

STANDARD MOLAR ENTHALPIES OF FORMATION OF [RE(Gly)₄(Im)(H₂O)](ClO₄)₃ (RE=Eu, Sm)

Y. R. Zhao^{1, 2}, J. X. Dong², Y. Liu^{2, *} and S. S. Qu²

¹Department of Chemistry, Xuchang College, Xuchang 461000, P. R. China

²Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China

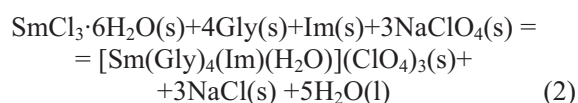
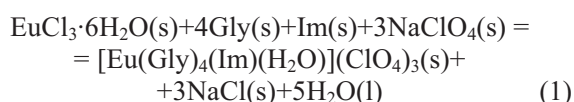
The two complexes, [RE(Gly)₄(Im)(H₂O)](ClO₄)₃(RE = Eu, Sm), have been synthesized and characterized. The standard molar enthalpies of reaction for the following reactions, RECl₃·6H₂O(s)+4Gly(s)+Im(s)+3NaClO₄(s) = [RE(Gly)₄(Im)(H₂O)](ClO₄)₃(s)+3NaCl(s)+5H₂O(l), were determined by solution-reaction calorimetry. The standard molar enthalpies of formation of the two complexes at T = 298.15 K were derived as Δ_fH_m^o{Eu(Gly)₄(Im)(H₂O)}(ClO₄)₃(s) = -(3396.6±2.3) kJ mol⁻¹ and Δ_fH_m^o{Sm(Gly)₄(Im)(H₂O)}(ClO₄)₃(s) = -(3472.7±2.3) kJ mol⁻¹, respectively.

Keywords: complex of rare earth, glycine, imidazole, solution-reaction calorimetry, standard molar enthalpy of formation

Introduction

A lot of binary complexes of rare earth with amino acids have been investigated in recent years [1–5]. However, little research on the ternary complexes of rare earth with amino acids and imidazole has been carried out. Some research work showed that some complexes of rare earth with amino acids possess functions of disinfection, elimination of inflammation, decline the level of blood sugar and anti-cruor, etc. Imidazole is a wreath compound, which presents unique biological activities. Some work showed that ternary complexes of rare earth with amino acids and imidazole have more powerful disinfection [6–8]. They will be widely used in agriculture, medicine, food and many other fields. In order to make a deep research into the complexes and provide a theory support for their bioactivity mechanisms, it is necessary to study their basic thermodynamics properties.

Two complexes, [RE(Gly)₄(Im)(H₂O)](ClO₄)₃(s) (RE = Eu, Sm), were synthesized in this paper. With a solution-reaction isoperibol calorimeter, the standard molar enthalpies of reaction for the following two reactions,



were determined and the standard molar enthalpies of the two complexes were derived.

Experimental

Materials

Chemicals

RE₂O₃ (with purities higher than 99.9%), EuCl₃·6H₂O, SmCl₃·6H₂O, HClO₄, glycine (abbreviated as Gly), and imidazole (abbreviated as Im) were of A. R. grade and obtained from Shanghai Chemical Reagent Co., Shanghai, P. R. China. KCl, with purity higher than 99.99%, was purchased from Shanghai No. 1 Reagent Factory, Shanghai, P. R. China. It was dried in a vacuum oven at 500 K for 6 h prior to use. Double-distilled water was used to prepare 2.0 mol dm⁻³ HCl(aq).

Sample preparation

RE₂O₃ was dissolved into HClO₄ with the molar ratio 1:6 at room temperature. Then the solutions were filtered, and the concentrations of rare earths in the filtrates were titrated by EDTA. The synthesis and purification of the complexes were carried out as described in literature [9–12]. RE(ClO₄)₃, Gly and Im reacted in water according to the molar ratio in a water bath at T=360 K for 7–8 h. The mixtures were concentrated by evaporation, and then be subsequently cooled and filtered. The colatures were placed into a desiccator with 98% sulfuric acid until crystalline products appeared from the solutions. The crystals were filtered out and washed with absolute alcohol for three times. Finally, the products were recrystallized from methanol, and the collected crystals were desiccated in a desiccator with P₄O₁₀ until their masses became constant.

* Author for correspondence: profliuyi@163.com, zhaoyanru58@yahoo.com.cn

Methods

Instrumental methods

The FT-IR spectra of the two crystals in the range of 4000–400 cm^{-1} were obtained from KBr pellets using FT-IR spectrophotometer (Model Avatar 360, Thermo Nicolet, USA). The infrared data for ligands and the complexes were listed in Table 1. The contents of rare earths in the two complexes were determined by EDTA titration. The two complexes were checked by an Elemental Analyzer (Model 1106, Carlo Erba Strumentazione, Italy). The elemental analysis data were presented in Table 2.

The TG-DTA test was performed in a Thermal Analyzer (Model DT-20B) in nitrogen atmosphere with a heating rate of 4 K min^{-1} [13, 14]. Satisfactory results of thermal analysis were obtained. The chemical formula of the complexes were determined as $[\text{RE}(\text{Gly})_4(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3$.

Solution-reaction calorimetry

The solution-reaction isoperibol calorimeter used for this study was constructed in the laboratory and was adapted to determine the enthalpies of solid-liquid and liquid-liquid interactions. The volume of the reaction vessel was 100 cm^3 . The water thermostat was maintained at $T=(298.15\pm 0.001)$ K, and the resolution of temperature measurement was ± 0.0001 K. More comprehensive descriptions and

detailed procedure of the calorimeter can be found in details [15–17].

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. The molar enthalpy of solution of KCl in double-distilled water was (17560 ± 21) J mol^{-1} at $T=298.15$ K, which was in good agreement with the published values in literatures [18, 19]. The uncertainty and the inaccuracy of the experimental results were within $\pm 0.3\%$ compared with the recommended reference data.

Determination of the final states

UV-Vis spectrums and refractive indexes of dissolution products of Solution B₁ and Solution C₁ (or Solution B₂ and Solution C₂) were determined. We discovered the repeatability of UV-Vis spectrums and the equal refractive indexes ($\eta_{25^\circ\text{C}} = 1.3510$, Reaction (1) and $\eta_{25^\circ\text{C}} = 1.3521$, Reaction (2)). Thus, we believed that the values of $\Delta_f H_m^\ominus$ determined by solution-reaction calorimetry were reliable.

Determination of the enthalpies of dissolution

According to Hess's Law, the thermochemical cycles of the two reactions were described in Fig. 1.

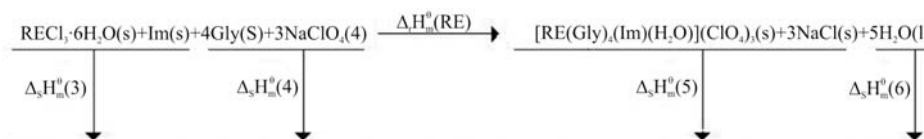
The chosen solvent (2.0 mol dm^{-3} HCl (aq)) can dissolve all the samples completely and rapidly. All

Table 1 Infrared data for $[\text{RE}(\text{Gly})_4(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3$, Gly and Im (cm^{-1})

Compound	$\nu(\text{HO}-)$	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{as}}(\text{NH}^{3+})$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{NH}^{3+})$	$\nu(-\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C}-)$
Gly		1590	3130	1403	1505			
Im						3115	1669	1542
Eu compound	3415	1629	3156	1411	1488	3156	1630–1620	1490–1450
Sm compound	3410	1624	3150	1411	1488	3150	1630–1620	1490–1450

Table 2 Experimental and calculated (calc.) values of elemental analysis for the two complexes

Sample	RE/%	C/%	N/%	H/%
$[\text{Eu}(\text{Gly})_4(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3$	17.91 (18.16)	15.46 (15.78)	9.64 (10.04)	3.08 (3.11)
$[\text{Sm}(\text{Gly})_4(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3$	17.64 (18.00)	15.95 (15.81)	9.59 (10.06)	3.02 (3.11)



The same final state

Fig. 1 Thermochemical cycles for measuring the molar enthalpies of reaction for Reaction (1) and (2)

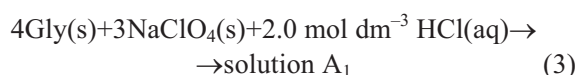
Table 3 The calorimetric results of reactions (3) to (5) at $T = 298.15 \text{ K}^a$

Reagents	Solvent	Solution	$\Delta_s H_m^\ominus / \text{kJ mol}^{-1}$
4Gly(s)+3NaClO ₄ (s)	2.0 mol dm ⁻³ HCl(aq)	A ₁	81.321±2.021
EuCl ₃ ·6H ₂ O(s)+Im(s)	A ₁	B ₁	-54.155±1.336
Eu compound(s)+3NaCl(s)	2.0 mol dm ⁻³ HCl(aq)	C ₁	87.759±1.122
4Gly(s)+3NaClO ₄ (s)	2.0 mol dm ⁻³ HCl(aq)	A ₂	81.776±1.701
SmCl ₃ ·6H ₂ O(s)+Im(s)	A ₂	B ₂	-54.158±1.703
Sm cocmpound(s)+3NaCl(s)	2.0 mol dm ⁻³ HCl(aq)	C ₂	79.028±1.206

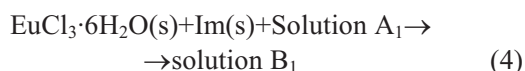
^a $\Delta_s H_m^\ominus$: the molar enthalpy of dissolution, and the uncertainty quoted for $\Delta_s H_m^\ominus$ corresponded to the standard deviation

the reactions were carried out at $T = 298.15 \text{ K}$. The calorimetric results were listed in Table 3, respectively. The detail method was as the following steps:

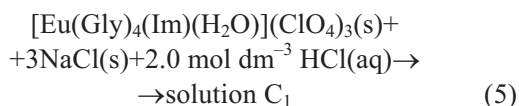
1.9129 mmol Gly(s) and 1.4341 mmol NaClO₄(s) were dissolved in 100.0 cm³ 2.0 mol dm⁻³ HCl(aq)



0.4780 mmol EuCl₃·6H₂O(s) and 0.4774 mmol Im(s) were dissolved in solution A₁



0.4781 mmol [Eu(Gly)₄(Im)(H₂O)](ClO₄)₃(s) and 1.4343 mmol NaCl(s) were dissolved in 100.0 cm³ 2.0 mol dm⁻³ HCl(aq)



Calorimetric results of reactions (3), (4) and (5) were listed in Table 3.

Standard enthalpy of reaction of the Sm 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 [18] were used in the calculation of all molar quantities.

Calculation of the standard molar enthalpy of reaction

The molar enthalpy of dissolution of 2.3944 and 2.3889 mmol H₂O(l) in 100.0 cm³ 2.0 mol dm⁻³ HCl(aq) at $T = 298.15 \text{ K}$ is too small and can be neglected.

$$\begin{aligned} \Delta_s H_m^\ominus (6) &\approx 0 \\ \Delta_r H_m^\ominus (\text{RE}) &= \Delta_s H_m^\ominus (3) + \Delta_s H_m^\ominus (4) - \\ &\quad - \Delta_s H_m^\ominus (5) - \Delta_s H_m^\ominus (6) \end{aligned}$$

Table 4 Standard enthalpies of reaction at $T = 298.15 \text{ K}^b$

Reaction	$\Delta_r H_m^\ominus (\text{RE}) / \text{kJ mol}^{-1}$
Eu Complex	-(60.593±1.541)
Sm Complex	-(51.410±1.554)

^b $\Delta_r H_m^\ominus (\text{RE})$ was standard molar enthalpies of reaction

Table 5 Ancillary data^b

Compound	$\Delta_f H_m^\ominus / \text{kJ mol}^{-1}$	Reference
H ₂ O(l)	-285.830±0.042	[20, 24]
EuCl ₃ ·6H ₂ O(s)	-2784.9±0.1	[20]
SmCl ₃ ·6H ₂ O(s)	-2870.2±0.1	[20]
Glycine(s)	-528.5±0.4	[21]
Imidazole(s)	49.8±0.6	[22]
NaClO ₄ (s)	-383.30	[20, 23]
NaCl(s)	-411.153	[20, 23]

^b $\Delta_f H_m^\ominus$ was the standard molar enthalpy of formation, and the uncertainty quoted for $\Delta_f H_m^\ominus$ corresponded to the standard deviation

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

Derivation of the standard molar enthalpy of formation

The standard molar enthalpies of formation of the two complexes were calculated from the standard molar enthalpies of reaction and various ancillary data were listed in Table 5.

$$\begin{aligned} \Delta_f H_m^\ominus \{[\text{Eu}(\text{Gly})_4(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3\text{(s)}\} &= \\ &= \Delta_f H_m^\ominus (\text{Eu}) + \Delta_f H_m^\ominus (\text{EuCl}_3 \cdot 6\text{H}_2\text{O, s}) + \\ &\quad + 4\Delta_f H_m^\ominus (\text{Gly, s}) + \Delta_f H_m^\ominus (\text{Im, s}) + \\ &\quad + 3\Delta_f H_m^\ominus (\text{NaClO}_4, \text{s}) - 3\Delta_f H_m^\ominus (\text{NaCl, s}) - \\ &\quad - 5\Delta_f H_m^\ominus (\text{H}_2\text{O, l}) = -60.593 + (-2784.9) + \\ &\quad + 4(-528.4) + 49.8 + 3(-383.30 - 3(-411.153)) - \\ &\quad - 5(-285.830) = -3396.6 \pm 2.3 \text{ kJ mol}^{-1} \\ \Delta_f H_m^\ominus \{\text{Sm}[(\text{Gly})_4(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3\text{(s)}\} &= \\ &= \Delta_f H_m^\ominus (\text{Sm}) + \Delta_f H_m^\ominus (\text{SmCl}_3 \cdot 6\text{H}_2\text{O, s}) + \\ &\quad + 4\Delta_f H_m^\ominus (\text{Gly, s}) + \Delta_f H_m^\ominus (\text{Im, s}) + \end{aligned}$$

$$\begin{aligned}
& +3\Delta_f H_m^\ominus(\text{NaClO}_4, \text{s}) - 3\Delta_f H_m^\ominus(\text{NaCl}, \text{s}) - \\
& -5\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}) = -51.410 + (-2870.2) + \\
& +4(-528.4) + 49.8 + 3(-383.30) - 3(-411.153) - \\
& -5(-285.830) = -3472.7 \pm 2.3 \text{ kJ mol}^{-1}
\end{aligned}$$

As the author of literature discussed, we found the same phenomena in the experiments that glycine and NaClO₄ dissolved in solvent *S*₁ was endothermic, but imidazole and RECl₃·6H₂O (*RE* = Sm, Eu) dissolved in solvent *S*₁ was exothermic, and the difference of absolute quantities of endothermic and exothermic effects is relatively small. So, the value of the signal is relatively small if all four kinds of reactants were dissolved in solvent *S*₁ at the 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.

The final results were summarized in Table 6 for comparison. Compared with the standard molar enthalpies of formation of $\Delta_f H_m^\ominus[\text{RE}(\text{Ala})_2(\text{Im})(\text{H}_2\text{O})](\text{ClO}_4)_3(\text{s})$ (*Ala*=alanine, *RE*=Sm, Eu) in literature [25], the difference between the standard molar enthalpies of formation of [RE(Gly)₄(Im)(H₂O)](ClO₄)₃(s) may be attributed to lanthanide contraction (ionic radius: 62, Sm³⁺ 95.8 pm; 63, Eu³⁺ 94.7 pm, the data from the literature [26]) which caused the difference among the standard molar enthalpies of formation of RECl₃·6H₂O(s), [RE(Gly)₄(Im)(H₂O)](ClO₄)₃(s) and [RE(Ala)₂(Im)(H₂O)](ClO₄)₃(s), which can be seen from Table 5 to Table 6 too.

Table 6 the standard molar enthalpies of formation of [RE(Gly)₄(Im)(H₂O)](ClO₄)₃(s) and [RE(Ala)₂(Im)(H₂O)](ClO₄)₃(s) [25]

Compound	$\Delta_f H_m^\ominus/\text{kJ mol}^{-1}$
[Eu(Gly) ₄ (Im)(H ₂ O)](ClO ₄) ₃ (s)	-3396.6±2.3
[Sm(Gly) ₄ (Im)(H ₂ O)](ClO ₄) ₃ (s)	-3472.7±2.3
[Eu(Ala) ₂ (Im)(H ₂ O)](ClO ₄) ₃ (s)	-2360.3±3.3
[Sm(Ala) ₂ (Im)(H ₂ O)](ClO ₄) ₃ (s)	-2448.1±3.3

Acknowledgements

This work was financially supported by the Teaching and Research Award Program for Outstanding Young Professors in High Education Institute, Ministry of Education, P. R. China.

References

- 1 H. C. Aspinall, *Chem. Rev.*, 102 (2002) 1870.
- 2 X. B. Li, A. R. Zhou and W. F. Yu, *J. Chin. Rare Earths*, 21 (2000) 156.

- 3 E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sava and S. Zorzet, *Inorg. Chem.*, 27 (1988) 4099.
- 4 J. Lnanaga, H. Furuno and T. Hayano, *Chem. Rev.*, 102 (2002) 2211.
- 5 B. P. Liu, Z. C. Tan, H. G. Yu, Z. G. Chen, L. X. Sun, X. Z. Lan, P. Liu and Y. Y. Di, *Chin. J. Chem.*, 21 (2003) 396.
- 6 S. Y. Heng, J. L. Chen, W. P. Zhang, X. R. Liu and D. S. Song, *J. Chin. Rare Earth Soc.*, 19 (2001) 80.
- 7 G. J. G. Dunn, *Thermochim. Acta*, 390 (2002) 1.
- 8 A. Palasz and P. J. Czekaj, *Acta Biochim. Pol.*, 47 (2000) 1107.
- 9 Y. M. Dan, Y. R. Zhao, Y. Li and S. S. Qu, *J. Therm. Anal. Cal.*, 84 (2006) 331.
- 10 J. Torres, C. Kremer and E. Kremer, *J. Chem. Soc.*, (2002) 4035.
- 11 S. L. Gao, S. P. Chen, H. Y. Li, X. W. Yang and Q. Z. Shi, *J. Chin. Rare Earth Soc.*, 5 (2001) 385.
- 12 Y. R. Zhao, A. X. Hou, J. X. Dong, Y. Li and S. S. Qu, *Chin. J. Chem.*, 22 (2004) 1267.
- 13 T. S. Martins, J. R. Matos, G. Vicentini and P. C. Isolani, *J. Therm. Anal. Cal.*, 82 (2005) 77.
- 14 T. S. Martins, J. R. Matos, G. Vicentini and P. C. Isolani, *J. Therm. Anal. Cal.*, 86 (2006) 351.
- 15 H. G. Yu, Y. Liu, Z. C. Tan, J. X. Dong, T. J. Zou, X. M. Huang and S. S. Qu, *Thermochim. Acta*, 401 (2003) 217.
- 16 P. O. Dunstan, *J. Therm. Anal. Cal.*, 79 (2005) 355.
- 17 V. P. Nesterenko, *J. Therm. Anal. Cal.*, 80 (2005) 575.
- 18 R. Rychly and V. Pekarek, *J. Chem. Thermodyn.*, 9 (1977) 391.
- 19 R. L. Montgomery, R. A. Melaugh, C. C. Lau, G. H. Meier, H. H. Chan and F. D. Rossini, *J. Chem. Thermodyn.*, 9 (1977) 915.
- 20 D. D. Wagmon, W. H. Evans, V. B. Parker, R. H. Schumm, I. B. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *The NBS tables of Chemical Thermodynamic Properties*, *J. Phys. Chem. Ref. Data* (Suppl. 2), (1982) 11.
- 21 J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds*, Thermodynamics Research Center Data Series, Vol. 1, Thermodynamics Research Center, College Station, 1994.
- 22 P. Jimenez, M. V. Roux and C. Turrion, *J. Chem. Thermodyn.*, 19 (1987) 985.
- 23 J. A. Den, *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, 1985.
- 24 E. Giera, *J. Chem. Thermodyn.*, 32 (2000) 821.
- 25 Y. M. Dan, H. G. Yu, Q. Long, A. X. Hou, Y. Li, S. S. Qu, *Thermochim. Acta*, 419 (2004) 169.
- 26 K. B. Yatsimir and N. K. Davidenko, *Cood. Chem. Rev.*, 27 (1979) 223.

Received: July 25, 2006

Accepted: November 1, 2006

OnlineFirst: February 26, 2007

DOI: 10.1007/s10973-006-7900-z