COORDINATION REACTION OF ALANINE WITH NEODYMIUM(III) AND ERBIUM(III) NITRATE
Thermochemical study

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Abstract

The solid-state coordination reaction:

$$Nd(NO_3)_3 \cdot 6H_2O(s) + 4Ala(s) \rightarrow Nd(Ala)_4(NO_3)_3 \cdot H_2O(s) + 5H_2O(l)$$

$$Er(NO_3)_3 \cdot 6H_2O(s) + 4Ala(s) \rightarrow Er(Ala)_4(NO_3)_3 \cdot H_2O(s) + 5H_2O(l)$$

have been studied by classical solution calorimetry. The molar dissolution enthalpies of the reactants and the products in 2 mol L^{-1} HCl solvent of these two solid–solid coordination reactions have been measured using a calorimeter. From the results and other auxiliary quantities, the standard molar formation enthalpies of [Nd(Ala)$_4$(NO$_3$)$_3 \cdot$H$_2$O, s, 298.2 K] and [Er(Ala)$_4$(NO$_3$)$_3 \cdot$H$_2$O, s, 298.2 K] at 298.2 K have been determined to be $\Delta_f H_m^0$ [Nd(Ala)$_4$(NO$_3$)$_3 \cdot$H$_2$O, s, 298.2 K]$=-3867.2$ kJ mol^{-1}, and $\Delta_f H_m^0$ [Er(Ala)$_4$(NO$_3$)$_3 \cdot$H$_2$O, s, 298.2 K]$=-3821.5$ kJ mol^{-1}.

Keywords: alanine, erbium nitrate, isoperibol calorimetry, neodymium nitrate, standard molar formation enthalpy

Introduction

Rare earth ions possess some special functions in biological bodies. Amino acids are the basic units of protein. It is reported that La(Gly)$_3$Cl$_3 \cdot$3H$_2$O has an antitumor effect [1]. Therefore, study on the complexes of rare earth with amino acids is significant. In 1996, the preparation of the new complexes Nd(Ala)$_4$(NO$_3$)$_3 \cdot$H$_2$O [2] and Er(Ala)$_4$(NO$_3$)$_3 \cdot$H$_2$O [3] was reported, the preparation of the new coordination was reported. XRD, IR and element analyses have been used to characterize the solid complexes. However, the thermochemical properties of these two solid–solid reactions at ambient temperature have not been reported. The purpose of the present study is to determine the dissolution enthalpies of the reactants and the products by solution cal-

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orimetry, and to obtain the standard molar formation enthalpies of the two new complexes. The molar reaction enthalpies of the two solid-state coordination reactions were derived from the respective dissolution enthalpies, and from the result and other auxiliary quantities, the standard molar formation enthalpies of the complexes $Nd(Ala)_4(NO_3)_3 \cdot H_2O(s)$ and $Er(Ala)_4(NO_3)_3 \cdot H_2O$ were calculated.

Experimental

Chemical

All the chemicals (including the Ala, Nd_2O_3, Er_2O_3, HCl and KCl) used are of a. r. grade and obtained from Shanghai Reagent Factory. 2 mol L^{-1} HCl was chosen as calorimetric solvent.

$Nd(NO_3)_3 \cdot 6H_2O(s)$ and $Er(NO_3)_3 \cdot 6H_2O$ were obtained by Nd_2O_3 and Er_2O_3 with HNO_3 [4].

KCl (obtained from Shanghai Reagent Factory), a purity greater than 99.99%, was dried in a vacuum oven for 6 h at 135°C prior to use.

Preparations

$Nd(Ala)_4(NO_3)_3 \cdot H_2O$, a violet red solid, was prepared and analyzed according to the method given in [2].

$Er(Ala)_4(NO_3)_3 \cdot H_2O$, a reddish solid, was prepared and analyzed according to the method given in [3].

Calorimeter and calibration

The isoperibol reaction calorimeter used for this study was constructed in this laboratory and was adapted for measuring enthalpies of solid–liquid, liquid–liquid reactions. The reactor was made by glass, and the volume of the reaction vessel is 100 cm³. The precision of temperature control and measurement are ±0.001 and 0.0001 K, respectively. All calorimetric determinations were carried out in this isoperibol calorimeter as described previously [5].

The calorimetric system was tested by measuring the dissolution enthalpy of KCl (calorimetric primary standard) in water at 298.2 K. The measured mean dissolution enthalpy of KCl(s) in water at 298.2 K was 17651±27 kJ mol⁻¹, which is in agreement with the corresponding published data [6].

Determination of the dissolution enthalpies

Determination of the dissolution enthalpies of the reactants in 2 mol L^{-1} HCl solvent

The symbol *RE* stands for rare earth ions Nd and Er, the two solid–solid coordination reaction are abbreviated as:

$$RE(NO_3)_3 \cdot 6H_2O(s) + 4Ala(s) \rightarrow RE(Ala)_4(NO_3)_3 \cdot H_2O(s) + 5H_2O(l)$$
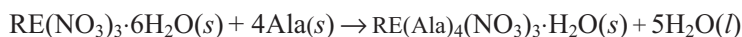
RE(NO$_3$)$_3$·6H$_2$O(s) and Ala(s) was weighed accurately for mole ratio n[RE(NO$_3$)$_3$· 6H$_2$O]:n[Ala]=1:4. The enthalpies of dissolution of [RE(NO$_3$)$_3$·6H$_2$O(s) +4Ala(s)] (mole ratio 1:4) in 100 mL 2 mol L^{-1} HCl were measured and presented in Table 1.

Table 1 Dissolution enthalpies of [Nd(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)] and [Er(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)] in 2 mol L^{-1} HCl solvent at 298.2 K

System	No.	Mass$_{RE(NO_3)_3·6H_2O}$/g	Mass$_{Ala}$/g	$\Delta_s H_m^0$/kJ mol^{-1}
Nd(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)	1	0.1320	0.1071	33.451
	2	0.1313	0.1071	33.519
	3	0.1313	0.1065	33.580
	4	0.1313	0.1067	33.425
	5	0.1315	0.1068	33.490
$\Delta_s H_m^0$[Nd(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)]=33.493±0.027 kJ mol^{-1}				
Er(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)	1	0.2307	0.1778	12.451
	2	0.2309	0.1780	12.397
	3	0.2305	.0.1777	12.450
	4	0.2305	0.1784	12.481
	5	0.2312	0.1783	12.519
$\Delta_s H_m^0$[Er(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)]=12.460±0.020 kJ mol^{-1}				

Determination of the dissolution enthalpies of the products in 2 mol L^{-1} HCl solvent

Distilled water was weighed accurately for mole ratio n[H$_2$O]:n[RE(NO$_3$)$_3$·6H$_2$O]= 5:1, and added in 100 mL 2 mol L^{-1} HCl RE(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s) was weighed accurately for mole number n[RE(Ala)$_4$(NO$_3$)$_3$·H$_2$O]=n[RE(NO$_3$)$_3$·6H$_2$O]. The enthalpies of dissolution of RE(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s) in the HCl solvent diluted above are measured, and the results are shown in Table 2.

Table 2 Dissolution enthalpies of Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s) and Er(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s) in (100 mL 2 mol^{-1} HCl+5H$_2$O) solvent at 298.2 K

System	No.	Mass/g	$\Delta_s H_m^0$/kJ mol^{-1}
Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s)	1	0.2108	4.479
	2	0.2114	4.550
	3	0.2105	4.519
	4	0.2117	4.543
	5	0.2111	4.453
$\Delta_s H_m^0$ [Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O s, 298.2 K]=4.509±0.019 kJ mol^{-1}			
Er(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s)	1	0.3640	−5.350
	2	0.3643	−5.397
	3	0.3638	−5.300
	4	0.3639	−5.345
	5	0.3635	−5.309
$\Delta_s H_m^0$ [Er(Ala)$_4$(NO$_3$)$_3$·H$_2$O s, 298.2 K]= −5.340±0.017 kJ mol^{-1}			

Results and discussion

Evaluation of the standard molar enthalpy of formation of Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s)

According to Hess' law, a thermochemical cycle was designed as shown in Table 3.

Table 3 Reaction scheme for the standard molar formation enthalpy of Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O at the temperature 298.2 K. The solvent 'A' was 2 mol L^{-1} HCl (*aq*). $\Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3$

Reaction	$\Delta_f H_m^0$/kJ mol^{-1}
1. [Nd(NO$_3$)$_3$·6H$_2$O (*s*)+4Ala(*s*)]+'A'=[Nd(NO$_3$)$_3$·4Ala·6H$_2$O])(sln in 'A')	33.493±0.027
2. 5H$_2$O(*l*)+'A'=5H$_2$O(sln in 'A') (according to [10])	−0.001
3. [Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O(*s*)]+5H$_2$O(sln in 'A')= [Nd(NO$_3$)$_3$·4Ala·6H$_2$O](sln in 'A')	4.509±0.019
4. Nd(NO$_3$)$_3$·6H$_2$O(*s*)+4Ala(*s*)=Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O(*s*)+5H$_2$O(*l*)	28.985

UV spectroscopy and the date of the refrangibility have confirmed that the final state 1 and state 3 are thermodynamically equivalent. So, the reaction enthalpy of:

$$Nd(NO_3)_3·6H_2O(s)+4Ala(s) \rightarrow Nd(Ala)_4(NO_3)_3·H_2O(s)+5H_2O(l) \qquad (1)$$

can be calculated as $\Delta_r H_m^0(1)=\Delta H_4=\Delta H_1-\Delta H_2-\Delta H_3=28.985$ kJ mol^{-1}.

The standard molar formation enthalpy of Nd(Ala)$_4$(NO$_3$)$_3$·H$_2$O has not been reported. In order to obtain this value, using the above results and other auxiliary quantities, it was calculated.

According thermodynamic principle, for the reaction (1):

$$\Delta_r H_m^0(1)=\Delta_f H_m^0 [Nd(Ala)_4(NO_3)_3·H_2O, s, 298.2 K]+$$
$$+5\Delta_f H_m^0 [H_2O, l, 298.2 K]-\Delta_f H_m^0[Nd(NO_3)_3·6H_2O, s, 298.2 K]-$$
$$-4\Delta_f H_m^0 [Ala, s, 298.2 K]$$

according to [7]: $\Delta_f H_m^0$ [H$_2$O, *l*, 298.2 K]= −285.83 kJ mol^{-1}
according to [8]: $\Delta_f H_m^0$ [Nd(NO$_3$)$_3$·6H$_2$O, *s*, 298.2 K]= −3071.1 kJ mol^{-1}
according to [9]: $\Delta_f H_m^0$ [Ala, *s*, 298.2 K]= −563.580 kJ mol^{-1}
so that

$$\Delta_f H_m^0 [Nd(Ala)_4(NO_3)_3·H_2O, s, 298.2 K]= -3867.2 \text{ kJ mol}^{-1}$$

Evaluation of standard molar formation enthalpy of Er(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s)

Using the same method as described above. The reaction chemical cycle was used to derive the standard molar formation enthalpy of Er(Ala)$_4$(NO$_3$)$_3$·H$_2$O(*s*) is presented in Table 4.

Table 4 Reaction scheme for the standard molar formation enthalpy of $Er(Ala)_4(NO_3)_3 \cdot H_2O$ at the temperature 298.2 K. The solvent 'A' was 2 mol L^{-1} HCl (aq). $\Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3$

Reaction	$\Delta_f H_m^0$/kJ mol^{-1}
1. $[Er(NO_3)_3 \cdot 6H_2O(s) + 4Ala(s)] + 'A' = [Er(NO_3)_3 \cdot 4Ala \cdot 6H_2O](sln\ in\ 'A')$	12.460 ± 0.020
2. $5H_2O(l) + 'A' = 5H_2O(sln\ in\ 'A')$ (according to [10])	-0.001
3. $Er(Ala)_4(NO_3)_3 \cdot H_2O(s) + 5H_2O(sln\ in\ 'A') = [Er(NO_3)_3 \cdot 4Ala \cdot 6H_2O](sln\ in\ 'A')$	-5.340 ± 0.017
4. $Er(NO_3)_3 \cdot 6H_2O(s) + 4Ala(s) = Er(Ala)_4(NO_3)_3 \cdot H_2O(s) + 5H_2O(l)$	17.800

States 1 and 3 are of thermodynamically equivalent, as confirmed by UV spectroscopy and refrangibility data. The reaction enthalpy of the reaction:

$$Er(NO_3)_3 \cdot 6H_2O(s) + 4Ala(s) \rightarrow Er(Ala)_4(NO_3)_3 \cdot H_2O(s) + 5H_2O(l) \qquad (2)$$

$$\Delta_r H_m^0(2) = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 = 17.800\ kJ\ mol^{-1}.$$
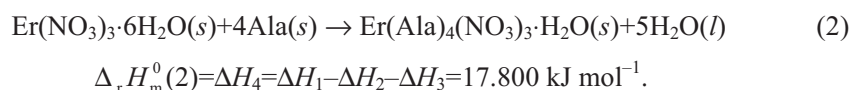
The standard molar formation enthalpy of $Er(Ala)_4(NO_3)_3 \cdot H_2O(s)$ has also not been reported. In order to obtain this value, the same method described above was used.

$$\Delta_r H_m^0(2) = \Delta_f H_m^0\ [Er(Ala)_4(NO_3)_3 \cdot H_2O,\ s,\ 298.2\ K] +$$

$$5\Delta_f H_m^0\ [H_2O,\ l,\ 298.2\ K] - \Delta_f H_m^0 [Er(NO_3)_3 \cdot 6H_2O,\ s,\ 298.2\ K]$$

$$- 4\Delta_f H_m^0\ [Ala,\ s,\ 298.2\ K]$$

according to [7]: $\Delta_f H_m^0 [H_2O,\ l,\ 298.2\ K] = -285.83\ kJ\ mol^{-1}$.
according to [8]: $\Delta_f H_m^0\ [Er(NO_3)_3 \cdot 6H_2O,\ s,\ 298.2\ K] = -3014.2\ kJ\ mol^{-1}$.
according to [9]: $\Delta_f H_m^0\ [Ala,\ s,\ 298.2\ K] = -563.580\ kJ\ mol^{-1}$
then,

$$\Delta_f H_m^0\ [Er(Ala)_4(NO_3)_3 \cdot H_2O,\ s,\ 298.2\ K] = -3821.5\ kJ\ mol^{-1}.$$

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