Journal of Thermal Analysis and Calorimetry, Vol. 73 (2003) 285–291

A THERMOCHEMICAL STUDY OF THE COORDINATION REACTIONS OF La(III) WITH ALANINE AND GLYCINE

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(Received September 25, 2002; in revised form January 7, 2003)

Abstract

The solid-state coordination reactions of lanthanum chloride with alanine and glycine, and lanthanum nitrate with alanine 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 three solid–solid coordination reactions have been measured using an isoperibol calorimeter. From the results and other auxiliary quantities, the standard molar formation enthalpies have been determined to be $\Delta_f H_m^\theta$[La(Ala)$_3$Cl$_3$·3H$_2$O(*s*), 298.2 K]= –3716.3 kJ mol^{-1}, $\Delta_f H_m^\theta$[La(Gly)$_3$Cl$_3$·5H$_2$O(*s*), 298.2 K]= –4223.0 kJ mol^{-1} and $\Delta_f H_m^\theta$[La(Ala)$_4$(NO$_3$)$_3$·H$_2$O(*s*), 298.2 K]= –3867.57 kJ mol^{-1}, respectively.

Keywords: alanine, glycine, lanthanum chloride, lanthanum nitrate, solid-state coordination, standard molar formation enthalpy

Introduction

Rare earth ions possess some special functions in biology, and amino acids are the basic units of protein. It was reported that La(Gly)$_3$Cl$_3$·3H$_2$O has antitumor action [1]. Therefore, study of the complexes of rare earth with amino acids has significance. During 1990–1994, the preparations of the new complexes La(Ala)$_3$Cl$_3$·3H$_2$O [2], La(Gly)$_3$Cl$_3$·5H$_2$O [3] and La(Ala)$_4$(NO$_3$)$_3$·H$_2$O [4] have been reported. XRD, IR and elemental analyses have been used to characterize the solid complexes. However, the thermochemical properties of these three 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 calorimetry, and obtain the standard molar formation enthalpies of the three new complexes. The molar reaction enthalpies of the three solid-state coordination reactions were derived from the respective dissolution enthalpies, and from the results and other auxiliary quanti-

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1388–1650/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ties, the standard molar enthalpies of formation of the complexes $La(Ala)_3Cl_3\cdot 3H_2O$, $La(Gly)_3Cl_3\cdot 5H_2O$ and $La(Ala)_4(NO_3)_3\cdot H_2O$ were calculated.

Experimental

Chemicals

All the chemicals (including the Alanine, Glycine, La_2O_3, HCl, HNO_3 and KCl) used are of A.R. grade and were obtained from the Shanghai Reagent Factory. 2 mol L^{-1} HCl was chosen as the calorimetric solvent.

$LaCl_3\cdot 7H_2O$ [5] and $La(NO_3)_3\cdot 6H_2O$ [6] were obtained by reacting La_2O_3 with HCl and with HNO_3, respectively.

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

Preparations

$La(Ala)_3Cl_3\cdot 3H_2O$, $La(Gly)_3Cl_3\cdot 5H_2O$ and $La(Ala)_4(NO_3)_3\cdot H_2O$ are all white solids. $La(Ala)_3Cl_3\cdot 3H_2O$ was prepared and analyzed according to the method given in [2], $La(Gly)_3Cl_3\cdot 5H_2O$ according to [3] and $La(Ala)_4(NO_3)_3\cdot H_2O$ according to [4].

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 and liquid–liquid reactions. The reactor was made of glass, and the volume of the reaction vessel is 100 cm^3. 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 [7].

$KCl(s)$ and $H_2O(l)$ were weighed accurately for mole ratio $n[KCl]:n[H_2O]=1:1110$. The calorimetric system was tested by measuring the dissolution enthalpy of $KCl(s)$ (calorimetric primary standard) in water at 298.2 K. The measured mean value was 17651±21 J mol^{-1}, which is in agreement with the corresponding published data [8].

Determination of the dissolution enthalpies

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

Using the symbol *M* for Cl and NO_3, and *A* for Ala and Gly, the three solid–solid coordination reactions are abbreviated as:

$$LaM_3\cdot xH_2O(s)+aA(s)\rightarrow La(A)_aM_3\cdot mH_2O(s)+(x-m)H_2O(l)$$

$LaM_3\cdot xH_2O(s)$ and $aA(s)$ were weighed accurately for mole ratio $n[LaM_3\cdot xH_2O]:n[A]=1:a$. The enthalpies of dissolution of $[LaM_3\cdot xH_2O(s)+aA(s)]$ (mole ratio 1:a) in 100 mL 2 mol L^{-1} HCl were measured, and are presented in Table 1.

Table 1 Dissolution enthalpies of [$LaCl_3 \cdot 7H_2O(s)$+4Ala(s)], [$LaCl_3 \cdot 7H_2O(s)$+3Gly(s)] and [$La(NO_3)_3 \cdot 6H_2O(s)$+4Ala($s$)] in 2 mol L^{-1} HCl solvent at 298.2 K

System	No	$m_{LaM_3 \cdot xH_2O}$/g	m_{Ala}/g	Q/J	$\Delta_s H_m^\theta$/ kJ mol^{-1}
	1	0.1859	0.1339	3.130	6.251
	2	0.1857	0.1337	3.122	6.243
$LaCl_3 \cdot 7H_2O(s)$+3Ala(s)	3	0.1856	0.1335	3.169	6.342
	4	0.1858	0.1340	3.152	6.295
	5	0.1859	0.1338	3.187	6.367
$\Delta_s H_m^\theta$[$LaCl_3 \cdot 7H_2O(s)$+3Ala(s)]=6.300±0.024 kJ mol^{-1}					
	1	0.1858	0.1132	5.394	10.762
	2	0.1857	0.1123	5.439	10.888
$LaCl_3 \cdot 7H_2O(s)$+3Gly(s)	3	0.1857	0.1125	5.414	10.831
	4	0.1856	0.1130	5.426	10.841
	5	0.1859	0.1130	5.401	10.780
$\Delta_s H_m^\theta$[$LaCl_3 \cdot 7H_2O(s)$+3Gly(s)]=10.820±0.023 kJ mol^{-1}					
	1	0.2168	0.1785	15.382	30.713
	2	0.2161	0.1779	15.334	30.718
$La(NO_3)_3 \cdot 6H_2O(s)$+4Ala($s$)	3	0.2162	0.1780	15.338	30.711
	4	0.2165	0.1783	15.364	30.716
	5	0.2164	0.1781	15.352	30.715
$\Delta_s H_m^\theta$[$La(NO_3)_3 \cdot 6H_2O(s)$+4Ala($s$)]=30.715±0.001 kJ mol^{-1}					

note: m – mass of sample; Q – heat effect; $\Delta_s H_m^\theta$ – molar dissolution enthalpy

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

Distilled water was weighed accurately for mole ratio $n[H_2O]:n[LaM_3 \cdot xH_2O]=(x-m):1$, and was added in 100 mL 2 mol L^{-1} HCl solution. $La(A)_aM_3 \cdot mH_2O(s)$ was weighed accurately for mole number $n[La(A)_aM_3 \cdot mH_2O]=n[LaM_3 \cdot xH_2O]$. The enthalpies of dissolution of $La(A)_aM_3 \cdot mH_2O(s)$ in the HCl solvent diluted above were measured, and the results are shown in Table 2.

Results

Evaluation of the standard molar formation enthalpy of $La(Ala)_3Cl_3 \cdot 3H_2O(s)$

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

UV spectroscopy and the optical refraction data confirmed that the final state 1 and state 3 are thermodynamically equivalent. So, the reaction enthalpy of:

$$LaCl_3 \cdot 7H_2O(s)+3Ala(s) \rightarrow La(Ala)_3Cl_3 \cdot 3H_2O(s)+4H_2O(l) \quad (1)$$

can be calculated as $\Delta_r H_m^\theta(1)=\Delta H_4=\Delta H_1-\Delta H_2-\Delta H_3=9.738$ kJ mol^{-1}.

The value of the standard molar formation enthalpy of $La(Ala)_3Cl_3\cdot 3H_2O$ has not been reported. The above results and other auxiliary quantities, were used to calculate a value.

Table 2 Dissolution enthalpies of $La(Ala)_3Cl_3\cdot 3H_2O$, $La(Gly)_3Cl_3\cdot 5H_2O$ and $La(Ala)_4(NO_3)_3\cdot H_2O$ in (100 mL 2 mol L^{-1} HCl+(x–m) H_2O) solvent at 298.2 K

System	No.	m/g	Q/J	$\Delta_s H_m^\theta$/ kJ mol^{-1}
	1	0.2832	1.740	–3.481
	2	0.2834	1.737	–3.473
$La(Ala)_3Cl_3\cdot 3H_2O$	3	0.2834	1.692	–3.383
	4	0.2832	1.701	–3.403
	5	0.2833	1.723	–3.446
	$\Delta_s H_m^\theta$[$La(Ala)_3Cl_3\cdot 3H_2O$(s) 298.2 K]=–3.437±0.019 kJ mol^{-1}			
	1	0.2810	7.611	15.182
	2	0.2806	7.587	15.156
$La(Gly)_3Cl_3\cdot 5H_2O$	3	0.2803	7.533	15.064
	4	0.2805	7.564	15.116
	5	0.2808	7.596	15.163
	$\Delta_s H_m^\theta$[$La(Gly)_3Cl_3\cdot 5H_2O$(s) 298.2 K]=15.136±0.021 kJ mol^{-1}			
	1	0.3472	4.698	9.462
	2	0.3501	4.741	9.470
$La(Ala)_3(NO_3)_3\cdot H_2O$	3	0.3493	4.729	9.467
	4	0.3497	4.729	9.457
	5	0.3491	4.723	9.461
	$\Delta_s H_m^\theta$[$La(Ala)_4\cdot(NO_3)_3\cdot H_2O$($s$) 298.2 K]=9.463±0.023 kJ mol^{-1}			

m – mass of samples

Table 3 Reaction scheme for the standard molar formation enthalpy of $La(Ala)_3Cl_3\cdot 3H_2O$ at 298.2 K

	Reaction	$\Delta_s H_m^\theta$/ kJ mol^{-1}
1	[$LaCl_3\cdot 7H_2O$(s)+3Ala(s)]+A=[$LaCl_3\cdot 3Ala\cdot 7H_2O$] (sln in A)	6.300±0.024
2	$4H_2O$(l)+A=$4H_2O$ (sln in A) (according to [11])	–0.001
3	$La(Ala)_3Cl_3\cdot 3H_2O$(s)+$4H_2O$ (sln in A)=[$LaCl_3\cdot 3Ala\cdot 7H_2O$] (sln in A)	–3.437±0.019
4	$LaCl_3\cdot 7H_2O$(s)+3Ala(s)=$La(Ala)_3Cl_3\cdot 3H_2O$(s)+$4H_2O$(l)	9.738

The solvent A was 2 mol L^{-1} HCl (aq); $\Delta H_4=\Delta H_1-\Delta H_2-\Delta H_3$

According to thermodynamic principles, for the reaction (1):

$$\Delta_r H_m^\theta(1) = \Delta_f H_m^\theta[\mathrm{La(Ala)_3Cl_3{\cdot}3H_2O}(s), 298.2\ \mathrm{K}] + 4\Delta_f H_m^\theta[\mathrm{H_2O}(l), 298.2\ \mathrm{K}] -$$

$$-\Delta_f H_m^\theta[\mathrm{LaCl_3{\cdot}7H_2O}(s), 298.2\ \mathrm{K}] - 3\Delta_f H_m^\theta[\mathrm{Ala}(s), 298.2\ \mathrm{K}]$$

according to [9]: $\Delta_f H_m^\theta[\mathrm{H_2O}(l), 298.2\ \mathrm{K}] = -285.83\ \mathrm{kJ\ mol^{-1}}$

$$\Delta_f H_m^\theta[\mathrm{LaCl_3{\cdot}7H_2O}(s), 298.2\ \mathrm{K}] = -3178.6\ \mathrm{kJ\ mol^{-1}}$$

according to [10]:

$$\Delta_f H_m^\theta[\mathrm{Ala}(s), 298.2\ \mathrm{K}] = -563.580\ \mathrm{kJ\ mol^{-1}}$$

so that $\Delta_f H_m^\theta[\mathrm{La(Ala)_3Cl_3{\cdot}3H_2O}(s), 298.2\ \mathrm{K}] = -3716.3\ \mathrm{kJ\ mol^{-1}}$

Evaluation of the standard molar formation enthalpy of $\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}(s)$

Using the same method as described above, the reaction cycle was used to derive a value for the standard molar formation enthalpy of $\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}$. The results are presented in Table 4.

Table 4 Reaction scheme for the standard molar formation enthalpy of $\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}$ at 298.2 K

	Reaction	$\Delta_s H_m^\theta$/ kJ mol^{-1}
1	$[\mathrm{LaCl_3{\cdot}7H_2O}(s)+3\mathrm{Gly}(s)]+A=[\mathrm{LaCl_3{\cdot}3Gly{\cdot}7H_2O}](\mathrm{sln\ in}\ A)$	10.820±0.023
2	$2\mathrm{H_2O(l)}+A=4\mathrm{H_2O}$ (sln in A) (according to [11])	–0.0004
3	$\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}(s)+2\mathrm{H_2O}$ (sln in A)$=[\mathrm{LaCl_3{\cdot}3Gly{\cdot}7H_2O}]$ (sln in A)	15.136±0.021
4	$\mathrm{LaCl_3{\cdot}7H_2O}(s)+3\mathrm{Gly}(s)=\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}(s)+2\mathrm{H_2O}(l)$	–4.356

The solvent A was 2 mol L^{-1} HCl (*aq*); $\Delta H_4=\Delta H_1-\Delta H_2-\Delta H_3$

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

$$\mathrm{LaCl_3{\cdot}7H_2O}(s)+3\mathrm{Gly}(s)\rightarrow\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}(s)+2\mathrm{H_2O}(l) \qquad (2)$$

$$\Delta_r H_m^\theta(2) = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 = -4.356\ \mathrm{kJ\ mol^{-1}}.$$

The standard molar formation enthalpy of $\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}$ has also not been reported. In order to obtain this value, the same method described above was used.

$$\Delta_r H_m^\theta(2) = \Delta_f H_m^\theta[\mathrm{La(Gly)_3Cl_3{\cdot}5H_2O}(s), 298.2\ \mathrm{K}] + 2\Delta_f H_m^\theta[\mathrm{H_2O}(l), 298.2\ \mathrm{K}] -$$

$$-\Delta_f H_m^\theta[\mathrm{LaCl_3{\cdot}7H_2O}(s), 298.2\ \mathrm{K}] - 3\Delta_f H_m^\theta[\mathrm{Gly}(s), 298.2\ \mathrm{K}]$$

according to [9]: $\Delta_f H_m^\theta[\mathrm{H_2O}(l), 298.2\ \mathrm{K}] = -285.83\ \mathrm{kJ\ mol^{-1}}$

$$\Delta_f H_m^\theta[\mathrm{LaCl_3{\cdot}7H_2O}(s), 298.2\ \mathrm{K}] = -3178.6\ \mathrm{kJ\ mol^{-1}}$$

according to [10]: $\Delta_f H_m^\theta$[Gly(s), 298.2 K]= –537.23 kJ mol^{-1}

then, $\Delta_f H_m^\theta$[La(Gly)$_3$Cl$_3$·5H$_2$O(s), 298.2 K]= –4223.0 kJ mol^{-1}

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

Using the same method as described here, a thermochemical cycle was designed as shown in Table 5.

Table 5 Reaction scheme for the standard molar formation enthalpy of La(Ala)$_4$(NO$_3$)$_3$·H$_2$O at 298.2 K

	Reaction	$\Delta_s H_m^\theta$/ kJ mol^{-1}
1	[La(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)]+A=[La(NO$_3$)$_3$·4Ala·6H$_2$O] (sln in A)	30.715±0.001
2	5H$_2$O(l)+A=5H$_2$O (sln in A) (according to [11]	–0.001
3	La(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s)+5H$_2$O (sln in A)= =[La(NO$_3$)$_3$·4Ala·6H$_2$O] (sln in A)	9.463±0.0023
4	La(NO$_3$)$_3$·6H$_2$O(s)+4Ala(s)=La(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s)+5H$_2$O(l)	21.253

The solvent A was 2 mol L^{-1} HCl (aq); $\Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3$

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

$$\mathrm{La(NO_3)_3\cdot 6H_2O}(s)+4\mathrm{Ala}(s)\rightarrow \mathrm{La(Ala)_4(NO_3)_3\cdot H_2O}(s)+5\mathrm{H_2O}(l) \qquad (3)$$

$$\Delta_r H_m^\theta(3) = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 = 21.253 \text{ kJ mol}^{-1}.$$

According to Hess' law:

$$\Delta_r H_m^\theta(3) = \Delta_f H_m^\theta[\mathrm{La(Ala)_4(NO_3)_3\cdot H_2O)}(s), 298.2\text{ K}] + 5\Delta_f H_m^\theta[\mathrm{H_2O}(l), 298.2\text{ K}] -$$

$$-\Delta_f H_m^\theta[\mathrm{La(NO_3)_3\cdot 6H_2O}(s), 298.2\text{ K}] - 4\Delta_f H_m^\theta[\mathrm{Ala}(s), 298.2\text{ K}].$$

according to [9]: $\Delta_f H_m^\theta$[H$_2$O(l), 298.2 K]= –285.83 kJ mol^{-1}.
according to [11]: $\Delta_f H_m^\theta$[La(NO$_3$)$_3$·6H$_2$O(s), 298.2 K]= –3063.65 kJ mol^{-1}.
according to [10]: $\Delta_f H_m^\theta$[Ala(s), 298.2 K]= –563.580 kJ mol^{-1}.

then, $\Delta_f H_m^\theta$[La(Ala)$_4$(NO$_3$)$_3$·H$_2$O(s), 298.2 K]= –3867.57 kJ mol^{-1}.

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