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Standard Enthalpies of Formation of Rare Earth L-Proline Chloride Complexes $[RE(L\text{-}Pro)_2(H_2O)_5]Cl_3$ (RE = Ho, Er)

Xinmin Wu, Jinxiu Huang, Haiyan Li, and Wei Li*

College of Chemical Engineering, Beijing Institute of Petro-chemical Technology, Beijing 102617, China

ABSTRACT: Two crystalline compounds of rare-earth chlorides coordinated with L-proline, $[RE(L\text{-}Pro)_2(H_2O)_5]Cl_3$ (RE = Ho, Er), were synthesized. Their structures were characterized using thermogravimetric analysis (TG), differential thermal analysis (DTA), and chemical analytical methods, the purities of the $[RE(L\text{-}Pro)_2(H_2O)_5]Cl_3$ (RE = Ho, Er) complexes were determined to be 98.85 % and 98.62 %, respectively. After the measurement of the dissolving heat of the two systems, $[RE(NO_3)_3 \cdot 6H_2O + 2L\text{-}Pro + 3NaCl]$ and $\{[RE(L\text{-}Pro)_2(H_2O)_5]Cl_3 + 3NaNO_3\}$, at 298.15 K in 2 $mol \cdot dm^{-3}$ HCl solvent by using a conduction microcalorimeter, the standard enthalpies of formation of the two crystalline compounds at 298.15 K were determined to be $\Delta_f H_m^{\ominus}\{[Ho(L\text{-}Pro)_2(H_2O)_5]Cl_3, s, 298.15\ K\} = (-3675.0 \pm 1.3)\ kJ \cdot mol^{-1}$ and $\Delta_f H_m^{\ominus}\{[Er(L\text{-}Pro)_2(H_2O)_5]Cl_3, s, 298.15\ K\} = (-3655.9 \pm 1.6)\ kJ \cdot mol^{-1}$, respectively.

INTRODUCTION

Rare earth elements have drawn more and more attention for their special biological effects. In the 19th century, it was found that cerium salts can be used as a preservative and pregnancy antitoxicity medication.[1] Then, many other properties of rare earth materials were found, such as anticoagulation effects, influence on the activity of enzyme and the metabolism process of fat, and strong affinity between rare earth and chondriosomes, macromolecules, protein and amino acids, and so forth. All of these properties have been utilized widely nowadays.[2] At present, rare earths have been used widely in the fields of catalysis, coloration, agriculture, environment, and so forth. However, there is lack of fundamental physicochemical properties of rare earth compounds. Although there have been some reports about the synthesis, structural analysis, and thermodynamic analysis of rare earth complexes,[3−5] the important thermodynamic values, such as the enthalpies of formation of such kind of complexes, are lacking;[6] more work is needed.

In this paper, rare earth chloride complexes coordinated with L-proline (L-Pro) were synthesized, and the structures were characterized to be $[RE(L\text{-}Pro)_2(H_2O)_5]Cl_3$ (RE = Ho, Er). By using the calorimetric method, the solution enthalpies of the reactants and products of a designed thermochemical cycle were measured in 2 $mol \cdot dm^{-3}$ HCl solvent with a RD496-2000 microcalorimeter, for the purpose of finally calculating the standard formation enthalpy of the complex $[RE(L\text{-}Pro)_2(H_2O)_5]Cl_3$ at 298.15 K.

EXPERIMENTAL SECTION

Instruments and Reagents. A HCT-1 microprocessor thermal balance (Beijing Hengjiu Scientific Instrument Factory, China), WZS-1 Abbe refractometer (Shanghai Experimental Instrument Factory, China), UV-16 UV−vis spectrometer (Shimadzu, Japan), and RD496-2000 microcalorimeter (Mianyang Instrument Factory, Chinese Academy of Sciences) were used.

Ho_2O_3, Er_2O_3 (Tianjin Jinke Institute of Fine Chemicals, Tianjin, China) had a purity of ≥ 99.99 %, L-proline (Tianjin Fuchen Chemical Reagent Factory, Tianjin, China) a purity ≥ 99.0 %, and NaCl, $NaNO_3$, HCl, and HNO_3 were analytically pure. All solid samples have been dried before the experiment, and redistilled water was used for all experiments.

Synthesis and Determination of Rare Earth Chloride Compound with L-Proline. The synthesis process is according to refs 7 and 8. A portion of 1.1053 g of Ho_2O_3 and 1.2659 g of Er_2O_3 was weighed and dissolved in 1:1 hydrochloric acid solution. Then a certain amount of $RECl_3$ (RE = Ho, Er) solution and L-proline with a molar ratio of 1:2 were dissolved in distilled water, after adjusting the pH value to around 4; the mixed solution was stirred for 8 h in a water bath at 333 K and then concentrated by evaporation in the water bath at 323 K. After cooling, the solution was placed in a dryer, and crystals appeared after about 3 weeks of evaporation. The crystals were dried to constant weight in a desiccator, and finally the crystal products $[RE(L\text{-}Pro)_2(H_2O)_5]Cl_3$ (RE = Ho, Er) were obtained. The purity analysis of the products was performed with an ethylenediaminetetraacetic acid (EDTA) complexometric titration, and the thermogravimetric and differential thermal analysis were performed by a HCT-1 microprocessor thermal balance.

Synthesis and Determination of $RE(NO_3)_3 \cdot 6H_2O$. According to ref 9, 2 g of the oxides of Ho and Er were dissolved in heated concentrated HNO_3 solutions (oxides were a little in excess). After the reaction, the remaining unreacted oxides were filtered, and the filtrate was cooled to get nitrate crystals. The crystals were put into a vacuum desiccator at room temperature for 48 h, then placed in a desiccator with 45 % H_2SO_4, and dried to constant weight. At last, light yellow holmium nitrate crystals and pink erbium nitrate were obtained. The component of the

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products was analyzed with an EDTA titration and a HCT-1 thermal balance, and so forth.

Determination of Dissolution Enthalpies. The determination of the dissolution enthalpy was performed by a RD496-2000 microcalorimeter. In the RD496-2000 conduction microcalorimeter, there are 496 pairs of thermocouple sensors between the reaction cell and constant-temperature block, and the thermocouple sensors are in charge of heat conduction and temperature determination. When a reaction begins, the reaction will induce a temperature difference and heat transfer between the reaction cell and constant-temperature block, and after the reaction, thermal equilibrium between the reaction cell and constant-temperature block will be reached again. The thermal effect of the whole process can be obtained by integrating the thermal electromotive force with respect to time. The temperature control precision of the microcalorimeter is $\pm 1 \cdot 10^{-3}$ K at 298.15 K, the measurement sensitivity can reach 1 μW. The microcalorimeter needs to be calibrated before the experiments, and the calibration parameter was found to be $S = 63.04 \pm 0.05$ $\mu\text{V} \cdot \text{mW}^{-1}$ after electrical calibration using a Joule cell at 298.15 K. Choosing KCl (working standard) as a standard substance, the dissolution enthalpy of KCl in deionized water was determined to be 17.23 ± 0.03 $\text{kJ} \cdot \text{mol}^{-1}$, which agrees well with the value of 17.24 ± 0.02 $\text{kJ} \cdot \text{mol}^{-1}$ from ref 10. The determination error of the dissolution enthalpy in deionized water was less than 0.5 %. A 15 cm^3 steel reservoir with an inner separable glass sleeve was used as the sample pool and reference pool.[11] The pools were put into the calorimeter chamber at 298.15 K. When the baseline was steady (fluctuation less than ± 0.00001 mV), the firing pin was triggered to make the sample mix with the solution. The chamber was then kept at 298.15 K until the thermodynamical curve went parallel to the baseline with a very small fluctuation which shows the completion of reaction, and then the experimental data were saved.

The final dissolution states were determined with an Abel refractometer and UV spectrometer.

■ RESULTS AND ANALYSIS

Content and Structures of Rare Earth Nitrates and Rare Earth Complexes with Proline. It can be seen from the TG/DTA curves that there exist two main steps in the thermal decomposition process of the holmium complex with proline. There are two endothermal peaks in the 323 K to 418 K range (peak value at 342 K) and the 548 K to 723 K (peak value at 614 K), respectively. The weight loss in the two periods is 15.77 % and 40.01 %, respectively, which agrees with the fact that the complex loses five crystallization water molecules first and two proline molecules second. The erbium complex has a similar thermal behavior: there are two endothermal peaks in the 333 K to 403 K (peak value at 394 K) and 503 K to 773 K ranges, respectively, with mass losses of 15.71 % and 39.80 %, respectively. It was found from further investigation of the TG curves that the two proline molecules are lost step by step. According to refs 6 and 7, the sample structure is characterized as $[\text{Ho}(\text{L-Pro})_2(\text{H}_2\text{O})_5]\text{Cl}_3$ and $[\text{Er}(\text{L-Pro})_2(\text{H}_2\text{O})_5]\text{Cl}_3$, respectively. The molecular weight (M) for above the two structures is 591.629 $\text{g} \cdot \text{mol}^{-1}$ and 593.958 $\text{g} \cdot \text{mol}^{-1}$, respectively. The content of the rare earth ions was measured by the method of EDTA titration, and the sample purities were calculated to be 98.85 % and 98.62 %, respectively.

Table 1. Dissolution Heat of $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, L-Pro, NaCl in 2.4 cm^3 of 2 $\text{mol} \cdot \text{dm}^{-3}$ HCl[a]

	no.	m_1/mg	m_2/mg	m_3/mg	$-Q_{s1}$/J
RE = Ho	1	58.0	29.1	22.2	1.217
	2	58.3	29.2	22.3	1.256
	3	58.5	29.3	22.3	1.169
	4	58.8	29.5	22.4	1.324
	5	59.0	29.6	22.5	1.145
	ave	$\overline{Q}_{s1} = (-1.222 \pm 0.054)$ J			
RE = Er	1	58.5	29.2	22.2	1.339
	2	58.3	29.1	22.1	1.197
	3	58.0	29.0	22.0	1.272
	4	58.7	29.3	22.3	1.195
	5	59.0	29.4	22.4	1.230
	ave	$\overline{Q}_{s1} = (-1.247 \pm 0.047)$ J			

[a] m_1, m_2, and m_3 represent the mass of $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, L-Pro, and NaCl, respectively; $n_{\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}}/n_{\text{L-Pro}}/n_{\text{NaCl}} = 1{:}2{:}3$.

A TG and EDTA analysis of the two rare-earth nitrates has been also done, and it was concluded that the content of water in Ho and Er nitrates was 23.6 % and 23.2 %, respectively, and their structural formulas were determined to be $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (M = 459.036 $\text{g} \cdot \text{mol}^{-1}$) and $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (M = 461.366 $\text{g} \cdot \text{mol}^{-1}$).

Design of the Thermochemistry Cycle. To get the standard reaction enthalpy ($\Delta_r H^\ominus$) of the following reaction,

$$\begin{aligned} &\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{s}) + 2\text{L-Pro}(\text{s}) + 3\text{NaCl}(\text{s}) \\ &\quad = [\text{RE}(\text{L-Pro})_2(\text{H}_2\text{O})_5]\text{Cl}_3(\text{s}) + 3\text{NaNO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \end{aligned} \tag{1}$$

Three reaction schemes were designed as follows:

$$\begin{aligned} &[\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{s}) + 2\text{L-Pro}(\text{s}) + 3\text{NaCl}(\text{s})] + \text{s} \\ &\quad = \text{state}_1 \quad (\text{reaction enthalpy}, \Delta_s H_1) \end{aligned} \tag{2}$$

$$\text{s} + \text{H}_2\text{O} = \text{s-H}_2\text{O} \quad (\text{reaction enthalpy}, \Delta_d H) \tag{3}$$

$$\begin{aligned} &\{[\text{RE}(\text{L-Pro})_2(\text{H}_2\text{O})_5]\text{Cl}_3(\text{s}) + 3\text{NaNO}_3(\text{s})\} + \text{s-H}_2\text{O} \\ &\quad = \text{state}_2 \quad (\text{reaction enthalpy}, \Delta_s H_2) \end{aligned} \tag{4}$$

where s refers to the solvent of 2.4 cm^3 of 2 $\text{mol} \cdot \text{dm}^{-3}$ HCl. If state_1 was the same as state_2, according to the Hess Law, under the conditions of constant temperature and pressure, there exists the relation that eqs 1 + 3 + 4 = 2, and so $\Delta_r H^\ominus = \Delta_s H_1 - \Delta_s H_2 - \Delta_d H$, where $\Delta_d H$ represents the dilution enthalpy of the process of adding a little water into 2.4 cm^3 of 2 $\text{mol} \cdot \text{dm}^{-3}$ HCl. The value of $\Delta_d H$ was found to be small enough to be ignored, so the value of $\Delta_r H^\ominus$ could be calculated after gaining $\Delta_s H_1$ and $\Delta_s H_2$.

Calculation of $\Delta_s H_1$. The quantity of the reactants was determined according to the stoichiometric relationship in chemical reaction 1 and the solubility of RD496-2000 microcalorimeter; the detailed data are: $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 58.2 mg; L-Pro, 29.2 mg; NaCl, 22.3 mg; and $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 58.3 mg; L-Pro, 29.2 mg; NaCl, 22.3 mg. The weighed reactants were put into the sample pool, and the solution heat Q_{s1} was measured during the dissolving process with 2.4 cm^3 of 2 $\text{mol} \cdot \text{dm}^{-3}$ HCl

Table 2. Dissolution Heat of $[RE(\text{L-Pro})_2(H_2O)_5]Cl_3$ and $NaNO_3$ in 2.4 cm^3 of 2 $mol \cdot dm^{-3}$ HCl[a]

	no.	m_4/mg	m_5/mg	Q_{s2}/J
RE = Ho	1	75.0	32.32	7.670
	2	75.1	32.38	7.502
	3	75.5	32.54	7.732
	4	75.3	32.45	7.767
	5	75.4	32.50	7.842
	ave		$\overline{Q_{s2}} = (7.703 \pm 0.093)$ J	
RE = Er	1	75.5	32.2	7.192
	2	75.3	32.4	7.477
	3	75.7	32.3	7.018
	4	75.0	32.2	7.420
	5	75.0	32.2	7.305
	ave		$\overline{Q_{s2}} = (7.282 \pm 0.142)$ J	

[a] m_4 and m_5 represent the mass of $[RE(\text{L-Pro})_2(H_2O)_5]Cl_3$ and $NaNO_3$, respectively; $n_{[RE(\text{L-Pro})_2(H_2O)_5]Cl_3}/n_{NaNO_3} = 1:3$.

solution. The experimental data of five parallel experiments are presented in Table 1.

Calculation of $\Delta_s H_2$. Also according to the stoichiometric relationship in chemical reaction 1, 75.0 mg of $[Ho(\text{L-Pro})_2(H_2O)_5]Cl_3$, 32.2 mg of $NaNO_3$, or 75.0 of mg $[Er_2(\text{L-Pro})_6(H_2O)_4](ClO_4)_6$, and 32.2 mg of $NaNO_3$ were weighed and put into a reactor, and then Q_{s2} was determined under the same conditions as those in determining Q_{s1}. The experimental data and the average results are shown in Table 2.

Reaction Enthalpy of Chemical Reaction 1 and the Standard Formation Enthalpy of $[RE(\text{L-Pro})_2(H_2O)_5]Cl_3$. According to thermochemistry law and the relationship between Q and ΔH, it is known that

$$\Delta_r H^\ominus = \Delta_s H_1 - \Delta_s H_2 - \Delta_d H = \overline{Q}_{s1} - \overline{Q}_{s2} - Q_d = \overline{Q}_{s1} - \overline{Q}_{s2}$$

The reaction enthalpy of chemical reaction 1, in which RE = Ho, is calculated as follows:

$$\Delta_r H^\ominus = \overline{Q}_{s1} - \overline{Q}_{s2} = -1.222 \text{ J} - 7.703 \text{ J} = (-8.925 \pm 0.108) \text{ J}$$

Then

$$\Delta_r H_m^\ominus = Q \cdot M/W = (-70.1 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$$

The reaction enthalpy of chemical reaction 1, in which RE = Er, is:

$$\Delta_r H^\ominus = \overline{Q}_{s1} - \overline{Q}_{s2} = -1.247 \text{ J} - 7.282 \text{ J} = (-8.529 \pm 0.150) \text{ J}$$

Then

$$\Delta_r H_m^\ominus = Q \cdot M/W = (-67.3 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$$

For the formation reaction of $[RE(\text{L-Pro})_2(H_2O)_5]Cl_3$,

$$\begin{aligned}\Delta_r H_m^\ominus = {} & \Delta_f H_m^\ominus([RE(\text{L-Pro})_2(H_2O)_5]Cl_3, \text{s}, 298.15 \text{ K}) \\ & + 3\Delta_f H_m^\ominus(NaNO_3, \text{s}, 298.15 \text{ K}) \\ & + \Delta_f H_m^\ominus(H_2O, \text{l}, 298.15 \text{ K}) \\ & - \Delta_f H_m^\ominus(RE(NO_3)_3 \cdot 6H_2O, \text{s}, 298.15 \text{ K}) \\ & - 2\Delta_f H_m^\ominus(\text{L-Pro}, \text{s}, 298.15\text{K}) \\ & - 3\Delta_f H_m^\ominus(NaCl, \text{s}, 298.15 \text{ K})\end{aligned}$$

According to refs 12 to 14:

$$\Delta_f H_m^\ominus(NaNO_3, \text{s}, 298.15 \text{ K}) = -467.85 \text{ kJ} \cdot \text{mol}^{-1}, \text{ref } 12$$

$$\Delta_f H_m^\ominus(H_2O, \text{l}, 298.15 \text{ K}) = (-285.83 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}, \text{ref } 13$$

$$\Delta_f H_m^\ominus(\text{L-Pro}, \text{s}, 298.15 \text{ K}) = (-515.18 \pm 0.52) \text{ kJ} \cdot \text{mol}^{-1}, \text{ref } 14$$

$$\Delta_f H_m^\ominus(NaCl, \text{s}, 298.15 \text{ K}) = -411.15 \text{ kJ} \cdot \text{mol}^{-1}, \text{ref } 12$$

According to ref 9:

$$\Delta_f H_m^\ominus[Ho(NO_3)_3 \cdot 6H_2O, \text{s}, 298.15 \text{ K}] = -3030.5 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_m^\ominus[Er(NO_3)_3 \cdot 6H_2O, \text{s}, 298.15 \text{ K}] = -3014.2 \text{ kJ} \cdot \text{mol}^{-1}$$

So the standard formation enthalpy of $[RE(\text{L-Pro})_2(H_2O)_5]Cl_3$ is:

$$\Delta_f H_m^\ominus([Ho(\text{L-Pro})_2(H_2O)_5]Cl_3, \text{s}, 298.15 \text{ K} = (-3675.0 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_m^\ominus([Er(\text{L-Pro})_2(H_2O)_5]Cl_3, \text{s}, 298.15 \text{ K} = (-3655.9 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$$

DISCUSSION

Calculation of Dilution Enthalpy $\Delta_d H$. To get the dilution enthalpy of the process of adding 2.3101 mg of H_2O into 2.4 cm^3 of 2 $mol \cdot dm^{-3}$ HCl solution (the molality before and after adding water was 0.0365 $mol \cdot kg^{-1}$ and 0.0370 $mol \cdot kg^{-1}$, respectively), the data provided by ref 15 were used to obtain a linear equation $\varphi_L = 29.252 + 1868.171m - 9976.341m^2$ in the molality range (0.01850 to 0.0617) $mol \cdot kg^{-1}$ by using a least-squares fitting method (the correlation coefficient is $R = 0.99916$).

After further mathematical treatment,

$$\begin{aligned}\Delta_d H_{0.0370 \to 0.0365} & = \Delta_d H_{0.0370 \to 0} - \Delta_d H_{0.0365 \to 0} \\ & = (\varphi_{L(0.0370)} - \varphi_{L(0.0365)}) \cdot 0.20000 \cdot 10^{-3} \cdot 4.184 \text{ J} \\ & = -(84.716 - 84.149) \cdot 0.20000 \cdot 10^{-3} \cdot 4.184 \text{ J} \\ & = -1.1387 \cdot 10^{-5} \text{ J}\end{aligned}$$

The calculated results show that it is feasible to ignore the dilution enthalpy during calculating the reaction enthalpy $\Delta_r H^\ominus$.

Identification Test for the Final Dissolved Material. A WZS-1 Abbe refractometer and UV-16 ultraviolet–visible spectrophotometer were used to study the refractive index and ultraviolet spectrum of the reactant $[RE(NO_3)_3 \cdot 6H_2O + 2\text{L-Pro} + 3NaCl]$ and the product $\{[RE(\text{L-Pro})_2(H_2O)_5]Cl_3 + 3NaNO_3 + H_2O\}$ in 2.4 cm^3 of 2 $mol \cdot dm^{-3}$ HCl solution, the results show that the reactant and product have the same refractive index and ultraviolet spectrum. So we concluded that the tested states have the same final thermochemistry state in the experiments, which means the design of the thermochemical cycle is reasonable.[16]

Comparison between $\Delta_f H_m^{\ominus}$ of $[Ho(L\text{-}Pro)_2(H_2O)_5]Cl_3$ and $[Er(L\text{-}Pro)_2(H_2O)_5]Cl_3$. $[Ho(L\text{-}Pro)_2(H_2O)_5]Cl_3$ and $[Er(L\text{-}Pro)_2(H_2O)_5]Cl_3$ are compounds of the same series, and the result that the $-\Delta_f H_m^{\ominus}$ value of the Ho salt is a little larger than $-\Delta_f H_m^{\ominus}$ value of Er salt is consistent with the conclusion in ref 17.

AUTHOR INFORMATION

Corresponding Author

*E-mail: liwei77@bipt.edu.cn.

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