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Synthesis and determination of standard molar enthalpies of formation for complexes of rare earth isothiocyanates with alanine

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Abstract

Four solid complexes of rare earth isothiocyanates with alanine were prepared. They were characterized by chemical analysis, elemental analysis, infrared spectra, X-ray powder diffraction and TG analysis. Their chemical formulae were found to be $RE(NCS)_3 \cdot 3Ala$, where RE are La, Ce, Pr and Nd, and Ala is *dl*-α-alanine. The integral heats of solution of $RE(NCS)_3 \cdot 7H_2O$ in aqueous alanine solution, of $RE(NCS)_3 \cdot 3Ala$ in water and of alanine in water were measured calorimetrically at 298.15 K. By means of a thermochemical cycle suggested in this paper, the standard molar enthalpies of formation for $RE(NCS)_3 \cdot 3Ala(c)$ were obtained and their lattice energies were calculated.

INTRODUCTION

The rare earth elements are widely used as spectroscopic probes in systems of biological importance [1]. Studies on the coordination effects of rare earth elements with amino acids that form proteins are of great importance in researching the physiological effects of rare earth elements in biological systems. Some solid complexes of rare earth compounds with glycine have been prepared [2, 3]. In the previous works [4, 5], we studied the complexes of rare earth isothiocyanates with glycine. In this paper, four new solid complexes of rare earth isothiocyanates with alanine, $RE(NCS)_3 \cdot 3Ala$, were prepared.

We suggest the following thermochemical cycle for deriving the standard molar enthalpies of formation for the complexes $RE(NCS)_3 \cdot 3Ala$.

$$RE(NCS)_3 \cdot 7H_2O(c) + 3Ala \cdot 800H_2O(aq) \xrightarrow{\Delta H_1} RE(NCS)_3 \cdot 3Ala \cdot 807H_2O(aq) \quad (1)$$

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$$RE(NCS)_3 \cdot 3Ala(c) + 807H_2O(l) \xrightarrow{\Delta H_2} RE(NCS)_3 \cdot 3Ala \cdot 807H_2O(aq) \tag{2}$$

$$Ala(c) + 800/3H_2O(l) \xrightarrow{\Delta H_3} (3Ala \cdot 800H_2O)/3(aq) \tag{3}$$

eqn. (1) + 3 eqn. (3) − eqn. (2) → eqn. (4)

$$RE(NCS)_3 \cdot 7H_2O(c) + 3Ala(c) \xrightarrow{\Delta H_4} RE(NCS)_3 \cdot 3Ala(c) + 7H_2O(l) \tag{4}$$

$$\Delta H_4 = \Delta H_1 + 3\Delta H_3 - \Delta H_2$$

$$\begin{aligned}&\Delta H_f^\circ RE(NCS)_3 \cdot 3Ala(c)\\ &\quad = \Delta H_4 + \Delta H_f^\circ RE(NCS)_3 \cdot 7H_2O(c)\ [6] + 3\Delta H_f^\circ Ala(c)\ [7]\\ &\qquad - 7\Delta H_f^\circ H_2O(l)\ [8]\end{aligned}$$

EXPERIMENTAL

Purification of reagents and synthesis of complexes

Alanine was recrystallized twice from distilled water. The complexes $RE(NCS)_3 \cdot 7H_2O$ (RE are La, Ce, Pr, Nd) were prepared as previously described [6].

The complexes $RE(NCS)_3 \cdot 3Ala$ were prepared in the following steps. $RE(NCS)_3 \cdot 7H_2O$ and alanine (in molar ratio 1:3) were dissolved separately in distilled water; each $RE(NCS)_3 \cdot 7H_2O$ was mixed with the alanine solution, and the mixed solutions were then concentrated at 50–55°C. When the solutions became sticky, absolute alcohol was added, and then the precipitates appeared. The precipitates were filtered off, washed with absolute alcohol and dried over phosphorus pentoxide in a desiccator until their weights became constant.

Component analysis and physical measurements

The RE^{3+} content in the complexes was determined by EDTA titration. The NCS^- content was determined by Volhard's method. The contents of C, H and N in the complexes were determined by a Perkin-Elmer 240C elemental analyser (USA).

Infrared spectra were taken on a Nicolet 20SX IR spectrophotometer (USA) using the KBr disc technique.

The X-ray powder diffraction analyses of the complexes, $RE(NCS)_3 \cdot 3Ala$, and the corresponding hydrates, $RE(NCS)_3 \cdot 7H_2O$, were carried out on a D/Hax-rA X-ray diffractometer (Japan) with Cu radiation and identical conditions.

Thermogravimetric analyses of the complexes were performed on a Perkin-Elmer TGS-2 (USA), with a nitrogen flow rate of 20 ml min^{-1}, in the temperature range 40–900°C and with a linear heating rate of 5.00°C min^{-1}.

Calorimeter and calorimetric experiments

A modified RD-1 heat-conducting automatic calorimeter (The Scientific Instruments Factory of Sichuan University, People's Republic of China) was used for the calorimetric measurements. Heat changes of up to 2 J could be measured exactly. Details of the apparatus, principles and calorimetry of the calorimeter have been published elsewhere [6, 9].

The reliability of the calorimetric system was monitored in the present experiments by measuring the integral heat of solution of 1 mole of KCl (Merck) in 200 moles of H_2O at 298.15 K. The measured value is 17.64 ± 0.07 kJ mol^{-1}, which is consistent with the literature value of 17.524 ± 0.028 kJ mol^{-1} [10].

According to the thermochemical cycle mentioned above, we measured the integral heats of solution of $RE(NCS)_3 \cdot 7H_2O$ in aqueous alanine solution (ΔH_1), of $RE(NCS)_3 \cdot 3Ala$ in water (ΔH_2) and of alanine in water (ΔH_3).

The experimental results in this paper were expressed as $x = \bar{x} \pm 2\sigma_a$. The results determined indirectly were obtained by transfer formulae of standard uncertainty. ΔH_1, ΔH_2 and ΔH_3 were generally measured nine times.

RESULTS AND DISCUSSION

Results of component analysis and physical measurements

The results of the component analyses of the complexes are given in Table 1. The formulae weights of all four complexes agree with the general formula $RE(NCS)_3 \cdot 3Ala$.

The IR wavenumbers of some group vibrations in the complexes and of free alanine are listed in Table 2. The data in Table 2 show that the IR

TABLE 1

The results of component analysis and elemental analysis of $RE(NCS)_3 \cdot 3Ala$

RE	RE (%)		NCS (%)		C (%)		H (%)		N (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
La	23.93	23.83	30.02	29.95	24.83	24.80	3.65	3.58	14.48	14.72
Ce	24.06	24.01	29.96	30.00	24.78	24.85	3.64	3.60	14.45	14.81
Pr	24.19	24.10	29.92	30.01	24.75	25.08	3.63	3.61	14.43	14.21
Nd	24.62	24.28	29.75	29.44	24.61	24.34	3.61	3.65	14.35	14.67

TABLE 2

Wavenumbers (cm^{-1}) of some group vibrations in the complexes RE(NCS)$_3$ · 3Ala and alanine

Approximate description of mode	Ala [11]	RE				Intensity
		La	Ce	Pr	Nd	
Vibrations of NH_3^+ group of alanine						
Stretch		3118	3086	3087	3107	s
		3081			3084	
Asymmetric bend	1623	1665	1668	1670	1671	s
		1623	1622	1623	1625	
Symmetric bend	1534	1575	1563	1575	1569	s
		1565		1565		
Rock	1113	1114	1113	1114	1111	m
Twist	492	533	534	534	535	m
Vibrations of COO^- group of alanine						
Asymmetric stretch	1597	1665	1668	1670	1671	s
		1606	1606	1605	1605	
Symmetric stretch	1412	1422	1421	1422	1421	s
Bend	648	637	635	637	637	w
Vibrations of CH_3 group of alanine						
Asymmetric bend	1455	1488	1487	1488	1492	s
		1470	1470		1465	
Symmetric bend	1355	1351	1351	1351	1350	s
		1371				
Rock	1026	985	984	985	985	m
Vibrations of CH group of alanine						
Bend	1308	1302	1302	1303	1302	m
Vibrations of $C-N^+$ group of alanine						
Asymmetric bend	1148	1201	1201	1201	1202	m
Symmetric bend	918	928	928	928	928	w
	852	844	843	844	844	
Vibrations of NCS^- group						
Stretch of C≡N		2071	2072	2074	2071	s
Bend		474	473	473	473	w
Vibrations of RE–O						
Stretch		407	406	407	405	w

group vibrations occur in all four complexes which indicates that the structures of the four complexes are similar.

The data of Table 2 also indicate that the characteristic frequencies of $-NH_3^+$ and $-COO^-$ of alanine appear in both the free and complexed forms; alanine retains its zwitterion structure in these complexes. This excludes the possibility of the coordination of the nitrogen in alanine to the rare earth cations.

The frequencies at $\approx 2070\,\mathrm{cm}^{-1}$ and $\approx 475\,\mathrm{cm}^{-1}$ prove that in the complexes, the NCS^- groups are coordinated through the nitrogen to the rare earth cations [12].

The anti-symmetric stretch of carboxylic group of alanine in its complexes shows a shoulder in addition to the main peak. This could be due to more than one kind of binding of oxygen in complexes with rare earth cations, which may be achieved by polymerization of the monomer species.

Comparing the X-ray diffraction data of $La(NCS)_3 \cdot 7H_2O$ and $La(NCS)_3 \cdot 3Ala$ we can conclude that the two compounds belong to different phases.

The TG results show that all the four $RE(NCS)_3 \cdot 3Ala$ complexes begin to decompose at 136–170°C. The TG results of the hydrates $RE(NCS)_3 \cdot 7H_2O$ show that they begin to decompose at about 50°C. Therefore, we can conclude that the complexes $RE(NCS)_3 \cdot 3Ala$ are, in fact, formed.

Results of calorimetric experiments

The experimental data obtained for the integral heats ΔH_1, ΔH_2, and ΔH_3 in the thermochemical cycle mentioned above, and the calculated total heats of reaction, ΔH_4, are summarized in Table 3.

The standard molar enthalpies of formation of the complexes, $RE(NCS)_3 \cdot 3Ala$, were calculated using the values of ΔH_4 and the data below: the results are given in Table 4.

$\Delta H_f^\circ \mathrm{Ala(c)} = -563.6 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$ [7]

$\Delta H_f^\circ \mathrm{H_2O(l)} = -285.83\,\mathrm{kJ\,mol^{-1}}$ [8]

TABLE 3

The results of ΔH_1, ΔH_2, ΔH_3 and ΔH_4 ($\mathrm{kJ\,mol^{-1}}$)

RE	ΔH_1	ΔH_2	ΔH_3	ΔH_4
La	17.59 ± 0.11	5.98 ± 0.02	9.50 ± 0.05	40.11
Ce	18.20 ± 0.07	8.51 ± 0.04	9.50 ± 0.05	38.19
Pr	18.43 ± 0.17	7.66 ± 0.06	9.50 ± 0.05	39.27
Nd	18.65 ± 0.12	8.41 ± 0.06	9.50 ± 0.05	38.74

TABLE 4

The results of standard molar enthalpies of formation ΔH_f° (kJ mol^{-1}) and lattice energies ΔU_L° (kJ mol^{-1}) of the complexes RE(NCS)$_3$ · 3Ala

Re	ΔH_f° RE(NCS)$_3$ · 7H$_2$O(c)	ΔH_f° RE^{3+}(g)	ΔH_f° Re(NCS)$_3$ · 3Ala(c)	ΔU_L° RE(NCS)$_3$ · 3Ala(c)
La	−2491.7	3905.6	−2141.6	−4308.4
Ce	−2483.0	3958.7	−2134.8	−4354.7
Pr	−2488.3	4003.5	−2139.0	−4403.7
Nd	−2479.2	4042.5	−2130.5	−4434.2

Using the standard molar enthalpies of formation of RE(NCS)$_3$ · 3Ala and the relative data in the references, we also calculated the lattice energies ΔU_L° of RE(NCS)$_3$ · 3Ala. The results are summarized in Table 4.

$$\mathrm{RE^{3+}(g) + 3NCS^-(g) + 3Ala(g) \xrightarrow{\Delta H_L^\circ} RE(NCS)_3 \cdot 3Ala(c)}$$

$$\begin{aligned}\Delta U_L^\circ &= \Delta H_L^\circ - \Delta nRT\\ &= \Delta H_f^\circ \mathrm{RE(NCS)_3 \cdot 3Ala(c)} - 3\Delta H_f^\circ \mathrm{Ala(g)}\\ &\quad - 3\Delta H_f^\circ \mathrm{NCS^-(g)} - \Delta H_f^\circ \mathrm{RE^+(g)} - \Delta nRT\end{aligned}$$

In the above equation, $\Delta n = -7$, $R = 8.314$ J mol^{-1} K^{-1}, ΔH_f°NCS$^-$(g) = −81.71 kJ mol^{-1} [6], $T = 298.15$ K; ΔH_f°RE^{3+}(g) [6] are listed in Table 4.

$$\mathrm{Ala(c) \xrightarrow{\Delta H_s^\circ} Ala(g)}$$

$$\Delta H_s^\circ = 17.1 \text{ kcal mol}^{-1} = 71.5 \text{ kJ mol}^{-1} \text{ [13]}$$

$$\Delta H_f^\circ \mathrm{Ala(c)} = -563.6 \text{ kJ mol}^{-1} \text{ [7]}$$

Thus,

$$\Delta H_f^\circ \mathrm{Ala(g)} = -492.1 \text{ kJ mol}^{-1}.$$

The data in Table 4 suggest that the lattice energies $-\Delta U_L^\circ$ are inversely proportional to the radii of the rare earth cations.

REFERENCES

1 R.B. Martin and F.S. Richardson, Q. Rev. Biophys., 12 (1979) 181.
2 B.S. Mathur and T.S. Srivastava, J. Inorg. Nucl. Chem., 32 (1970) 3277.
3 Wu Ji-Gui, Deng Ru-Wen, Wang Liu-Fang and Yu Ming, J. Lanzhou Univ., 20(3) (1984) 69 (in Chinese).
4 Yin Jing-Zhi, Jiang Ben-Gao and Yang Shu-Rong, Chem. J. Chinese Univ., 6(1) (1990) 56 (in English).
5 Shu-Rong Yang, Jian-Hua Zhang, Ben-Gao Jiang and Zhao-He Yang, Thermochim. Acta, 176 (1991) 209.

6 Jing-Zhi Yin, Ben-Gao Jiang, Tong-Shan Sun and Yu-Feng Liu, Thermochim. Acta, 123 (1988) 43.

7 J.B. Pedley, R.D. Naylor and S.P. Kirby, Thermochemical Data of Organic Compounds, 2nd edn., Chapman and Hall, London, 1986, p. 174.

8 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, Selected values of chemical thermodynamic properties, Natl. Bur. Stand. (U.S.), Tech. Note, 270-3, U.S. Department of Commerce, Washington, DC, 1968.

9 An-Min Tian, Zi-Ming Qin, Xian-Cheng Zeng, Shu-Guang Zhan and Yu Deng, Chem. J. Chinese Univ., 2(1981), 244, (in Chinese).

10 R. Rychly and V. Pekarek, J. Chem. Thermodyn., 9 (1977) 391.

11 K. Fukushima, T. Onishi, T. Shimanouchi and S. Mizushima, Spectrochim. Acta, 15 (1959) 236.

12 A. Sabatini and I. Bertini, Inorg. Chem., 4 (1965) 959.

13 J.A. Dean, Handbook of Organic Chemistry, McGraw-Hill, New York, 1987, p. 5.