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Synthesis and thermo-decomposition mechanism of rare earth complexes with phenylacetic acid[1]

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Abstract

Rare earth complexes with phenylacetic acid ($LnL_3 \cdot nH_2O$, Ln is Ce, Nd, Pr, Ho, Er, Yb and Y, L is phenylacetate, $n = 1$–2) were prepared and characterized by elemental analysis, IR spectroscopy, chemical analysis, and X-ray crystal structure. The mechanism of thermal decomposition of the complexes was studied by means of TG–DTG, DTA and DSC. The activation energy and enthalpy change for the dehydration and melting processes were determined.

Keywords: Phenylacetic acid; Rare earth complex; Thermo-decomposition mechanism

1. Introduction

Rare earth complexes with carboxylic acids and β-diketones have unusual structures and interesting luminescent property [1–3]. Some rare earth complexes with carboxylic acids have been applied in agriculture as luminescent materials. As a continuation of our research, rare earth complexes of phenylacetate, which have not been reported in the literature, were synthesized and characterized. The thermal analysis of the complexes was studied by TG–DTG, DTA and DSC.

2. Experimental

An aqueous solution of $LnCl_3$ (5.0 mmol) was added to an aqueous solution of phenylacetic acid (15.0 mmol). The pH of the resulting solution was adjusted to 5 with aqueous ammonia solution, followed by stirring for 2 h in a water bath (65°C). After

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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filtration, the filtrate was kept in air for several days. The solid complex that separated out was collected by filtration, washed with alcohol and dried over phosphorus (V) oxide in a desiccator. Elemental analysis of the complexes was performed with a 1106 model elemental analyzer. IR spectra were recorded on a Perkin-Elmer 580B model infrared spectrophotometer using KBr pellets, and X-ray diffraction analysis were made on a Nicolet R3m/E. TG–DTG curves were recorded on a Shimadizu DT-30 model thermal analyzer. Sample masses of 10 mg and dynamic air atmosphere with a flow rate of 50 ml min^{-1} were used. The heating rate was 10°C min^{-1}. DSC was performed with a Perkin-Elmer DSC-7 thermal analyzer in a dry N_2 atmosphere (flow rate of 50 ml min^{-1}) at a heating rate of 10°C min^{-1}. Indium metal was used as the calibration material for DSC.

3. Results and discussion

3.1. Characterization of rare earth complexes

The carbon and hydrogen contents were determined by elemental analysis, and rare earth contents by titration with EDTA. The elemental analysis data are presented in Table 1, which shows that the phenyl acetates of Ce, Pr and Nd were prepared as monohydrates, and the phenyl acetates of Y, Ho, Er and Yb were prepared as dihydrates. The experimental results approximate closely to the calculated values.

The IR spectra of the complexes are similar to one another. Analyses of IR spectra also confirm the suggested composition of the complexes. When acid is converted into salt, the COOH groups of absorption band at 1695 cm^{-1} disappears, and two groups of bands arising from asymmetric and symmetric vibration of COO^- appear at 1550–1590 cm^{-1} and 1385–1440 cm^{-1}, respectively. The asymmetric (ν_{as}) and symmetric (ν_s) bands of the COO^- group are split, which suggests that the COO^- groups are bonded in different ways in the same complex molecule. An absorption band at 3100–3200 cm^{-1} indicates the presence of water in the complex. The results of the IR spectra are also confirmed by the crystal structure analysis [4,5].

Table 1
Elemental analysis data of rare earth complexes (%)

Complex	RE		C		H	
	Found	Calcd.	Found	Calcd.	Found	Calcd
$CeL_3 \cdot H_2O$	25.00	24.87	50.97	51.15	3.92	4.08
$PrL_3 \cdot H_2O$	24.80	24.99	50.96	51.08	3.96	4.08
$NdL_3 \cdot H_2O$	25.00	25.44	50.72	50.97	4.00	4.06
$HoL_3 \cdot 2H_2O$	27.01	27.22	47.26	47.53	4.10	4.13
$ErL_3 \cdot 2H_2O$	27.13	27.49	47.05	47.35	4.13	4.11
$YbL_3 \cdot 2H_2O$	28.40	28.18	46.60	46.90	4.10	4.07
$YL_3 \cdot 2H_2O$	17.01	16.78	54.10	54.35	4.92	4.72

The crystal structures of the Nd and Er complexes also confirm the suggested composition. For the Nd complex, two carboxyl groups coordinate as oxygen bridging chelate tridentate ligands, the third serves as a bridging bidentate ligand; for the Er complex, two carboxyl groups coordinate as chelate ligands, only one serving as the oxygen bridging chelate tridentate ligand. The Nd complex forms an infinite chain structure, but the Er complex forms a dimer structure.

3.2. Thermo-decomposition mechanism of rare earth complexes

Fig. 1 shows TG–DTG and DTA curves of three rare earth complexes. From Fig. 1, it can be seen that the thermal decomposition of the rare earth complexes consists of three processes: dehydration, melting and decomposition.

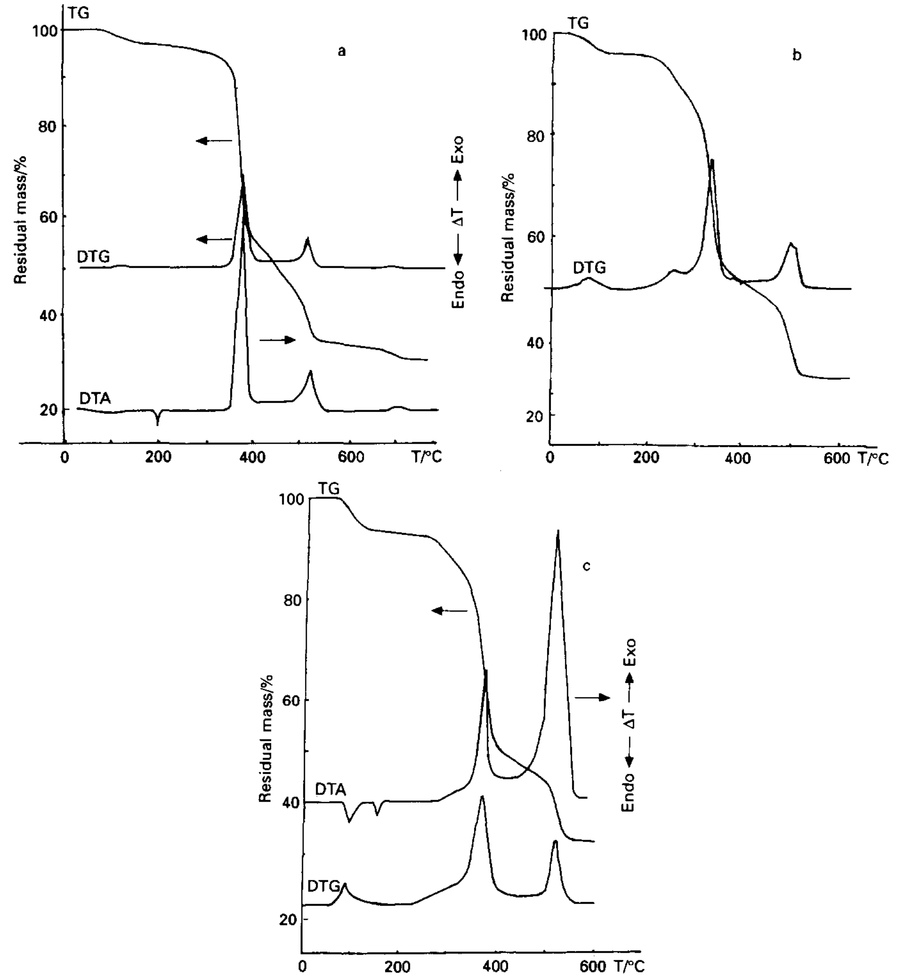

Fig. 1. The TG-DTG and DTA curves of rare earth complexes a. NdL_3H_2O b. HoL_32H_2O c. ErL_32H_2O

3.2.1. Dehydration processes

From the thermal decomposition curves of the complexes, it can be seen that a well-defined weight loss in the temperature range from 60 to 140°C appears in the TG–DTG curves, and a corresponding endothermic process is noted in the DTA curves. The experimental mass loss accords with the theoretically calculated water contents of the complexes (as shown in Table 2). The IR spectra of the dehydration products indicate that the absorption bands of O–H at 3100–3200 cm^{-1} disappear [6], which confirms that this is a dehydration process. Since the dehydration temperature of the complexes is higher and interreaction between the rare earth and water molecules of the complex is strong, it may be suggested that the water molecule in the complexes must be coordinated to the rare earth ions. The dehydration temperature of light rare earth complexes is higher than that of heavy rare earth complexes. This may be due to differences in the rare earth ion orbit, the coordination mode of the carboxylic group, and the number of coordinated water molecules between light and heavy rare earth complexes.

In order to investigate the kinetics of the dehydration process of the rare earth complexes, the Freeman–Carroll [7] method was used to calculate the activation energies for the dehydration

$$\Delta \lg(\mathrm{d}\alpha/\mathrm{d}t)/\Delta \lg(1-\alpha) = -E\Delta(1/T)/2.3R\Delta \lg(1-\alpha) + n$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the reaction rate, R the universal gas constant, E the activation energy, T the absolute temperature, α the degree of conversion, and n the order of reaction. A plot of $\Delta \lg(\mathrm{d}\alpha/\mathrm{d}t)/\Delta \lg(1-\alpha)$ vs.Δ $(1/T)\Delta/\lg(1-\alpha)$ should result in a straight line with slope $-$ E/2.3 R, and then the activation energies can be obtained. Meanwhile, the enthalpy changes for dehydration of rare earth complexes were determined by DSC. Enthalpy changes and activation energy data are listed in Table 2.

3.2.2. Melting and decomposition processes

When the anhydrous complex is heated up to 180°C, a sharp endothermic peak appears in the DTA curve, but there is no corresponding weight change in the TG–DTG curve. By observing the intermediate which was cooled quickly, it was found

Table 2
Dehydration process data for rate earth complexes

Complex	Dehydration temperature range/°C			Weight loss		ΔH/ kJ mol^{-1}	E/ kJ mol^{-1}
	Onset	Peak	Offset	Found	Calcd.		
$\mathrm{CeL_3 \cdot H_2O}$	70.1	80.0	137.1	3.2	3.2	29.3	80.1
$\mathrm{PrL_3 \cdot H_2O}$	70.0	98.0	145.0	3.1	3.2	36.2	89.0
$\mathrm{NdL_3 \cdot H_2O}$	88.5	135.0	148.2	3.1	3.2	30.3	84.0
$\mathrm{HoL_3 \cdot 2H_2O}$	60.0	105.1	130.8	6.0	5.9	80.1	76.3
$\mathrm{ErL_3 \cdot 2H_2O}$	61.0	78.0	125.0	5.9	5.9	82.4	97.2
$\mathrm{YbL_3 \cdot 2H_2O}$	70.0	86.0	120.0	5.8	5.8	66.4	79.6
$\mathrm{YL_3 \cdot 2H_2O}$	60.1	80.0	130.0	6.9	6.8	74.3	89.0

Table 3
Data on the melting and decomposition process of rare earth complexes

Complex	Melting point/ °C	Melting enthalpy/ kJ mol^{-1}	Melting entropy/ J mol^{-1}K^{-1}	Temp. range of decomposition/°C			Mass loss %		Intermediate
				Onset	Peak	Offset	Found	Calcd.	
CeL_3	145.0	24.6	58.8	270	330	435	44.0	45.1	CeOL
				435	467	557	22.3	21.1	CeO_2
PrL_3	180.0	27.2	60.0	280	330	425	43.8	45.0	PrOL
				425		540	20.0	18.6	$Pr_2O_2CO_3$
				580	650	700	2.8	2.9	Pr_6O_{11}
NdL_3	201.1	25.7	53.4	310	340	405	43.0	44.8	NdOL
				405	507	530	20.4	18.5	$Nd_2O_2CO_3$
				630	660	700	3.7	3.8	Nd_2O_3
HoL_3	188.0	36.2	78.5	250	335	418	40.7	41.9	HoOL
				418	520	590	22.2	21.0	Ho_2O_3
ErL_3	155.9	38.1	88.9	280	390	437	40.9	41.8	ErOL
				437	509	543	21.7	20.8	Er_2O_3
YbL_3	144.0	34.1	81.7	255	340	420	40.6	41.4	YbOL
				420	570	600	21.6	20.7	Yb_2O_3
YL_3	162.0	33.0	75.8	230	390	437	46.8	48.0	YOL
				437	510	590	26.3	24.0	Y_2O_3

that the rare earth complex had melted. The melting enthalpies of the complexes were determined by DSC. According to the equation $\Delta S = \Delta H/T_m$ [8], where ΔS is the melting entropy, ΔH the melting enthalpy, and T_m the melting temperature, the entropy changes for the melting process of the rare earth complexes were obtained (see Table 3). From Table 3, it can be seen that the melting enthalpy changes of heavy rare earth complexes are higher than those of light rare earth complexes.

The mechanisms of the thermal decomposition of rare earth complexes are classified into two kinds, LnL_3 (Ln is Pr, Nd) decompose in three steps. In the first step, at about 380°C, the complexes begin to decompose, losing two ligands and forming unstable intermediates of LnOL. In the second step, the intermediates LnOL decompose continuously and form stable intermediates of $Ln_2O_2CO_3$. The mass loss for the complexes agrees with calculated values based on the composition of $Ln_2O_2CO_3$. It can be seen from the IR spectra of $Ln_2O_2CO_3$ that characteristic absorption bands for the ligand disappear and the absorption bands at 1480–1400 and 880–850 cm^{-1} arising from CO_3^{2-} appear. The final step of the thermal decomposition of these complexes is the conversion of $Ln_2O_2CO_3$ to the corresponding rare earth metal oxides.

LnL_3 (Ln is Ce, Y, Er, Ho and Yb) decomposes in two steps. First, the complexes lose two ligands and form stable intermediate products of LnOL; then the intermediate products decompose to the oxide directly without forming $Ln_2O_2CO_3$. The formation temperature of the oxides of light rare earth complexes, except that of Ce, is higher than that of heavy rare earth complexes. Although a Ce is a light rare earth, the decomposition process of the Ce complex consists of two steps; this is due to the valence change of Ce ion during decomposition and a large exothermic process.

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