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Synthesis and calorimetric study of rare earth complexes $[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$ (RE: Sm, Eu, Dy, Er)

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Abstract

The crystals of four complexes of rare earth perchlorate with DL-α-alanine and imidazole were synthesized and characterized. The components of them were determined to be $[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$ (RE: Sm, Eu, Dy, Er) by FT-IR, chemical, elemental and thermal analysis. The enthalpies of dissolution of $[2C_3H_7NO_2(s) + 3NaClO_4(s)]$, $[C_3H_4N_2(s) + RECl_3{\cdot}6H_2O(s)]$ and [3NaCl(s)], $\{[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3(s)\}$ were determined by a solution–reaction isoperibol calorimeter at $T = 298.15$ K, respectively. According to Hess's law, the standard molar enthalpies of reaction of four reactions, $RECl_3{\cdot}6H_2O(s) + 2C_3H_7NO_2(s) + C_3H_4N_2(s) + 3NaCl(s) = [RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3(s) + 3NaCl(s) + 5H_2O(l)$ (RE: Sm, Eu, Dy, Er) were determined to be 4.87 ± 0.20, 7.23 ± 0.19, 0.96 ± 0.27 and 12.88 ± 0.32 kJ mol^{-1}, respectively. The standard molar enthalpies of formation of the four complexes at $T = 298.15$ K, $\Delta_f H_m^{\ominus}$ $\{[Re(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3(s)\}$ (RE: Sm, Eu, Dy, Er), were determined to be $-(2448.1 \pm 3.3)$, $-(2360.3 \pm 3.3)$, $-(2451.8 \pm 3.3)$ and $-(2444.3 \pm 3.3)$ kJ mol^{-1}, respectively.

Keywords: Standard enthalpy of formation; Solution–reaction calorimetry; Complexes of rare earth; DL-α-Alanine; Imidazole

1. Introduction

Biologists, chemists and pharmacologists were interested in the biological effects of rare earth ions and their complexes for a long time [1–3]. The binary systems of rare earth and amino acid have been extensively investigated in recent decades. The ternary complexes of rare earth, amino acid and imidazole have been seldom studied. Imidazole has the activities of antibacterial and anticoagulant, and some medicines, such as metronidazole, ketoconazole and clotrimazole, contain imidazole unit [4]. As a biologically important N-ligand and a segment of histidine, imidazole plays a very significant role in many biological processes. Deep investigations of complexes of metal ions and imidazole are very important in the enzyme simulation. We know that the active centers of many enzymes, such as Zinc enzyme and SOD enzyme, are made of histidine unit and metal ions through coordination effect.

In this paper, the crystals of $[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$ (RE: Sm, Eu, Dy, Er) have been synthesized and characterized. The standard molar enthalpies of formation of the four complexes have been determined and discussed.

2. Experimental

2.1. Chemicals

KCl (mass fraction above 0.9999), RE_2O_3 (RE: Sm, Eu, Dy, Er, mass fraction above 0.995), DL-α-alanine ($C_3H_7NO_2$, mass fraction above 0.990), imidazole ($C_3H_4N_2$, mass fraction above 0.990), $NaClO_4$ (mass fraction above 0.998) and NaCl (mass fraction above 0.999) were purchased from Shanghai Chemical Reagent Co., Shanghai, PR China. $RECl_3{\cdot}6H_2O$ (RE: Sm, Eu, Dy, Er) used for calorimetric determination, were prepared from the respective oxides and characterized as previously described in detail elsewhere [5]. KCl, NaCl and $NaClO_4$ were dried in a vacuum at 410 K for 8 h prior to use. All reagents were maintained in desiccators over phosphorus pentoxide

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

Compound	ν(OH)	$\nu_{as}(NH_3^+)$	ν(CH)	$\nu_s(COO^-)$	$\rho(COO^-)$	$\delta(COO^-)$	ν(NH)	ν(C=N)
Alanine		3090	1458	1412	769	643		
Imidazole							3097	1667
$[Sm(Ala)_2(Im)(H_2O)](ClO_4)_3$	3415	3126	1481	1427	776	622	3146	1629
$[Eu(Ala)_2(Im)(H_2O)](ClO_4)_3$	3406	3145	1491	1424	774	630	3145	1630
$[Dy(Ala)_2(Im)(H_2O)](ClO_4)_3$	3428	3128	1501	1430	772	627	3145	1635
$[Er(Ala)_2(Im)(H_2O)](ClO_4)_3$	3425	3130	1495	1431	772	629	3148	1632

(P_4O_{10}) or silica gel before the calorimetric measurements. Hydrochloric acid (analytical grade) and double-distilled water were used to prepare all of the calorimetric solvents.

2.2. Synthesis and characterization of the four complexes

The synthesis and purification of the four complexes were carried out according to literature [6]. An amount of RE_2O_3 (RE: Sm, Eu, Dy, Er) was dissolved in six molar amount of $HClO_4$ (analytical grade). After the reactions were complete, the methanol solution of two equivalent molar amounts of imidazole with four equivalent molar amounts of DL-α-alanine were added into the solution of $RE(ClO_4)_3$ in a water bath at $T = 353$ K. The mixtures refluxed for 8–10 h. The mixtures were concentrated by evaporation, and the solutions were subsequently cooled and filtered, the crystals were filtered out and washed with ether for three times. Finally, the products were recrystalled from methanol for three times, and the collected crystals were desiccated for 30 days in a desiccator with P_4O_{10} until their masses became constant.

The FT-IR spectra of the four compounds in the range of 4000–400 cm^{-1} were obtained from KBr pellets using a FT-IR spectrophotometer (Model Avatar 360, Thermo Nicolet, USA). As can be observed in Table 1, RE^{3+} (RE: Sm, Eu, Dy, Er) are coordinated by the nitrogen atom ($-NH_2$) and oxygen atoms (COO^-) of DL-α-alanine, as well as by the nitrogen atom (C=N–) of imidazole. The TG-DTA tests were performed in a thermal analyzer (Model Setsys 16, Setaram, France) and under dynamic atmosphere of N_2. The contents of rare earth in the four complexes were determined by EDTA titration, and the element carbon, nitrogen and hydrogen of the four complexes were checked by an element analyzer (Model 1106, Carlo Erba Strumentazione, Italy), which were agreement with the proposed formula established for the four complexes, as shown in Table 2.

2.3. Solution–reaction isoperibol calorimeter

A solution–reaction isoperibol calorimeter constructed in the Laboratory of Thermochemistry, Department of Chemistry, Wuhan University, PR China, was used to determine the enthalpy of dissolution. More comprehensive description and detailed procedure of the calorimeter can be found in the literature [7].

In order 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. The molar 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 [8,9]. The uncertainty and the inaccuracy of the experimental results were within ±0.3% compared with the recommended reference data.

2.4. Determination of the enthalpies of dissolution

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

0.0911 g Ala and 0.1877 g $NaClO_4$ were dissolved in 100.0 cm^3 2.0 mol dm^{-3} HCl(aq) at $T = 298.15$ K.

$$[2\mathrm{Ala(s)} + 3\mathrm{NaClO_4(s)}] + 2.0\,\mathrm{mol\,dm^{-3}\,HCl(aq)} \rightarrow \mathrm{Solution\,A_1} \quad (1)$$

0.0348 g Im and 0.1864 g $SmCl_3{\cdot}6H_2O$ were dissolved in Solution A_1 at $T = 298.15$ K.

$$[\mathrm{SmCl_3 \cdot 6H_2O(s) + Im(s)}] + \mathrm{Solution\,A_1} \rightarrow \mathrm{Solution\,B_1} \quad (2)$$

0.0896 g NaCl was dissolved in 100.0 cm^3 2.0 mol dm^{-3} HCl(aq) at $T = 298.15$ K.

$$[3\mathrm{NaCl(s)}] + 2.0\,\mathrm{mol\,dm^{-3}\,HCl(aq)} \rightarrow \mathrm{Solution\,C_1} \quad (3)$$

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

Compound	RE (%)	C (%)	N (%)	H (%)
$[Sm(Ala)_2(Im)(H_2O)](ClO_4)_3$	21.00 (21.09)	15.05 (15.16)	7.93 (7.86)	2.81 (2.83)
$[Eu(Ala)_2(Im)(H_2O)](ClO_4)_3$	21.12 (21.27)	15.01 (15.13)	7.90 (7.84)	2.81 (2.82)
$[Dy(Ala)_2(Im)(H_2O)](ClO_4)_3$	22.38 (22.41)	15.01 (14.91)	7.68 (7.73)	2.71 (2.78)
$[Er(Ala)_2(Im)(H_2O)](ClO_4)_3$	22.81 (22.92)	14.90 (14.81)	7.61 (7.68)	2.72 (2.76)

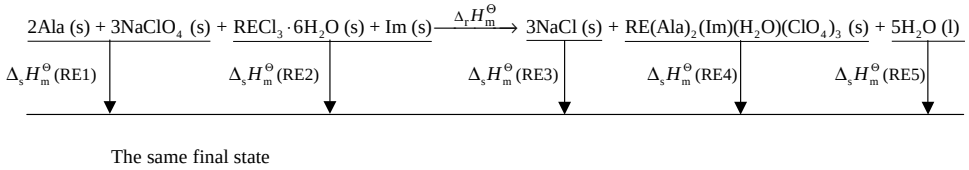

Fig. 1. The general thermochemical cycles for measuring the standard molar enthalpies of reaction.

0.3643 g $[Sm(Ala)_2(Im)(H_2O)](ClO_4)_3$ was dissolved in Solution C_1 at $T = 298.15$ K.

$$[Sm(Ala)_2(Im)(H_2O)](ClO_4)_3(s) + \text{Solution } C_1 \rightarrow \text{Solution } B_1 \quad (4)$$

The calorimetric results of reactions (1), (2), (3) and (4) are listed in Table 3.

The standard molar enthalpies of reaction of the other three reactions were determined by the same method, and the calorimetric results are listed in Table 3.

3. Results and discussion

The standard atomic masses recommended by the IUPAC Commission in 2001 [10] were used in the calculation of all molar quantities.

3.1. Calculation of the standard molar enthalpy of reaction

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

$$\Delta_r H_m^\Theta(RE) = \Delta_s H_m^\Theta(RE1) + \Delta_s H_m^\Theta(RE2) - \Delta_s H_m^\Theta(RE3) - \Delta_s H_m^\Theta(RE4) - \Delta_s H_m^\Theta(RE5)$$

where $\Delta_s H_m^\Theta$ (RE1) was the enthalpy of dissolution of "2Ala(s) + Im(s)", $\Delta_s H_m^\Theta$ (RE2) the enthalpy of dissolution of "$RECl_3{\cdot}6H_2O$(s) + Im(s)", $\Delta_s H_m^\Theta$ (RE3) the enthalpy of dissolution of "3NaCl(s)", $\Delta_s H_m^\Theta$ (RE4) the enthalpy of dissolution of " $[RE(Ala)_2(Im)(H_2O)](ClO_4)_3$(s)", and $\Delta_s H_m^\Theta$ (RE5) was the enthalpy of dissolution of "$5H_2O$(l)". The value of $\Delta_s H_m^\Theta$ (RE5) was very little (about 10^{-5} kJ mol^{-1}) and can be neglected [11].

The results of the standard molar enthalpies of reaction are summarized in Table 4.

3.2. Derivation of the standard molar enthalpy of formation

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

$$\begin{aligned}\Delta_f H_m^\Theta\{&[RE(Ala)_2(Im)(H_2O)](ClO_4)_3(s)\} \\ &= \Delta_r H_m^\Theta(RE) + \Delta_f H_m^\Theta[RECl_3 \cdot 6H_2O(s)] \\ &+ 2\Delta_f H_m^\Theta[Ala(s)] + \Delta_f H_m^\Theta[Im(s)] \\ &+ 3\Delta_f H_m^\Theta[NaClO_4(s)] - 3\Delta_f H_m^\Theta[NaCl(s)] \\ &- 5\Delta_f H_m^\Theta[H_2O(l)]\end{aligned}$$

The final results of the standard molar enthalpies of formation are summarized in Table 6.

Table 3
The calorimetric results of [2Ala(s) + $3NaClO_4$(s)], [$RECl_3{\cdot}6H_2O$(s) + Im(s)], [3NaCl(s)] and $[RE(Ala)_2(Im)(H_2O)](ClO_4)_3$(s) at $T = 298.15$ K[a]

No.	Reagent	Solvent	Solution	$\Delta_s H_m^\Theta$ (kJ mol^{-1})
1	2Ala(s) + $3NaClO_4$(s)	2.0 mol dm^{-3} HCl	A_1	51.82 ± 0.14
2	Im(s) + $SmCl_3{\cdot}6H_2O$(s)	A_1	B_1	−(55.25 ± 0.09)
3	3NaCl(s)	2.0 mol dm^{-3} HCl	C_1	19.99 ± 0.03
4	Sm complex(s)	C_1	B_1	−(28.29 ± 0.12)
5	2Ala(s) + $3NaClO_4$(s)	2.0 mol dm^{-3} HCl	A_2	52.00 ± 0.11
6	Im(s) + $EuCl_3{\cdot}6H_2O$(s)	A_2	B_2	−(59.66 ± 0.07)
7	3NaCl(s)	2.0 mol dm^{-3} HCl	C_2	19.72 ± 0.07
8	Eu complex(s)	C_2	B_2	−(34.61 ± 0.12)
9	2Ala(s) + $3NaClO_4$(s)	2.0 mol dm^{-3} HCl	A_3	51.27 ± 0.05
10	Im(s) + $DyCl_3{\cdot}6H_2O$(s)	A_3	B_3	−(59.43 ± 0.20)
11	3NaCl(s)	2.0 mol dm^{-3} HCl	C_3	20.49 ± 0.08
12	Dy complex(s)	C_3	B_3	−(29.61 ± 0.15)
13	2Ala(s) + $3NaClO_4$(s)	2.0 mol dm^{-3} HCl	A_4	51.67 ± 0.24
14	Im(s) + $ErCl_3{\cdot}6H_2O$(s)	A_4	B_4	−(58.97 ± 0.12)
15	3NaCl(s)	2.0 mol dm^{-3} HCl	C_4	19.97 ± 0.11
16	Er complex(s)	C_4	B_4	−(40.15 ± 0.13)

[a] $\Delta_s H_m^\Theta$ was the standard molar enthalpy of dissolution.

Table 4
The standard molar enthalpies of reaction[a]

Reaction (RE)	$\Delta_r H_m^\Theta$ (kJ mol^{-1})
Sm	(4.87 ± 0.20)
Eu	(7.23 ± 0.19)
Dy	(0.96 ± 0.27)
Er	(12.88 ± 0.32)

[a] $\Delta_r H_m^\Theta$ was the standard molar enthalpy of reaction.

Table 5
Ancillary data[a]

Compound	$\Delta_f H_m^\Theta$ (kJ mol^{-1})	References
$SmCl_3{\cdot}6H_2O$(s)	−(2870.2 ± 0.1)	[5,14,15]
$EuCl_3{\cdot}6H_2O$(s)	−(2784.8 ± 0.1)	[14]
$DyCl_3{\cdot}6H_2O$(s)	−(2870.0 ± 0.1)	[14,15]
$ErCl_3{\cdot}6H_2O$(s)	−(2874.4 ± 0.1)	[5,14,15]
$NaClO_4$(s)	−383.30	[16]
NaCl(s)	−411.12	[16]
DL-α-Alanine(s)	−(572.57 ± 1.61)	[17]
Imidazole(s)	(49.8 ± 0.6)	[18]
H_2O(l)	−(285.830 ± 0.042)	[19,20]

[a] $\Delta_f H_m^\Theta$ was the standard molar enthalpy of formation.

3.3. Discussion

In the experiments, we found that DL-α-alanine and $NaClO_4$ dissolved in 2.0 mol dm^{-3} HCl(aq) was endothermic, but imidazole and $RECl_3{\cdot}6H_2O$ (RE: Sm, Eu, Dy, Er) dissolved in 2.0 mol dm^{-3} HCl(aq) was exothermic, and the difference of absolute quantities of endothermic and exothermic effects are relatively small. So, the magnitude of the signal is relatively small if all four kinds of reactants were dissolved in 2.0 mol dm^{-3} HCl(aq) at same time, and the experimental errors are relatively large. In order to reduce the errors, the enthalpies of dissolution of reactants had to be determined in two groups, respectively. To the same cause, the enthalpy of dissolution of products had also to be determined in two groups, respectively.

The corresponding uncertainties of $\Delta_r H_m^\Theta$ and $\Delta_f H_m^\Theta$ were calculated by the method previously described in the literature [12]. There are no reported associated uncertainties of $\Delta_f H_m^\Theta$ for NaCl and $NaClO_4$, so we did not consider the uncertainties of them in calculation of $\Delta_f H_m^\Theta$ for $[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$. The final results were summarized in Table 6 for comparison. The difference among the standard molar enthalpies of formation of $[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$ (RE: Sm, Eu, Dy, Er) may be attributed to the lanthanide contraction (ionic radius: Sm^{3+} 96.4 pm, Eu^{3+} 95.0 pm, Dy^{3+} 90.8 pm, Er^{3+} 88.1 pm, the data from the literature [13]) and special electron configuration (Sm^{3+} $4f^5$, Eu^{3+} $4f^6$, Dy^{3+} $4f^9$, Er^{3+} $4f^{11}$).

Table 6
The standard molar enthalpies of formation of of $[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$

Compound	$\Delta_f H_m^\Theta$ (kJ mol^{-1})
$[Sm(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$(s)	−(2448.1 ± 3.3)
$[Eu(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$(s)	−(2360.3 ± 3.3)
$[Dy(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$(s)	−(2451.8 ± 3.3)
$[Er(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$(s)	−(2444.3 ± 3.3)

4. Conclusion

In the present work, four complexes were synthesized and characterized, the components of them were determined to be $[RE(C_3H_7NO_2)_2(C_3H_4N_2)(H_2O)](ClO_4)_3$ (RE: Sm, Eu, Dy, Er). The data of standard molar enthalpies of formation of them were determined.

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