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THERMAL BEHAVIOUR OF RE(HIS)$(NO_3)_3 \cdot H_2O$

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Abstract

The thermal decomposition behaviour of the complexes of rare earth metals with histidine: RE(His)$(NO_3)_3 \cdot H_2O$ (*RE*=La–Nd, Sm–Lu and Y; *His*=histidine) was investigated by means of TG-DTG techniques. The results indicated that the thermal decomposition processes of the complexes can be divided into three steps. The first step is the loss of crystal water molecules or part of the histidine molecules from the complexes. The second step is the formation of alkaline salts or mixtures of nitrates with alkaline salts after the histidine has been completely lost from the complexes. The third step is the formation of oxides or mixtures of oxides with alkaline salts. The results relating to the three steps indicate that the stabilities of the complexes increase from La to Lu.

Keywords: *L*-α-histidine, rare earth, thermal decomposition, thermal stability

Introduction

Rare earth (RE) ions possess special functions in biological organisms, and α-amino acids are the basic units of proteins. In order to explore the metabolism and biological effects of the rare earth ions in biological organisms, studies on the coordination behaviour of rare earth salts with amino acids have been become popular in bio-inorganic chemistry in the past twenty years. Wang Ruiyao [1], Ma Aizeng [2] and Gao Shengli [3] reported the structures, synthesis and properties of the complexes of rare earths with amino acids in detail. However, studies on the complexes of rare earths with histidine have rarely been reported [4, 5].

In the present work, a series of solid complexes RE(His)$(NO_3)_3 \cdot H_2O$ (which have not been reported previously) were prepared, and their thermal decomposition processes were investigated by using TG-DTG techniques. The thermal stabilities of the complexes were determined.

Experimental

Preparation and composition of the complexes

$RE(NO_3)_3 \cdot nH_2O$ and *L*-α-histidine (in a mole ratio of 1:1) were dissolved in water (pH≈6.5), and reacted together on a water-bath, and the mixture was concentrated until a crystal membrane formed on the surface. It was then placed in a desic-

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cator containing concentrated H_2SO_4 until crystals separated out. These were filtered off and washed with a little alcohol (95%) and then with acetone. The crystals were next placed in a desiccator containing P_4O_{10} until the mass of the crystals became constant. The products were powders. The analytic results on the compositions are given in Table 1.

Experimental apparatus and conditions

TG and DTG data were obtained simultaneously by using a Perkin Elmer thermogravimetric analyser. All TG-DTG tests were carried out under a dynamic atmosphere of dry oxygen at a flow rate of 60 ml min^{-1}. The heating rate used was 10 deg min^{-1}. Sample masses were about 1 mg.

The IR spectra of the intermediates and final products of heating of the complexes were obtained with the use of an IR-440 Model Infrared Spectrophotometer (KBr Paller) (Japan).

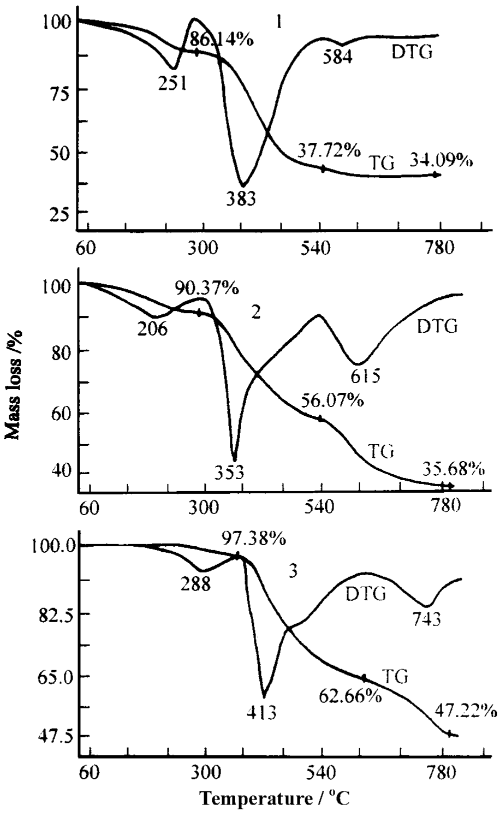

Fig. 1 TG-DTG curves for the complexes; 1 – $Pr(His)(NO_3)_3 \cdot H_2O$; 2 – $Dy(His)(NO_3)_3 \cdot H_2O$ and 3 – $Yb(His)(NO_3)_3 \cdot H_2O$

Table 1 Analytical results on compositions of the complexes (%)

Complex	RE		His		C		H		N	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.
$La(His)(NO_3)_3 \cdot H_2O$	27.57	27.89	31.17	31.15	14.21	14.47	2.14	2.23	16.92	16.87
$Ce(His)(NO_3)_3 \cdot H_2O$	28.22	28.06	32.28	31.07	14.07	14.43	2.12	2.22	16.89	16.83
$Pr(His)(NO_3)_3 \cdot H_2O$	27.91	28.18	30.90	31.03	14.10	14.41	2.07	2.22	16.72	16.80
$Nd(His)(NO_3)_3 \cdot H_2O$	28.53	28.65	30.72	30.82	14.02	14.32	2.03	2.20	16.54	16.69
$Sm(His)(NO_3)_3 \cdot H_2O$	29.54	29.51	30.65	30.45	13.98	14.14	2.05	2.18	16.28	16.49
$Eu(His)(NO_3)_3 \cdot H_2O$	29.57	29.73	30.14	30.36	13.92	14.10	1.99	2.17	16.16	16.44
$Gd(His)(NO_3)_3 \cdot H_2O$	30.44	30.45	29.96	30.04	14.14	13.95	2.32	2.15	16.03	16.27
$Tb(His)(NO_3)_3 \cdot H_2O$	30.91	30.67	30.07	29.95	14.05	13.91	2.20	2.14	16.31	16.22
$Dy(His)(NO_3)_3 \cdot H_2O$	31.23	31.15	29.40	29.74	13.89	13.81	2.24	2.13	16.24	16.11
$Ho(His)(NO_3)_3 \cdot H_2O$	31.77	31.47	29.44	29.60	13.64	13.75	2.11	2.12	16.07	16.03
$Er(His)(NO_3)_3 \cdot H_2O$	31.42	31.77	29.43	29.47	13.78	13.69	1.96	2.11	15.82	15.96
$Tm(His)(NO_3)_3 \cdot H_2O$	31.54	31.99	29.31	29.33	13.50	13.65	1.99	2.10	16.02	15.91
$Yb(His)(NO_3)_3 \cdot H_2O$	32.43	32.51	28.83	29.51	13.38	13.54	1.89	2.08	15.63	15.79
$Lu(His)(NO_3)_3 \cdot H_2O$	32.51	32.76	29.01	29.05	13.29	13.49	1.94	2.08	15.80	15.73
$Y(His)(NO_3)_3 \cdot H_2O$	19.82	19.84	34.25	34.63	15.96	16.08	2.53	2.47	18.84	18.75

RE^{3+} was determined complexometrically with EDTA, while His was analysed by the formalin method. Before it was titrated, the RE^{3+} was removed by precipitation with $K_2C_2O_4$. Carbon, hydrogen and nitrogen analyses were performed on a model 1106 elemental analyzer (Italy)

Results and discussion

Figure 1 presents the TG-DTG curves of the complexes $Pr(His)(NO_3)_3 \cdot H_2O$ (1), $Dy(His)(NO_3)_3 \cdot H_2O$ (2) and $Yb(His)(NO_3)_3 \cdot H_2O$ (3).

The TG curves of the other complexes are shown in Fig. 2. For comparison of the thermal behaviour of the complexes, the TG curves of complexes (1)–(3) in Fig. 1 are also shown in Fig. 2. The data on the decomposition products, decomposition temperatures and residue amounts obtained from Fig. 2 are listed in Table 2.

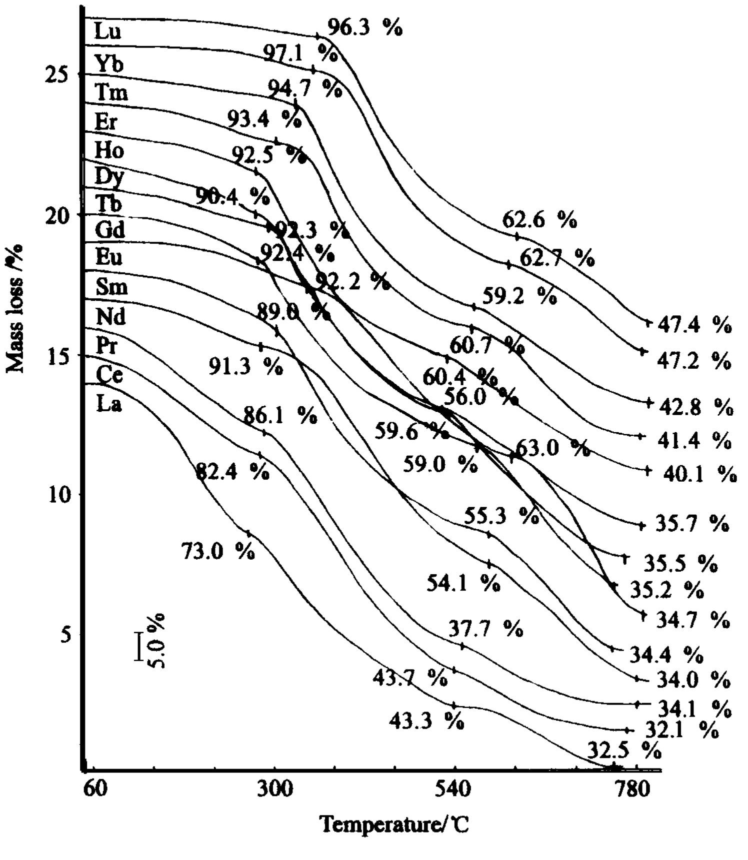

Fig. 2 TG curves for the complexes in an atmosphere of oxygen

Table 2 and Figs 1 and 2 allow the following observations:

1. The mass loss values in the processes of thermal decomposition are close to the calculated values. The compound listed in Table 2 are presumed decomposition products.

2. The thermal decomposition processes are similar for all complexes. They can be divided into three steps. The first step is the loss of crystal water or part of the his-

Table 2 Data on thermal decomposition of the complexes

Complex	Product Decomp. temp./°C Residue/%*		
$La(His)(NO_3)_3 \cdot H_2O$	$La(His)_{0.25}(NO_3)_3$ 51–186–271 73.0(73.0)	$LaONO_3$ 271–368–537 43.3(43.6)	La_2O_3 537–577–750 32.5(32.7)
$Ce(His)(NO_3)_3 \cdot H_2O$	$Ce(His)_{0.55}(NO_3)_3$ 51–201–288 82.4(82.4)	$CeONO_3$ 288–371–540 43.7(43.6)	CeO_3 540–581–776 34.0(34.5)
$Pr(His)(NO_3)_3 \cdot H_2O$	$Pr(His)_{0.67}(NO_3)_3$ 51–251–291 86.1(86.2)	$3PrONO_3 \cdot Pr_6O_{11}$ 291–383–551 37.7(37.3)	Pr_6O_{11} 551–584–783 34.1(34.9)
$Nd(His)(NO_3)_3 \cdot H_2O$	$Nd(His)_{0.88}(NO_3)_3$ 51–226–288 91.3(91.2)	$Nd(NO_3)_3 \cdot NdONO_3$ 288–400–591 54.1(54.9)	Nd_2O_3 591–678–783 34.0(33.4)
$Sm(His)(NO_3)_3 \cdot H_2O$	$Sm(His)_{0.76}(NO_3)_3$ 51–220–300 89.0(89.1)	$Sm(NO_3)_3 \cdot SmONO_3$ 300–401–587 55.3(55.4)	Sm_2O_3 587–621–753 34.4(34.2)
$Eu(His)(NO_3)_3 \cdot H_2O$	$Eu(His)_{0.85}(NO_3)_3$ 51–286–350 92.2(91.9)	$5Eu(NO_3)_3 \cdot EuONO_3$ 350–428–621 63.0(62.6)	Eu_2O_3 621–735–792 34.7(34.4)
$Gd(His)(NO_3)_3 \cdot H_2O$	$Gd(His)_{0.86}(NO_3)_3$ 51–158–290 92.4(92.3)	$2Gd(NO_3)_3 \cdot GdONO_3$ 290–375–578 59.0(59.5)	Gd_2O_3 578–611–756 35.2(35.1)
$Tb(His)(NO_3)_3 \cdot H_2O$	$Tb(His)_{0.86}(NO_3)_3$ 51–223–300 92.3(92.3)	$2Tb(NO_3)_3 \cdot TbONO_3$ 300–411–540 59.6(59.6)	Tb_2O_3 540–606–774 35.5(35.3)
$Dy(His)(NO_3)_3 \cdot H_2O$	$Dy(His)_{0.80}(NO_3)_3$ 51–206–285 90.4(90.6)	$Dy(NO_3)_3 \cdot DyONO_3$ 285–353–531 56.1(56.5)	Dy_2O_3 531–615–794 35.7(35.8)
$Ho(His)(NO_3)_3 \cdot H_2O$	$Ho(His)_{0.67}(NO_3)_3$ 51–220–291 92.5(92.7)	$2Ho(NO_3)_3 \cdot HoONO_3$ 291–360–540 60.4(60.1)	$HoONO_3 \cdot Ho_2O_3$ 540–653–801 40.1(39.5)
$Er(His)(NO_3)_3 \cdot H_2O$	$Er(His)_{0.90}(NO_3)_3$ 51–230–310 93.4(93.6)	$2Er(NO_3)_3 \cdot ErONO_3$ 310–381–568 60.7(60.3)	$2ErONO_3 \cdot Er_2O_3$ 568–678–791 41.4(41.5)
$Tm(His)(NO_3)_3 \cdot H_2O$	$Tm(His)_{0.97}(NO_3)_3$ 51–238–343 94.7(94.5)	$3Tm(NO_3)_3 \cdot 2TmONO_3$ 343–382–577 59.2(59.0)	$3TmONO_3 \cdot Tm_2O_3$ 577–700–793 42.8(42.5)
$Yb(His)(NO_3)_3 \cdot H_2O$	$Yb(His)(NO_3)_3$ 51–288–360 97.1(96.6)	$3Yb(NO_3)_3 \cdot YbONO_3$ 360–413–621 62.7(62.4)	$YbONO_3$ 621–743–796 47.4(47.2)

Table 2 Continued

Complex	Product Decomp. temp./°C Residue/%*		
$Lu(His)(NO_3)_3\cdot H_2O$	$Lu(His)(NO_3)_3$	$3Lu(NO_3)_3\cdot LuONO_3$	$LuONO_3$
	51–290–360	360–420–625	625–752–801
	96.3(96.6)	62.6(62.5)	47.4(47.3)
$Y(His)(NO_3)_3\cdot H_2O$	$Y(His)_{0.88}(NO_3)_3$	$Y(NO_3)_3\cdot YONO_3$	$YONO_3\cdot Y_2O_3$
	51–220–301	301–325–540	540–550–731
	84.3(84.3)	49.3(49.3)	29.0(29.2)

*The data in brackets are calculated values

tidine from the complexes. The second step is the formation of alkaline salts or mixtures of nitrates with alkaline salts after the histidine has been lost completely from the complexes. The third step is the formation of oxides or mixtures of oxides with alkaline salts.

3. The decomposition process for the complex $Y(His)(NO_3)_3\cdot H_2O$ is similar to those for the heavy rare earth series.

4. The results relating to the three steps indicate that the thermal stabilities of the complexes increase from La to Lu.

In order to examine the decomposition mechanism mentioned above, the intermediates and final products of the thermal decompositions of the complexes were identified via IR spectrophotometry and the solution properties in water. When the total crystal water or part of the histidine was lost from the complexes, the products dissolved in water; the IR spectra of the products were then similar to those of the complexes. The compounds mRE$(NO_3)_3\cdot n$REONO$_3$ were formed when the histidine was lost completely; it can be seen that a proportion of the compounds was soluble, and the IR spectra exhibit the characteristic peaks of the anhydrous salts and alkaline

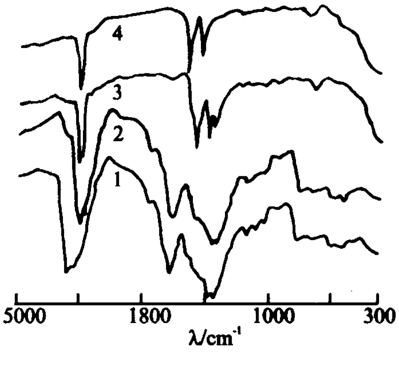

Fig. 3 IR spectra of the complex $Pr(His)(NO_3)_3\cdot H_2O$ at different stages during the thermal decomposition: step 1 – $Pr(His)(NO_3)_3\cdot H_2O$; step 2 – $Pr(His)_{0.67}(NO_3)_3$; step 3 – $3PrONO_3\cdot Pr_6O_{11}$ and step 4 – Pr_6O_{11}

salts at 1200 cm^{-1} [6]. If the compounds are xREONO$_3$·yRE$_2$O$_3$, they do not dissolve in water completely; the IR spectra show the characteristic peaks of the alkaline salts and oxides (Sadtler Standard). If the products are pure alkaline or oxides, they are easily identified. Figure 3 displays the IR spectra of the complex Pr(His)(NO$_3$)$_3$·H$_2$O at different stages during the thermal decomposition.

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