹, respectively.

Introduction

Rare earths were widely used in the metallurgical, glass, and ceramic industries, and to prepare many functional materials for advanced science and technology, such as catalysts in petrochemical engineering and selective organic synthesis, lanthanide lasers and amplifiers for optical communications, fluorescent materials, electroluminescent materials, magnetic materials, and superconducting materials. In recent decades, the applications of rare earths as additive elements of fertilizers in agriculture, dyeing promoters in the wool dyeing processes, and spectroscopic probes for calcium ion in biological system were attracting increasing interest. With the applications of rare earths, one inevitable trend is that rare earths diffuse into the environment and enter into the bodies of human beings. But affirmatory information about the long-term biological effects of rare earths has not been available till now. The biological effects of rare earths are ambiguous and have become a new field of inorganic biochemistry worthwhile to be explored in the future.

Amino acids are the basic units of peptides and proteins, and so their properties are of great importance in biology and pharmacy. Since Anghileri reported that the tumor inhibitory activity of lanthanum was enhanced when it was complexed by glycine in 1975,¹ coordination compounds of rare earths with amino acids have been extensively studied due to their unique physiological and biochemical effects. Nearly 200 coordination compounds of rare earths with amino acids have been synthesized, and over 50 crystal structures of these compounds have been determined. The thermodynamic stability constants of the complexes in solution have been investigated by NMR, luminescence, and titration methods. Better understanding of the interactions of rare earth metals with amino acids is of great importance in large numbers of biological processes. Knowledge of the energetics of the rare earth metal–amino acid bond can quantitatively provide biological effect and metabolism information of rare earths in living systems. We must determine many thermodynamic properties of these

complexes before exploring this new research field. Thus, the thermodynamic data for these complexes are needed in order to improve the technique of chemical synthesis and carry out relevant theoretical research.

The crystals of two coordination compounds, $[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (Ln = Pr, Nd; Gly = glycine), have been synthesized, and the crystal structure of $[\text{Pr}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ has been determined by single-crystal X-ray diffraction.² Heat capacities of the two compounds, $[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (Ln = Pr, Nd; Gly = glycine), were measured over the temperature range from $T = 78$ K to $T = 380$ K by Tan and his collaborators using adiabatic calorimetry. The thermal decompositions of the two compounds were studied through thermogravimetry (TG), and possible mechanisms of the decompositions were presented.³

In the present study, the standard molar enthalpies of formation of the two titled compounds, $[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (Ln = Pr, Nd; Gly = glycine), were determined by solution-reaction calorimetry, and their thermochemistry is discussed.

Experimental Section

KCl (mass fraction 0.9999) was purchased from Shanghai No.1 Reagent Factory, Shanghai, P. R. China. KCl was dried in a vacuum oven at $T = 500$ K for 6 h prior to use. Pr_6O_{11} (mass fraction 0.999) was commercially obtained from Tongji Institute of Trace Elements, Shanghai, P. R. China. Nd_2O_3 (mass fraction 0.999) and glycine (abbreviated as Gly, mass fraction 0.995) were supplied by Shanghai Chemical Reagent Co., Shanghai, P. R. China. $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (Ln = Pr, Nd) used for synthesis and calorimetric determination were prepared from the respective oxides and characterized as previously described in detail elsewhere.⁴ They were maintained in a desiccator over phosphorus pentoxide (P_2O_5) before the calorimetric measurements. Hydrochloric acid (analytical grade) and double-distilled water were used to prepare all of the calorimetric solutions.

The synthesis and purification of $[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (Ln = Pr, Nd; Gly = glycine) were carried out in

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Table 1. Infrared Bonds (cm⁻¹) for Glycine and [Ln(Gly)₃(H₂O)₂]Cl₃·2H₂O

compd	glycine	Ln = Pr	Ln = Nd
δ _s (H ₂ O)		1612	1612
δ _{as} (NH ₃ ⁺)	1614		
δ _{as} (COO ⁻)	1599	1601	1597
δ _s (NH ₃ ⁺)	1524	1520	1519
δ _s (CH ₂)	1445	1469	1470
ν _s (COO ⁻)	1413	1418	1420
ρ _w (CH ₂)	1333	1335	1334

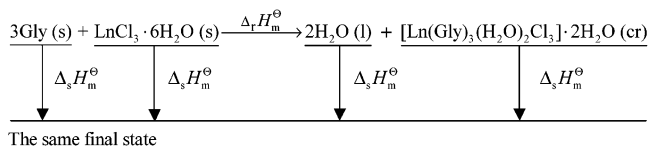
Table 2. Percentages of Experimental (Calculated) Values for Elemental Analysis of [Ln(Gly)₃(H₂O)₂]Cl₃·2H₂O

compd	Ln/%	C/%	N/%	H/%
Ln = Pr	25.8 (25.9)	13.0 (13.2)	7.5 (7.7)	4.4 (4.3)
Ln = Nd	26.3 (26.3)	12.9 (13.2)	7.5 (7.7)	4.5 (4.2)

accordance with the method as previously described in the literature.² The aqueous solutions of rare earth chlorides were mixed with glycine in the molar ratio 1:3, and appropriate amounts of a solution of NaOH were added to the mixed solutions till pH = 3. The mixtures were slowly concentrated by evaporation in a water bath at $T = 330$ K, and the resulting solutions were placed into a desiccator with fuming sulfuric acid at room temperature until crystalline products appeared from the solutions. The crystals were filtered out and washed with absolute alcohol three times. Green and pink needlelike crystals were obtained, respectively. Finally, the collected crystals were desiccated in a desiccator with P₂O₅ until their masses became constant. The FT-IR spectra of glycine and the two crystals were obtained from KBr pellets at room temperature using a FT-IR spectrophotometer (model Avatar 360, Thermo Nicolet, USA) (Table 1). The contents of rare earths in the two crystals were determined by EDTA titration. The purities of the two crystals were checked with an elemental analyzer (model 1106, Carlo Erba Strumentazione, Italy). The TG-DTA tests were performed in a thermal analyzer (model Setsys 16/18, Setaram, France) and under a dynamic atmosphere of N₂ (mass fraction 0.99999) with a flow rate of 60 cm³·min⁻¹ and a heating rate of 10 K·min⁻¹. Satisfactory results of TG-DTA measurement were obtained. The empirical formulas of the two crystals were determined to be [Pr(Gly)₃(H₂O)₂]Cl₃·2H₂O and [Nd(Gly)₃(H₂O)₂]Cl₃·2H₂O, respectively (Table 2). The mass fraction purities of the two coordination compounds were higher than 0.998, which were good enough to meet the requirements of the present calorimetric study.

A solution-reaction isoperibol calorimeter constructed in the laboratory was used to determine the enthalpy of dissolution. The calorimeter consisted of a water thermostat, a Pyrex-glass Dewar, a glass sample cell, a heater for calibration and equilibration purposes, a glass-sheathed thermistor probe, a data acquisition/switch unit, a 20-channel multiplexer module, a multifunction module (models 34970A, 34901A, and 34907A, Agilent, USA), and a personal computer for data acquisition and processing. During the experiments, the water thermostat was maintained at $T = 298.15$ K. The stability of temperature control of the water thermostat was $\pm 1 \times 10^{-3}$ K, and the resolution of the temperature measurement was $\pm 1 \times 10^{-4}$ K. A more comprehensive description and detailed procedure of the calorimeter can be found in the literature.⁵

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 double-distilled water was measured at $T = 298.15$ K.

**Figure 1.** General thermochemical cycle for measuring the standard molar enthalpies of reaction; reaction 1 is for Pr, and reaction 2 is for Nd.**Table 3. Standard Molar Enthalpy of Dissolution of Reactants and Products of Reaction 1 at $T = 298.15$ K^a**

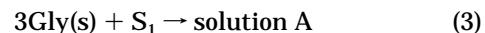
system	solvent	no.	m	$\Delta_s H_m^\ominus$
			g	kJ·mol ⁻¹
3Gly(s)	S ₁	1	0.1126	18.90
		2	0.1125	19.34
		3	0.1126	19.34
		4	0.1127	19.36
		5	0.1126	18.86
$\Delta_s H_m^\ominus[3\text{Gly}(\text{s})] = 19.16 \pm 0.26 \text{ kJ}\cdot\text{mol}^{-1}$				
PrCl ₃ ·6H ₂ O(s)	A	1	0.1779	-17.26
		2	0.1776	-17.52
		3	0.1778	-17.34
		4	0.1778	-16.84
		5	0.1779	-17.30
$\Delta_s H_m^\ominus[\text{PrCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})] = -(17.25 \pm 0.25) \text{ kJ}\cdot\text{mol}^{-1}$				
[Pr(Gly) ₃ (H ₂ O) ₂]Cl ₃ ·2H ₂ O(cr)	S ₂	1	0.2724	-17.14
		2	0.2723	-17.54
		3	0.2722	-17.18
		4	0.2723	-17.32
		5	0.2723	-17.28
$\Delta_s H_m^\ominus\{[\text{Pr}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\} = -(17.29 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1}$				

^a m is the mass of sample, $\Delta_s H_m^\ominus$ is the standard molar enthalpy of dissolution, and the uncertainty quoted for $\Delta_s H_m^\ominus$ corresponds to the standard deviation. Solvent S₁ is 100.0 cm³ of 3.0 mol·dm⁻³ HCl (aq), A is [100.0 cm³ of 3.0 mol·dm⁻³ HCl (aq) + 1.5 mmol of Gly], and S₂ is [100.0 cm³ of 3.0 mol·dm⁻³ HCl (aq) + 1.0 mmol of H₂O], respectively.

The molar enthalpy of solution of KCl in double-distilled water was $(17560 \pm 21) \text{ J}\cdot\text{mol}^{-1}$, which was in good agreement with the published values in the literature.^{6,7} The uncertainty and the inaccuracy of the experimental results were within $\pm 0.3\%$ compared with the recommended reference data.

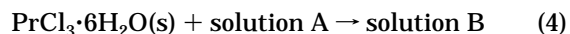
The general thermochemical cycle for measuring the standard molar enthalpies of reaction was depicted in Figure 1.

Gly(s) (1.5 mmol) was dissolved in 100.0 cm³ of 3.0 mol·dm⁻³ HCl(aq) at $T = 298.15$ K

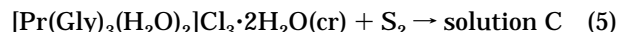


where S₁ was the calorimetric solvent.

PrCl₃·6H₂O(s) (0.5 mmol) was dissolved in [100.0 cm³ of 3.0 mol·dm⁻³ HCl (aq) + 1.5 mmol of Gly] at $T = 298.15$ K



[Pr(Gly)₃(H₂O)₂]Cl₃·2H₂O(cr) (0.5 mmol) was dissolved in [100.0 cm³ of 3.0 mol·dm⁻³ HCl(aq) + 1.0 mmol of H₂O] at $T = 298.15$ K



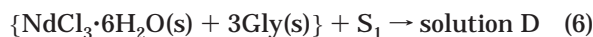
where S₂ was the calorimetric solvent.

The experimental data of reactions 3–5 were listed in Table 3.

Table 4. Standard Molar Enthalpy of Dissolution of Reactants and Products of Reaction 2 at $T = 298.15$ K

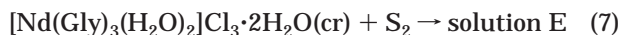
system	solvent	no.	m/g		$\Delta_s H_m^\ominus$
					$\text{kJ}\cdot\text{mol}^{-1}$
3Gly(s) + NdCl ₃ ·6H ₂ O(s)	S ₁	1	0.1125	0.1790	31.06
		2	0.1126	0.1792	31.30
		3	0.1127	0.1796	31.64
		4	0.1128	0.1794	31.04
		5	0.1126	0.1792	30.66
$\Delta_s H_m^\ominus[3\text{Gly(s)} + \text{NdCl}_3\cdot 6\text{H}_2\text{O(s)}] = 31.14 \pm 0.36 \text{ kJ}\cdot\text{mol}^{-1}$					
[Nd(Gly) ₃ (H ₂ O) ₂]Cl ₃ ·2H ₂ O(cr)	S ₂	1	0.2738		-32.24
		2	0.2741		-32.16
		3	0.2740		-32.48
		4	0.2737		-31.92
		5	0.2739		-32.64
$\Delta_s H_m^\ominus\{[\text{Nd}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}(\text{cr})\} = -(32.29 \pm 0.28) \text{ kJ}\cdot\text{mol}^{-1}$					

[NdCl₃·6H₂O(s) + 3Gly(s)] (0.5 mmol) was dissolved in 100.0 cm³ of 3.0 mol·dm⁻³ HCl (aq) at $T = 298.15$ K



where S₁ was the calorimetric solvent.

[Nd(Gly)₃(H₂O)₂]Cl₃·2H₂O(cr) (0.5 mmol) was dissolved in [100.0 cm³ of 3.0 mol·dm⁻³ HCl(aq) + 1.0 mmol H₂O] at $T = 298.15$ K



where S₂ was the calorimetric solvent.

The calorimetric results of reactions 4 and 5 were showed in Table 4.

Results and Discussion

The standard atomic masses recommended by the IUPAC Commission in 2001⁸ were used in the calculation of all molar quantities.

Evaluation of the Enthalpy of Dilution. The molar enthalpy of dissolution of 2 mol of H₂O(l) in [2000 × 100.0 cm³] of 3.0 mol·dm⁻³ HCl(aq) at $T = 298.15$ K was very small compared with the other enthalpies of dissolution, and it can be neglected. So, $\Delta_s H_m^\ominus \approx 0$.

Standard Molar Enthalpies of Reaction. From the standard molar enthalpies of dissolution, the standard molar enthalpies of reaction for the two reactions can be estimated

$$\begin{aligned} \Delta_r H_m^\ominus(1) &= \Delta_s H_m^\ominus(3) + \Delta_s H_m^\ominus(4) - \Delta_s H_m^\ominus(5) \\ &= [19.16] + [-17.25] - [-17.29] \\ &= 19.2 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r H_m^\ominus(2) &= \Delta_s H_m^\ominus(6) - \Delta_s H_m^\ominus(7) \\ &= [31.14] - [32.29] \\ &= 63.4 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The uncertainties, s , assigned to $\Delta_r H_m^\ominus$, were obtained considering the uncertainties of $\Delta_s H_m^\ominus$ and calculated from

the standard deviations:

$$s(\Delta_r H_m^\ominus) = \left\{ \sum [s(\Delta_s H_m^\ominus)]^2 \right\}^{1/2} \quad (8)$$

where $s(\Delta_s H_m^\ominus)$ was the corresponding uncertainty of the standard molar enthalpy of dissolution.

Standard Molar Enthalpies of Formation. From the standard molar enthalpies of reaction for the two reactions and various ancillary data, the standard molar enthalpies of formation of the two coordination compounds were calculated

$$\begin{aligned} \Delta_f H_m^\ominus\{[\text{Pr}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}(\text{cr})\} &= \\ \Delta_f H_m^\ominus[\text{PrCl}_3\cdot 6\text{H}_2\text{O}(\text{s})] + 3\Delta_f H_m^\ominus[\text{Gly}(\text{s})] - & \\ 2\Delta_f H_m^\ominus[\text{H}_2\text{O}(\text{l})] + \Delta_r H_m^\ominus(1) & \\ = [-2880.7] + 3[-528.61] - 2[-285.830] + [19.2] & \\ = -(3875.7 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1} & \end{aligned}$$

$$\begin{aligned} \Delta_f H_m^\ominus\{[\text{Nd}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}(\text{cr})\} &= \\ \Delta_f H_m^\ominus[\text{NdCl}_3\cdot 6\text{H}_2\text{O}(\text{s})] + 3\Delta_f H_m^\ominus[\text{Gly}(\text{s})] - & \\ 2\Delta_f H_m^\ominus[\text{H}_2\text{O}(\text{l})] + \Delta_r H_m^\ominus(2) & \\ = [-2874.4] + 3[-528.61] - 2[-285.830] + [63.4] & \\ = -(3825.2 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1} & \end{aligned}$$

The uncertainties of $\Delta_f H_m^\ominus\{[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}(\text{cr})\}$ (Ln = Pr, Nd) can be calculated from the following eq 9:

$$\begin{aligned} s\Delta_f H_m^\ominus\{[\text{Ln}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}(\text{cr})\} &= \\ \{s\Delta_f H_m^\ominus[\text{LnCl}_3\cdot 6\text{H}_2\text{O}(\text{s})]\}^2 + \{3s\Delta_f H_m^\ominus[\text{Gly}(\text{s})]\}^2 + & \\ \{2s\Delta_f H_m^\ominus[\text{H}_2\text{O}(\text{l})]\}^2 + \{s[\Delta_r H_m^\ominus]\}^2 & \quad (9) \end{aligned}$$

where $s[\Delta_f H_m^\ominus]$ was the corresponding uncertainty of the standard molar enthalpy of formation and $s[\Delta_r H_m^\ominus]$ was the corresponding uncertainty of the standard molar enthalpy of reaction.

The final results of the standard molar enthalpies of reaction and the standard molar enthalpies of formation were summarized in Tables 5 and 7, respectively. The ancillary data listed in Table 6 were used to calculate the standard molar enthalpies of formation.

The chosen calorimetric solvents in the calorimetric study could dissolve the chemicals in the sample cell of the calorimeter completely and relatively rapidly. Rigorous control of the stoichiometry was maintained through each series of experiments to ensure that the final solutions resulting from dissolution of the reactants were of the same composition of those from dissolution of the products. Solution B had the same thermodynamic state with solution C, and solution D had the same thermodynamic state with solution E, respectively.

Table 5. Standard Molar Enthalpies of Reaction for the Two Reactions at $T = 298.15$ K^a

reaction	$\Delta_r H_m^\ominus/\text{kJ}\cdot\text{mol}^{-1}$
$\text{PrCl}_3\cdot 6\text{H}_2\text{O}(\text{s}) + 3\text{Gly}(\text{s}) = [\text{Pr}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}(\text{cr}) + 2\text{H}_2\text{O}(\text{l})$	19.2 ± 0.4
$\text{NdCl}_3\cdot 6\text{H}_2\text{O}(\text{s}) + 3\text{Gly}(\text{s}) = [\text{Nd}(\text{Gly})_3(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}(\text{cr}) + 2\text{H}_2\text{O}(\text{l})$	63.4 ± 0.5

^a $\Delta_r H_m^\ominus$ is the standard molar enthalpy of reaction, and the uncertainty quoted for $\Delta_r H_m^\ominus$ corresponds to the standard deviation.

Table 6. Ancillary Data^a

compd	$\Delta_f H_m^\ominus/\text{kJ}\cdot\text{mol}^{-1}$	ref
H ₂ O(l)	-(285.830 ± 0.042)	9
PrCl ₃ ·6H ₂ O(s)	-(2880.7 ± 0.1)	4, 10
NdCl ₃ ·6H ₂ O(s)	-(2874.4 ± 0.1)	10, 11
glycine(s)	-(528.61 ± 0.34)	12

^a $\Delta_f H_m^\ominus$ is the standard molar enthalpy of formation.

Table 7. Standard Molar Enthalpies of Formation of the Two Compounds

compd	$\Delta_f H_m^\ominus/\text{kJ}\cdot\text{mol}^{-1}$
[Pr(Gly) ₃ (H ₂ O) ₂]Cl ₃ ·2H ₂ O(cr)	-(3875.7 ± 1.1)
[Nd(Gly) ₃ (H ₂ O) ₂]Cl ₃ ·2H ₂ O(cr)	-(3825.2 ± 1.1)

Literature Cited

- (1) Anghileri, L. J. On the Antitumor Activity of Gallium and Lanthanides. *Arzneim.-Forsch. (Drug Res.)* **1975**, *25*, 793–795.
- (2) Jin, T. Z.; Yang, C. Q.; Yang, Q. C.; Wu, J. G.; Xu, G. X. Studies on Rare Earth Complexes of Amino acids (–)-Synthesis and Crystal Structure of Triglycinato-Diaquo-Praseodymium Chlorides. *Chem. J. Chin. Univ.* **1989**, *10*, 118–122.
- (3) Liu, B. P.; Tan, Z. C.; Lu, J. L.; Lan, X. Z.; Sun, L. X.; Xu, F.; Yu, P.; Xing, J. Low-Temperature Heat Capacity and Thermodynamic Properties of Crystalline [RE(Gly)₃(H₂O)₂]Cl₃·2H₂O (RE = Pr, Nd; Gly = glycine). *Thermochim. Acta* **2003**, *397*, 67–73.
- (4) Santo, L. S., Jr.; Petrucelli, G. P.; Airoldi, C. Thermochemistry of 2, 2, 6, 6, 6-Tetramethyl-3, 5-Heptanedione Chelates of Lanthanide Group Elements. *Polyhedron* **1999**, *18*, 969–977.

- (5) 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 Ln(hq)₂Ac (Ln = La, Pr). *Thermochim. Acta* **2003**, *401*, 217–224.
- (6) Montgomery, R. L.; Melaugh, R. A.; Lau, C. C.; Meier, G. H.; Chan, H. H.; Rossini, F. D. Determination of the Energy Equivalent of a Water Solution Calorimeter with a Standard Substance. *J. Chem. Thermodyn.* **1977**, *9*, 915–936.
- (7) Archer, D. G. Thermodynamic Properties of the KCl + H₂O System. *J. Phys. Chem. Ref. Data* **1999**, *28*, 1–17.
- (8) Coplen, T. B. Atomic Weights of the Elements 1999 (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 667–683.
- (9) Cox, J. D.; Wagman, D. D.; Medvedev, V. A., Eds. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.
- (10) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I. B.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data (Suppl. 2)* **1982**, *11*.
- (11) Airoldi, C.; Santos, L. S., Jr. The Mean Enthalpy of the Lanthanide-Oxygen Bond in 2, 2, 6, 6-Tetramethyl-3, 5-Heptanedione Chelates of Praseodymium and Holmium. *Struct. Chem.* **1993**, *4*, 323–325.
- (12) Vasilev, V. P.; Borodin, V. A.; Kopnyshev, S. B. Calculation of the Standard Enthalpies of Combustion and of Formation of Crystalline Organic Acids and Complexones from the Energy Contributions of Atomic Group. *Russ. J. Phys. Chem.* **1991**, *65*, 29–32.

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