Different Thermal Decomposition Process of Lanthanide Complexes with *N*-Phenylanthranilic Acid in Air and Nitrogen Atmosphere

[a]B. YAN*, [b]H. J. ZHANG, [b]G. L. ZHOU, and [b]J. Z. NI

[a]*Department of Chemistry, Tongji University, Shanghai 200092, P. R. China*
e-mail: byan@tongji.edu.cn

[b]*Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China*

The thermal decomposition process and mechanism of lanthanide complexes with *N*-phenylanthranilic acid were studied. On heating in air atmosphere, the TG-DTA curves of La^{3+}, Pr^{3+}, Nd^{3+} complexes show three processes (two dehydrations and one decomposition), while the TG-DTA curves of Gd^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+} complexes show two processes (one dehydration and one decomposition), the final products are rare earth oxides. On heating in nitrogen atmosphere, the TG-DTA curves of all the complexes show two processes, the final products are the mixtures of lanthanide oxides and carbon.

In recent years, there has been a growing interest in the potential application of lanthanide coordination compounds as a luminescent material and luminescent probe for a variety of chemical and biological studies [1—3]. The lanthanide complexes with aromatic carboxylic acids offer an advantage of stability of luminescent properties owing to their infinite chain structure of chelation for practical application [4, 5]. Besides this, the luminescent complexes need excellent thermal stability, but little attention has been paid to the thermal analysis of lanthanide complexes with aromatic carboxylic acid except that *Brzyska* and the coworkers have done some work [6—8].

In the context, a series of lanthanide (La^{3+}, Nd^{3+}, Pr^{3+}, Gd^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+}) complexes with *N*-phenylanthranilic acid (*N*-HPA) were synthesized by homogeneous precipitation and characterized by elemental analysis and IR spectra. The thermal decomposition processes of these complexes in air and nitrogen were studied in detail.

The compositions of the prepared complexes were confirmed on the basis of the elemental analysis and the data are summarized in Table 1.

The IR spectra of the binary and ternary complexes differ from those of the free ligand (Table 2). In the lanthanide complexes the following bands present in the spectra of the free ligands $\nu(C{=}O)$ at 1657 cm^{-1} shift significantly according to the character of the coordination. The bands $\nu(OH)$ at 2863.3 cm^{-1}, 2732.6 cm^{-1}, 2640.2 cm^{-1}, and 2567.9 cm^{-1} in the spectra of the free ligands have disappeared in the spectra of complexes. The characteristic absorption band of NH_2 appeared in both complexes and ligand, which indicated that the rare earth ions are coordinated with *N*-PA through the oxygen atom of carboxyl group and not the nitrogen atom of amino group in lanthanide complexes. Besides this, the $\Delta(\nu_s - \nu_{as})$ value of COO^- in the IR spectra of lanthanide complexes was found less than that in the IR spectra of

Table 1. The Composition of Lanthanide Complexes

Complex	w_i(calc.)/% w_i(found)/%			
	C	H	N	RE
La(*N*-PA)₃ · 5H₂O	54.07	4.62	4.85	16.05
	54.13	4.80	4.80	16.18
Pr(*N*-PA)₃ · 5H₂O	53.88	4.60	4.84	16.24
	54.10	4.76	4.94	16.11
Nd(*N*-PA)₃ · 5H₂O	53.74	4.60	4.82	16.56
	53.89	4.77	4.96	16.43
Eu(*N*-PA)₃ · 4H₂O	54.38	4.41	4.88	17.68
	54.07	4.20	5.10	17.93
Gd(*N*-PA)₃ · 4H₂O	54.06	4.39	4.85	18.17
	53.98	4.11	5.08	18.36
Sm(*N*-PA)₃ · 4H₂O	54.48	4.42	4.89	17.50
	54.39	4.59	4.96	17.67
Tb(*N*-PA)₃ · 4H₂O	53.95	4.38	4.84	18.32
	53.64	4.09	5.04	18.04
Dy(*N*-PA)₃ · 4H₂O	53.72	4.37	4.82	18.65
	53.94	4.53	4.73	18.50

Table 2. Absorption Bands of IR Spectra for Lanthanide Complexes with N-Phenylanthranilic Acid[a]

Compound	$\tilde{\nu}/\text{cm}^{-1}$						
N-HPA	3333.6 m		1657.9 w	1409.7 s		1324.6 w	
Na(N-PA)	3322.0 m	3039.7 w	1610.8 w	1386.0 s	224.8	1317.6 w	427.8 w
La(N-PA)$_3 \cdot$5H$_2$O	3312.3 m	3040.2 w	1611.3 w	1393.7 s	217.6	1317.2 w	419.8 w
Pr(N-PA)$_3 \cdot$5H$_2$O	3312.7 m	3041.5 w	1611.7 w	1399.0 s	212.7	1316.5 w	420.7 w
Nd(N-PA)$_3 \cdot$5H$_2$O	3313.1 m	3040.8 w	1611.4 w	1398.5 s	212.9	1316.2 w	424.2 w
Eu(N-PA)$_3 \cdot$4H$_2$O	3308.9 m	3042.1 w	1609.9 w	1398.5 s	211.4	1318.3 w	414.9 w
Gd(N-PA)$_3 \cdot$4H$_2$O	3310.5 m	3041.3 w	1611.4 w	1395.2 s	214.2	1317.3 w	413.5 w
Sm(N-PA)$_3 \cdot$4H$_2$O	3309.4 m	3042.4 w	1612.1 w	1396.7 s	215.4	1316.2 w	411.4 w
Tb(N-PA)$_3 \cdot$4H$_2$O	3305.7 m	3040.5 w	1612.2 w	1398.5 s	213.7	1315.2 w	411.7 w
Dy(N-PA)$_3 \cdot$4H$_2$O	3318.9 m	3041.9 w	1610.9 w	1397.1 s	213.8	1316.2 w	412.3 w
Band assignment	$\nu_s(\text{NH}_2)$	$\nu_s(\text{C—H})$	$\nu_s(\text{COO}^-)$	$\nu_{as}(\text{COO}^-)$	$\Delta\nu(\nu_{as}-\nu_s)(\text{COO}^-)$	$\nu(\text{C=N})$	RE—O

a) s, m, and w represent strong, medium, and weak absorption bands of IR spectra, respectively.
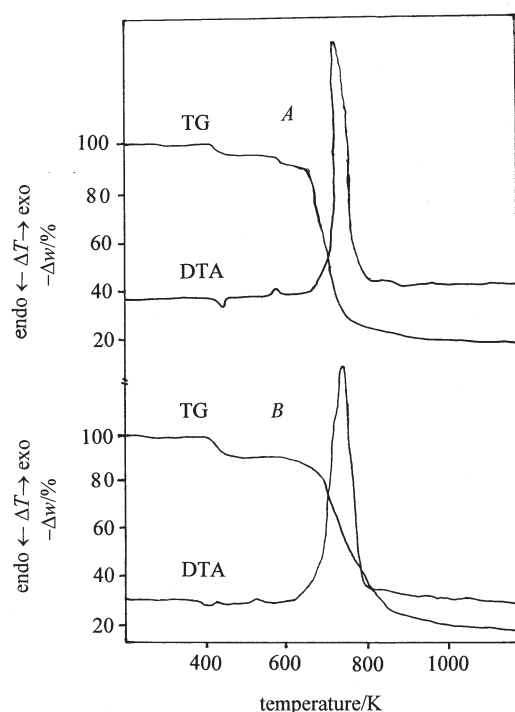

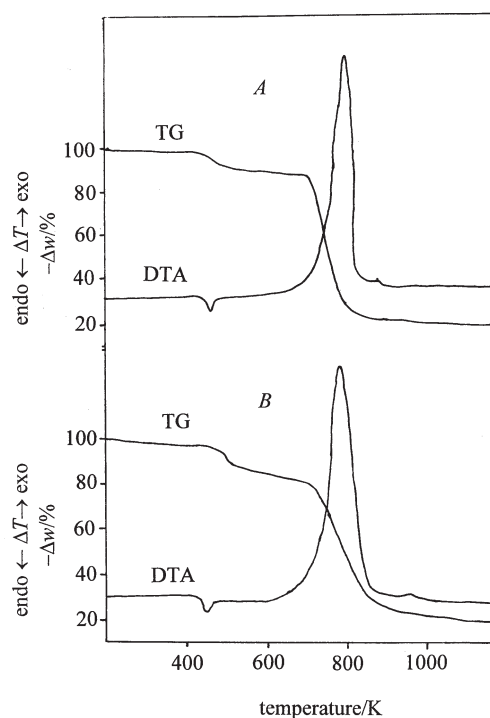**Fig. 1.** TG-DTA curves of La(N-PA)$_3 \cdot$5H$_2$O in air (A) and nitrogen (B) atmosphere.

Fig. 2. TG-DTA curves of Eu(N-PA)$_3 \cdot$4H$_2$O in air (A) and nitrogen (B) atmosphere.

the sodium salt of N-PA (at 224.8 cm^{-1}) at $\tilde{\nu}/\text{cm}^{-1}$ (217.6, 212.7, 212.9, 211.4, 214.2, 215.4, 213.7, 213.8), which implied that lanthanide complexes have bidentate coordination [9].

Figs. 1—3 show the TG-DTA curves of La(N-PA)$_3$ $\cdot$5H$_2$O, Eu(N-PA)$_3 \cdot$4H$_2$O, and Tb(N-PA)$_3 \cdot$4H$_2$O in air (A) and nitrogen (B) atmosphere, respectively. From these figures, the following results can be obtained. When heated in air atmosphere, the TG-DTA curves of lanthanide complexes with N-phenylanthranilic acid show different courses. The La^{3+}, Pr^{3+}, and Nd^{3+} complexes with N-HPA show three steps, they lose four water molecules and transform to the complexes with one water molecule with

endothermic effect, then lose the one water accompanied by endothermic effect, and at last, the anhydrous complexes decompose to be lanthanide oxides (La$_2$O$_3$, Pr$_6$O$_{11}$, Nd$_2$O$_3$) with the accomplishment of strong exothermic effect. On the other hand, the TG-DTA curves of Gd^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}, and Dy^{3+} complexes with N-HPA show two steps: the first is to lose crystallization water and yield the anhydrous salts to the accompaniment of endothermic effect; the second is that the anhydrous complexes then decompose to the oxides Gd$_2$O$_3$, Eu$_2$O$_3$, Sm$_2$O$_3$, Tb$_4$O$_7$, and Dy$_2$O$_3$ accompanied by strong exothermic effect. These oxides are stable in the temperature range 1163—1273 K. When heated in a nitrogen atmosphere, the TG-

DTA curves of all the hydrated complexes show two steps: one is dehydration process, another is decomposition process. The processes of dehydration are accompanied by endothermic effects and the decomposition processes are accompanied by strong exothermic effects. The final products of decomposition of the lanthanide complexes are mixtures of lanthanide oxides and carbon. The lanthanide oxides and carbon were identified by the combustion method and the content of carbon in the final products was determined by mass loss after the final mixed products of lanthanide oxides and carbon were fired in air atmosphere. Tables 3 and 4 show the TG-DTA data. The result of TG-DTA was in agreement with that of elemental analysis and IR spectra.

There are two phenyl groups in N-HPA molecule exhibiting larger steric hindrance effect than the aromatic carboxylic acid with one phenyl group, which leads to the different thermal decomposition process from the other reported lanthanide complexes [6—8]. The coordination of three N-HPA with lanthanide ions hinders the coordination of water molecule. Due to the lanthanide contraction, the radii of La^{3+}, Pr^{3+}, and Nd^{3+} are longer than those of other lanthanide ions (La^{3+}, Nd^{3+}, Pr^{3+}, Gd^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+}), it maybe predicted that La^{3+}, Pr^{3+}, and Nd^{3+} have one coordinated H_2O molecule while other lanthanide ions have no coordinated H_2O molecule. In the dehydration process La^{3+}, Pr^{3+}, and Nd^{3+} complexes with N-HPA first lose the four uncoordinated H_2O molecules and further lose the coordinated H_2O molecule, while the dehydration process of other lanthanide ions complexes with N-HPA shows losing only
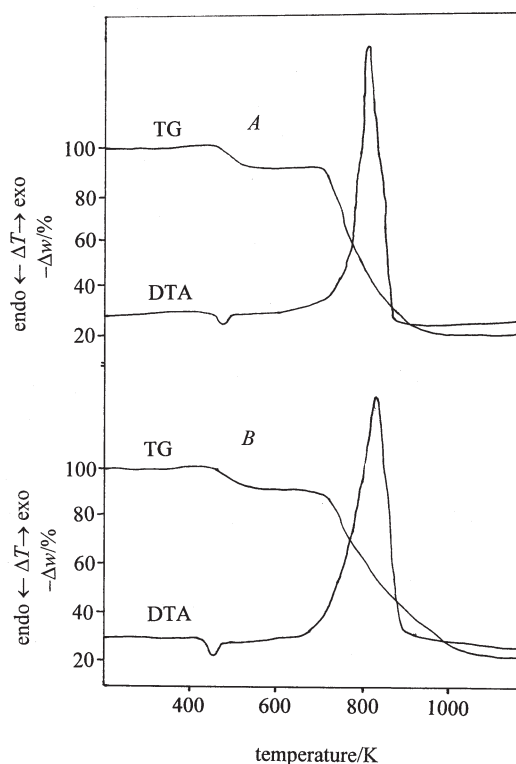

Fig. 3. TG-DTA curves of Tb(N-PA)$_3 \cdot 4H_2O$ in air (A) and nitrogen (B) atmosphere.

the four crystallized molecules. So TG-DTA curves of La^{3+}, Pr^{3+}, and Nd^{3+} complexes show three processes while the others show two processes.

Table 3. Temperature Range of Dehydration of Lanthanide Complexes with N-Phenylanthranilic Acid and the Products in Air (A) and Nitrogen (N) Atmosphere

Ln	Ln(N-PA)$_3 \cdot n$H$_2$O			Ln(N-PA)$_3 \cdot$ H$_2$O		
	Temp. range	n	Atmosphere	Temp. range	w_i(found)/%	w_i(calc.)/%
	K			K		
La	374—427	5	A	558—584	91.2	91.68
	362—433	5	N		90.7	91.68
Pr	376—416	5	A	533—583	90.7	91.70
	385—423	5	N		90.4	91.70
Nd	392—453	5	A	527—590	90.5	91.73
	392—453	5	N		90.5	91.73
Eu	398—505	4	A			
	428—520	4	N			
Gd	403—497	4	A			
	403—505	4	N			
Sm	411—533	4	A			
	411—517	4	N			
Tb	410—514	4	A			
	457—538	4	N			
Dy	417—538	4	A			
	417—538	4	N			

Table 4. Thermal Decomposition of Lanthanide Complexes with *N*-Phenylanthranilic Acid and their Products in Air (A) and Nitrogen (N) Atmosphere

Ln	Temp. range K	w_i(found)/%	w_i(calc.)/%	Temp. range K	w_i(found)/%	w_i(calc.)/%	C/%
	Ln(*N*-PA)$_3$			Ln$_2$O$_3$*			
La	660—783 A	89.5	89.60	783—1190	19.0	18.82	15.0
	649—844 N	89.0	89.60				
Pr	673—783 A	89.3	89.63	783—1183	20.0	19.62	6.5
	673—770 N	89.0	89.63				
Nd	678—783 A	89.0	89.67	783—1167	19.5	19.32	2.5
	678—783 N	89.0	89.67				
Eu	690—805 A	91.0	91.63	805—1168	21.0	20.45	5.5
	705—856 N	91.2	91.63				
Gd	678—816 A	90.8	91.69	816—1143	21.5	20.93	4.5
	680—816 N	90.5	91.69				
Sm	690—820 A	91.0	91.62	820—1143	21.0	20.30	4.0
	690—843 N	91.2	91.62				
Tb	706—935 A	90.5	91.70	935—1273	22.0	21.54	3.5
	724—978 N	90.8	91.70				
Dy	706—843 A	91.0	91.74	843—1273	22.0	21.41	6.5
	706—828 N	90.5	91.74				

*Ln$_2$O$_3$ (Ln = La, Nd, Eu, Sm, Gd, Dy), Pr$_6$O$_{11}$, and Tb$_4$O$_7$.

EXPERIMENTAL

Lanthanide oxide (99.99 %) was converted to its chloride by treating with concentrated hydrochloric acid. *N*-Phenylanthranilic acid and all other reagents were analytically pure.

Elemental analyses were carried out with an Erba 1106 elemental analyzer and the content of C, H, N was obtained, lanthanide ions content was determined by titration with EDTA using xylenol orange as the indicator and hexamethylene—tetramine as shock solution. Infrared spectra in the region $\tilde{\nu} = 400$—4000 cm^{-1} were recorded on a BIO-RAD infrared spetrophotometer (Model FTS-7) with KBr pellet technique. The thermal stability of the prepared complexes was studied. The TG and DTA curves were recorded on a Thermoflex DTA derivatograph at heating rate of 10 K min^{-1} and the samples were heated in air and nitrogen atmosphere at the sensitivities: TG – 10 mg, DTA $\pm$ 50 μV. The nitrogen flowed through gas washers filled with pyrogallol and silica gel, at a rate of 50 cm^3 min^{-1}. The numerical values (m/mg) of used sample masses for Ln(*N*-PA)$_3 \cdot n$H$_2$O (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy) are 20.5, 22.4, 21.5, 26.7, 24.7, 26.2, 30.7, 23.9, respectively in air atmosphere; and 23.2, 22.7, 20.8, 20.7, 23.3, 21.2, 25.9, 22.5, respectively in nitrogen.

Lanthanide Complexes

An aqueous solution of lanthanide chloride was added to a mixed alcoholic solution of *N*-phenylanthranilic acid (the mole ratio n(LnCl$_3 \cdot$6H$_2$O):n(*N*-phenylanthranilic acid) was 1:3), the pH value of which was adjusted to 6.0—7.0 by adding aqueous sodium hydroxide with stirring. The precipitate was filtered off, washed with water and ethanol, dried, then stored over silica gel desiccator.

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