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THERMOCHEMISTRY OF RARE EARTH COMPLEXES $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$ (*Ln*=Pr, Gd)

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The two complexes, $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$ (*Ln*=Pr, Gd), were synthesized and characterized. Using a solution-reaction isoperibol calorimeter, standard enthalpies of reaction of two reactions: $LnCl_3\cdot6H_2O(s)+2Ala(s)+Im(s)+3NaClO_4(s)=$ $=[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3(s)+3NaCl(s)+5H_2O(l)$ (*Ln*=Pr, Gd), at *T*=298.15 K, were determined to be (39.26±0.10) and (5.33±0.12) kJ mol^{-1}, respectively. Standard enthalpies of formation of the two complexes at *T*=298.15 K, $\Delta_f H_m^\ominus\{[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3(s)\}$ (*Ln*=Pr, Gd), were calculated as –(2424.2±3.3) and –(2443.4±3.3) kJ mol^{-1}, respectively.

Keywords: *complex of rare earth, DL-α-alanine, imidazole, solution–reaction calorimetry, standard enthalpy of formation*

Introduction

It is well known that China has plentiful of rare earth resources. Materials based on rare earth have many important applications and have attracted much attention from both industry and academia because of their outstanding properties [1, 2]. Although rare earth ions play very critical roles in biological systems, the mechanisms of rare earth in living systems, especially in enzyme systems, are challenges for medicinal inorganic chemistry and inorganic biochemistry.

Amino acids are basic units of proteins, and they help biological systems perform important biological functions. The imidazole moiety, as part of the side chain in histidine, plays a major role in the biological functions of many peptides and proteins. Substituted imidazoles also comprise an important class of pharmacologically active compounds with a wide range of interesting properties. In the last 3 decades a number of them were discovered and introduced in clinical practice. Members of this class of compounds are known to possess NO synthase inhibition and antifungal, antimycotic, antibiotic, antiulcerative, and CB_1 receptor antagonistic activities [3, 4].

Both amino acids and imidazole are biological ligands binding to many metal ions, but the chelating ability of imidazole is less than that of amino acids. Studies of complexes of rare earth with amino acids and imidazole can help us to understand some aspects of the problems of rare earth in biological systems. Many complexes of rare earth with amino acids were studied using various methods [5–7]. In recent years, some complexes of rare earth with amino acids were synthesized under near physiological conditions [5, 6]. However, the ternary complexes of rare earth with amino acid and imidazole were seldom studied [8, 9]. Aware of the various biological activities of imidazole compounds, we became interested in complexes of rare earth with amino acid and imidazole. Determination of the thermodynamic properties of the complexes cannot only enrich the thermochemical database, but also help to understand some other physico-chemical aspects of these complexes.

In our previous paper, we reported synthesis and calorimetric study of rare earth complexes, $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$ (*Ln*=Sm, Eu, Dy, Er) [9]. In the present study, the complexes of rare earth, $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$ (*Ln*=Pr, Gd), were synthesized and characterized. Standard enthalpies of formation of the two complexes were determined by solution–reaction calorimetry.

Experimental

Materials

KCl (mass fraction above 0.9999), NaCl (mass fraction above 0.999), $NaClO_4$ (mass fraction above 0.998), Pr_6O_{11} and Gd_2O_3 (mass fraction above 0.999), *DL*-α-alanine (mass fraction above 0.990, abbreviated as Ala), imidazole (mass fraction above 0.990, abbreviated as Im), and methanol, HCl, $HClO_4$ and H_2O_2 solutions (analytical grade) were supplied by Shanghai Chemical Reagent Co., Shanghai, P. R. China. $PrCl_3\cdot6H_2O$ and $GdCl_3\cdot6H_2O$ were prepared from the respective oxides, characterized as previously de-

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Table 1 FTIR data (cm^{-1}) for alanine, imidazole and $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$

Compound	ν_{OH}	$\nu_{as(NH_3^+)}$	ν_{CH}	$\nu_{s(COO^-)}$	$\nu_{as(COO^-)}$	$\nu_{Cl–O}$	ν_{NH}	$\nu_{C=N}$
alanine		3090	1458	1412	1592			
imidazole							3097	1667
Pr complex	3429	3135	1485	1425	1575	627, 1085	3142	1630
Gd complex	3415	3130	1490	1428	1572	625, 1084	3145	1635

Table 2 Percentages of experimental (calculated) values for elemental analysis of $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$

Compound	*Ln*/%	C/%	N/%	H/%
$[Pr(Ala)_2(Im)(H_2O)](ClO_4)_3$	20.02 (20.03)	15.32 (15.37)	7.94 (7.97)	2.85 (2.87)
$[Gd(Ala)_2(Im)(H_2O)](ClO_4)_3$	21.81 (21.85)	15.00 (15.01)	7.76 (7.78)	2.81 (2.80)

scribed in detail elsewhere [10], and maintained in desiccators over silica gel before use. KCl, NaCl and $NaClO_4$ were dried in a vacuum at 410 K for 8 h prior to calorimetric experiment. Double-distilled water was used to prepare all of the calorimetric solvents.

Synthesis and characterization of the two complexes

The synthesis and characterization of the two complexes were carried out according to literature [8]. $Ln(ClO_4)_3$ (*Ln*=Pr or Gd), *DL*-α-alanine and imidazole were mixed in a 1:2:1 mole ratio in methanol solution in a water bath, and refluxed for 8–10 h under stirring and heating at T=353 K. The mixed solution was concentrated by slow evaporation to form a precipitate, and the crystals were filtered and washed with ether for three times. The final products were desiccated for 30 days in a desiccator with P_4O_{10} until their masses became constant.

IR spectra were measured with a FT-IR spectrometer (Model Avatar 360, Thermo Nicolet, USA). Elemental analysis (C, H and N) was carried out with an elemental analyzer (Model 1106, Carlo Erba Strumentazione, Italy) and Ln^{3+} content was determined by EDTA titration. The results of FTIR spectroscopic and elemental analysis of the two products were list in Tables 1 and 2, respectively.

As seen in Table 1, the difference of the stretching vibration of the functional groups between free ligands and the complexes observed in the FTIR spectra were very obvious. ν(C=N) of the two complexes shifted to low wave number 37 and 32 cm^{-1} compared to that of free imidazole, respectively. Furthermore, in the metal complexes the amide NH stretch shifted to high wave number 45 and 48 cm^{-1} compared to that of free imidazole, respectively, suggesting complexation and no deprotonation. The existence of the characteristic bands of COO^- and NH_3^+ indicated that the zwitterion form of amino acid did not change before and after complexation. $\nu_{as}(NH_3^+)$ of the two complexes shifted to high wave number 55 and 60 cm^{-1} compared to that of free alanine, respectively. The carboxylate functional groups bands of the metal complexes at 1550–1575 cm^{-1} in the two complexes were assigned to the antisymmetric stretching vibration $\nu_{as}(COO^-)$. The bands in the 1419–1435 cm^{-1} region were the symmetric stretching vibration $\nu_s(COO^-)$. The free alanine, in which $\nu_{as}(COO^-)$ at 1592 cm^{-1} and $\nu_s(COO^-)$ at 1412 cm^{-1}. The difference between the symmetric and asymmetric stretching vibration of the carboxylate group (Δν) observed in the FTIR spectra was a diagnostic tool that provides structural insight into the coordination mode of the carboxylate group. Δν of the two complexes (150 and 144 cm^{-1}) were smaller than that of free alanine (180 cm^{-1}), which indicating bidentate chelating [11]. The strong peaks at about 3420 cm^{-1} suggested the presence of coordination water molecule.

Solution-reaction isoperibol calorimeter

A solution–reaction isoperibol calorimeter constructed in College of Chemistry and Molecular Sciences, Wuhan University, P. R. China, 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, an amplifier, a circuit used as an A/D converter and a personal computer for data acquisition and processing. The inevitable heat transfer and heat generation due to friction were compensated and the adiabatic temperature change (the corrected voltage change) was automatically calculated by the program Solution-Reaction Calorimetry System (SRCS) using the equal area method. More comprehensive description and detailed procedure of the calorimeter can be found in the literature [12]. During the experiments, the water thermostat was maintained at T=(298.15±0.001) K.

In order to verify the reliability of the calorimeter, the 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. The standard enthalpy of solution of KCl in double-distilled water was (17560±21) J mol^{-1}, which was in good agreement with the published values in the literatures [13, 14]. The uncertainty and the inaccuracy of the experimental results were within ±0.3% compared with the recommended reference data.

Determination of standard enthalpies of dissolution

The general thermochemical reaction for measuring the standard enthalpies of reaction was depicted in Fig. 1.

0.0919 g Ala and 0.1896 g $NaClO_4$ were dissolved in 100.0 cm^3 2.0 mol dm^{-3} HCl (aq) at T=298.15 K.

$$[2\text{Ala}(s)+3\text{NaClO}_4(s)]+2.0\ \text{mol dm}^{-3}\ \text{HCl(aq)}\rightarrow \rightarrow\text{Solution A}_1 \quad (1)$$

0.0351 g Im and 0.1834 g $PrCl_3{\cdot}6H_2O$ were dissolved in Solution A_1 at T=298.15 K.

$$[\text{PrCl}_3{\cdot}6\text{H}_2\text{O(s)}+\text{Im}(s)]+\text{Solution A}_1\rightarrow \rightarrow\text{Solution B}_1 \quad (2)$$

0.3630 g $[Pr(Ala)_2(Im)(H_2O)](ClO_4)_3$ and 0.0951 g NaCl was dissolved in 100.0 cm^3 2.0 mol dm^{-3} HCl (aq) at T=298.15 K.

$$\{[\text{Pr(Ala)}_2\text{(Im)(H}_2\text{O)](ClO}_4)_3(s)+3\text{NaCl}(s)\}+ +2.0\ \text{mol dm}^{-3}\ \text{HCl(aq)}\rightarrow\text{Solution C}_1 \quad (3)$$

Calorimetric results of reactions (1), (2) and (3) were listed in Table 3.

Standard enthalpy of reaction of the Gd complex was determined by the same method, and the calorimetric results were listed in Table 3.

Results and discussion

The standard atomic masses recommended by the IUPAC Commission in 2001 [15] were used in the calculation of all molar quantities.

Calculation of standard enthalpy of reaction

According to the general thermochemical reaction and Hess's law, $\Delta_r H_m^\ominus$(Ln) were calculated from the following equation:

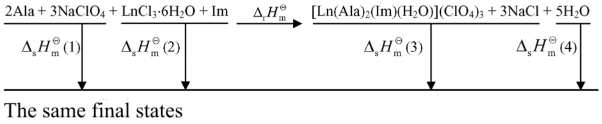

Fig. 1 The general thermochemical cycles for measuring standard enthalpies of reaction

$$\Delta_r H_m^\ominus(\text{Ln}) = \Delta_s H_m^\ominus(\text{Ln1}) + \Delta_s H_m^\ominus(\text{Ln2}) - - \Delta_s H_m^\ominus(\text{Ln3}) - \Delta_s H_m^\ominus(\text{Ln4})$$

where $\Delta_s H_m^\ominus$(Ln1) was standard enthalpy of dissolution of '$2Ala(s)+3NaClO_4(s)$', $\Delta_s H_m^\ominus$(Ln2) was standard enthalpy of dissolution of '$LnCl_3{\cdot}6H_2O(s)+Im(s)$', $\Delta_s H_m^\ominus$(Ln3) was the enthalpy of dissolution of '$[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3+3NaCl(s)$' and $\Delta_s H_m^\ominus$(Ln4) was standard enthalpy of dissolution of '$5H_2O(l)$'. The value of $\Delta_s H_m^\ominus$(Ln4) was very small compared with the other enthalpies of dissolution and can be neglected [16].

Results of standard enthalpies of reaction were summarized in Table 4.

Derivation of standard enthalpy of formation

From standard enthalpies of reaction for the two reactions and various ancillary data listed in Table 5, standard enthalpies of formation of the two complexes were calculated:

$$\Delta_f H_m^\ominus\{[\text{Ln(Ala)}_2\text{(Im)(H}_2\text{O)](ClO}_4)_3\ (s)\}= =\Delta_r H_m^\ominus(\text{Ln})+\Delta_f H_m^\ominus[\text{LnCl}_3{\cdot}6\text{H}_2\text{O}(s)]+2\Delta_f H_m^\ominus[\text{Ala}(s)]+ +\Delta_f H_m^\ominus[\text{Im}(s)]+3\Delta_f H_m^\ominus[\text{NaClO}_4(s)]- -3\Delta_f H_m^\ominus[\text{NaCl}(s)]-5\Delta_f H_m^\ominus[\text{H}_2\text{O}(l)]$$

The final results of standard enthalpies of formation were summarized in Table 6 for comparison. Standard enthalpies of formation of $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$ (*Ln*=Sm, Eu, Dy, Er) can be obtained from the literature [9]. Standard enthalpies of formation of $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3(s)$ (*Ln*=Pr, Sm, Eu, Gd, Dy and Er) in dependence on the atomic number was plotted in Fig. 2. The data were quite similar to each other, but there was an irregularity at the atom Eu.

Table 3 Calorimetric results of $[2Ala(s)+3NaClO_4(s)]$, $[LnCl_3{\cdot}6H_2O(s)+Im(s)]$ and $\{[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3(s)+3NaCl(s)\}$ at T=298.15 K[a]

No.	Reagents	Solvent	Solution	$\Delta_s H_m^\ominus$/kJ mol^{-1}
1	$2Ala(s)+3NaClO_4(s)$	2.0 mol dm^{-3} HCl	A_1	52.17±0.07
2	$Im(s)+PrCl_3{\cdot}6H_2O(s)$	A_1	B_1	–(48.57±0.06)
3	Pr complex(s)+3NaCl(s)	2.0 mol dm^{-3} HCl	C_1	–(35.66±0.05)
4	$2Ala(s)+3NaClO_4(s)$	2.0 mol dm^{-3} HCl	A_2	51.96±0.07
5	$Im(s)+GdCl_3{\cdot}6H_2O(s)$	A_2	B_2	–(58.91±0.08)
6	Gd complex(s)+3NaCl(s)	2.0 mol dm^{-3} HCl	C_2	–(12.28±0.05)

[a] $\Delta_s H_m^\ominus$ was standard enthalpy of dissolution

Table 4 Standard enthalpies of reaction[b]

Reaction (*Ln*)	$\Delta_r H_m^\Theta$ /kJ mol^{-1}
Pr complex	(39.26±0.10)
Gd complex	(5.33±0.12)

[b] $\Delta_r H_m^\Theta$ was standard enthalpy of reaction

Table 5 Ancillary data[c]

Compound	$\Delta_f H_m^\Theta$/kJ mol^{-1}	Reference
$PrCl_3\cdot 6H_2O(s)$	–(2880.7±0.1)	[17]
$GdCl_3\cdot 6H_2O(s)$	–(2866.0±0.1)	[10, 17, 18]
$NaClO_4(s)$	–383.30	[19]
$NaCl(s)$	–411.12	[19]
DL-α-alanine(*s*)	–(572.57±1.61)	[20]
imidazole(*s*)	(49.8±0.6)	[21]
$H_2O(l)$	–(285.830±0.042)	[22, 23]

[c] $\Delta_f H_m^\Theta$ was standard enthalpy of formation

Table 6 Standard enthalpies of formation of $[Ln(Ala)_2(Im)(H_2O)](ClO_4)_3$

Compound	$\Delta_f H_m^\Theta$/kJ mol^{-1}
$[Pr(Ala)_2(Im)(H_2O)](ClO_4)_3(s)$	–(2424.2±3.3)
$[Gd(Ala)_2(Im)(H_2O)](ClO_4)_3(s)$	–(2443.4±3.3)

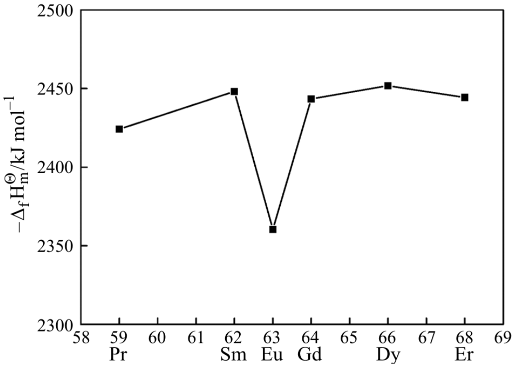

Fig. 2 Standard enthalpies of formation in dependence on the atomic number

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