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## New trivalent lanthanide complexes of phthalate-containing hydrazinium cation — preparation, and spectral and thermal studies

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### Abstract

Several new lanthanide complexes of the types,  $(\text{N}_2\text{H}_5)_2[\text{Ln}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$ , **A**, where Ln is La–Eu except Pm, and  $\text{N}_2\text{H}_5[\text{Ln}(\text{C}_6\text{H}_4(\text{COO})_2)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ , **B**, where Ln is Eu–Dy, have been prepared by crystallisation from concentrated aqueous solutions containing the metal nitrates and dihydrazinium phthalate in 1:6 molar ratio. The aqueous solutions of the compounds are acidic and exhibit high values of molar conductance. The complexes were characterised by analytical, magnetic, spectral, thermal and X-ray studies. The  $\text{OCO}^-$  groups of phthalate bridge in both mono- and bidentate fashion as evidenced by IR data. The N–N stretching frequency in the region  $960\text{--}965\text{ cm}^{-1}$  supports the non-coordination of  $\text{N}_2\text{H}_5^+$  ions. Both IR and thermal data confirm the presence of three coordinated and one lattice water molecules in the **B** complexes. Based on the results obtained, a nine-coordination for the lanthanide ions is proposed. Simultaneous TG–DTA of the complexes shows that they are thermally less stable and give metal oxides as the final product. X-ray powder patterns show isomorphism among the **A** and **B** complexes but not between them.

*Keywords:* Electronic spectra; Hydrazinium lanthanide phthalates; Thermal analysis; XRD

### 1. Introduction

The coordination chemistry of lanthanides, the hard acids, was limited initially to strongly chelating ligands with oxygen as donor atoms. The notion that neutral nitrogen bases precipitate the hydrous oxide or hydroxide of lanthanides [1] hindered the progress of the coordination chemistry of lanthanides. However, with the develop-

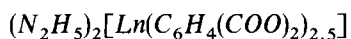
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ment of new synthetic techniques, some complexes of lanthanides (La–Nd, Sm, Dy, Er and Lu) with hydrazine and anions like halides, carbonate, nitrate, sulphate and perchlorate have been reported [2]. Similar types of complexes with carboxylate anions, like acetate [3] and oxalate [4], have been studied. There is a report on La, Ce and Nd complexes of phthalate with hydrazine [5]. The structures of these complexes have only been studied by chemical analysis and IR spectra. But the complexes  $N_2H_5Ln(SO_4)_2 \cdot H_2O$  (Ln is La–Tb, except Pm) have been characterised by spectral, magnetic, thermal and X-ray structural studies [6–8]. In these complexes,  $N_2H_5^+$  ion is coordinated. In view of the increasing interest and the dearth of complete and systematic studies on lanthanide complexes of phthalate and hydrazine, we here report such studies on the complexes  $(N_2H_5)_2[Ln(C_6H_4(COO)_2)_{2.5}]$ , **A**, where Ln is La–Eu except Pm, and  $N_2H_5[Ln(C_6H_4(COO)_2)_2(H_2O)_3] \cdot H_2O$ , **B**, where Ln is Eu–Dy.

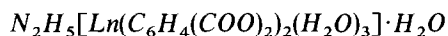
## 2. Experimental

The ligand dihydrazinium phthalate was prepared by the literature [9] method. The metal oxides (99%) of La to Dy (except Pm) were obtained from Indian Rare Earths Ltd., India and used as received. Hydrazine hydrate 99% (Glaxo India Ltd.) and phthalic acid (E. Merck India Ltd.) were also used as received.

### 2.1. Preparation



The metal oxides were dissolved in a minimum volume of 4 N  $HNO_3$  and evaporated to dryness. The metal nitrate solution obtained was mixed with the aqueous solution of dihydrazinium phthalate ( $0.06 \text{ mol dm}^{-3}$ ). The clear solution was concentrated on a thermostat at  $80^\circ\text{C}$  until the complexes were separated. It was filtered, washed with alcohol and ether and dried over  $P_2O_5$  in a vacuum desiccator.



The filtrate obtained, after separating the Eu complex  $(N_2H_5)_2[Eu(C_6H_4(COO)_2)_{2.5}]$ , as above, was concentrated further to the desired Eu complex. The other three complexes of Gd, Tb and Dy were obtained by adopting a method similar to that followed to prepare the **A** compounds. The complexes (**A** and **B**) were also prepared by crystallisation from a 1:6:6 molar mixture of lanthanide nitrate, hydrazine hydrate and phthalic acid in the aqueous solution.

The chemical compositions of the La and Ce compounds were in accord with those reported by Brzyska and Goral [5]. The composition of the Nd compound is slightly different. The three complexes  $Ln_2(C_8H_4O_4)_3 \cdot 4N_2H_4 \cdot 2C_8H_6O_4$  (Ln is La and Ce) and  $Nd_2(C_8H_4O_4)_3 \cdot 3N_2H_4$  were prepared by crystallisation from a 1:6:6 molar mixture of lanthanide salt, hydrazine hydrate and phthalic anhydride.

### 2.2. Physico-chemical techniques

The hydrazine content in the complexes was determined volumetrically [10] with  $0.025 \text{ M KIO}_3$  solution under Andrew's conditions. The metals, after destroying the

hydrazine and organic matter by treatment with concentrated  $\text{HNO}_3$  and evaporating the excess  $\text{HNO}_3$ , were determined volumetrically by EDTA titration [10] using xylenol orange indicator.

The magnetic moments of the complexes at room temperature were determined by Gouy's method using  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as the calibrant. Diamagnetic corrections were made using Pascal's constants.

The molar conductance of the  $10^{-3}$  M solutions in water was measured using an electrolytic conductivity bridge (open type) (P.I.Co., Madras-32, India) and an Elico conductivity cell (Type: CCO1) with an ear-telephone for detecting the null point.

The electronic absorption spectra in aqueous solvent were recorded on a Hitachi Perkin-Elmer 20/200 recording spectrophotometer.

Infrared spectra of the complexes were recorded with a Perkin-Elmer 597 infrared spectrophotometer in the range  $4000\text{--}200\text{ cm}^{-1}$  using KBr pellets of the samples.

Simultaneous TG-DTA analyses of the complexes were carried out in Shimadzu DT40 and STA 1500 thermal analysers. The experiments were carried out with 5–10 mg of the samples, in air using platinum cups as sample holders and with alumina as reference, at the heating rate of  $10^\circ\text{C min}^{-1}$ .

X-ray power diffraction patterns of the complexes were recorded in an X-ray diffractometer model Philips PW 1050/70 using  $\text{Cu K}\alpha$  radiation with an Ni filter.

### 3. Results and discussion

The stoichiometry of the complexes proposed are in accordance with the analytical data given in Table 1. They are less soluble in water and the resulting solutions are acidic to litmus. They are stable in air.

Table 1  
Analytical, magnetic and conductivity data

Compound	Colour	Yield %	Hydrazine(%)		Metal %		$\Lambda_M/\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	$\mu_{\text{eff}}/\text{BM}$
			Found	Calcd.	Found	Calcd.		
$(\text{N}_2\text{H}_5)_2[\text{La}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$	White	70	10.50	10.42	22.00	22.58	538.70	–
$(\text{N}_2\text{H}_5)_2[\text{Ce}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$	White	60	10.40	10.40	22.00	22.73	540.40	2.35
$(\text{N}_2\text{H}_5)_2[\text{Pr}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$	Light green	60	10.30	10.38	22.20	22.83	537.00	3.50
$(\text{N}_2\text{H}_5)_2[\text{Nd}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$	Light purple	65	10.30	10.33	23.00	23.24	533.20	3.55
$(\text{N}_2\text{H}_5)_2[\text{Sm}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$	Light yellow	70	10.35	10.23	23.50	23.99	540.50	1.55
$(\text{N}_2\text{H}_5)_2[\text{Eu}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$	White	40	10.25	10.20	24.50	24.18	533.80	3.50
$(\text{N}_2\text{H}_5)[\text{Eu}(\text{C}_6\text{H}_4(\text{COO})_2(\text{H}_2\text{O})_3)\cdot\text{H}_2\text{O}]$	White	30	5.30	5.48	26.00	25.96	214.00	3.55
$(\text{N}_2\text{H}_5)[\text{Gd}(\text{C}_6\text{H}_4(\text{COO})_2(\text{H}_2\text{O})_3)\cdot\text{H}_2\text{O}]$	White	60	5.80	5.43	27.00	26.63	213.50	7.70
$(\text{N}_2\text{H}_5)[\text{Tb}(\text{C}_6\text{H}_4(\text{COO})_2(\text{H}_2\text{O})_3)\cdot\text{H}_2\text{O}]$	Green	55	5.30	5.41	27.00	26.83	210.80	9.50
$(\text{N}_2\text{H}_5)[\text{Dy}(\text{C}_6\text{H}_4(\text{COO})_2(\text{H}_2\text{O})_3)\cdot\text{H}_2\text{O}]$	Green	60	5.50	5.38	27.50	27.27	210.10	10.40

### 3.1. Magnetic moments

The magnetic moment values (Table 1) of the complexes, except those of Sm and Eu, at room temperature, are found to be close to the values calculated using the formula [11]  $\mu = g\sqrt{J(J+1)}$ . This is due to the fact that in these ions the unpaired electrons in the 4f orbitals are quite deeply seated and hence are well shielded by 5s and 5p electrons from the effects of other atoms in the ligands. The relatively high values obtained in the case of Sm and Eu complexes are due to low J–J separation, which leads to a thermal population of higher energy levels and shows susceptibilities due to a first-order Zeeman effect [12].

### 3.2. Molar conductance

The molar conductance values (Table 1) of the complexes ( $10^{-3}$  M aqueous solution) were found to be in the range 533–541  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  for A type and 210–214  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  for B type complexes. These high values, as compared to 110  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  reported for a number of 1:1 Ln complexes [13], may be attributed to dissociation. It is also likely that some of the phthalate ligands in the complexes may exist as free acid in solution which is acidic to litmus.

### 3.3. Electronic spectra

The electronic spectra of lanthanides, constituting mainly Laporte-forbidden 4f-transitions, are not much influenced by the ligand environment, as in the case of d-block metal complexes. The electronic spectra of Pr, Nd and Sm complexes recorded in aqueous solvent were compared with those of aqueous metal nitrate solutions (Table 2). The data show not only shifts in band positions but also changes in intensity compared to those of the aquated lanthanide metal ions, i.e. the wave numbers at which the various bands appear are slightly greater. This shift, which is a measure of metal–ligand interaction, has been ascribed to the nephelauxetic effect [14, 15]. The Sinha's [16] covalency parameter ( $\% \delta$ ) was calculated using the expression

$$\delta = \frac{(1 - \beta)}{\beta} \times 100$$

where  $\beta = (1/n)\Sigma(v_{\text{complex}}^i/v_{\text{aquo}}^i)$ ;  $\beta$  is the average value of the ratio  $v_{\text{complex}}/v_{\text{aquo}}$  and  $n$  the number of transitions considered. The values of  $\delta$  (between 0.0 and  $-0.6$ ) are negative, indicating ionic bonding. However, the  $\beta$  values for these systems are very close to those reported for  $\text{N}_2\text{H}_5\text{Ln}(\text{SO}_4)_2\text{H}_2\text{O}$  complexes [6]. Moreover, the values of Sinha's covalency parameter presented here are less than those [16] for  $[\text{Nd}(\text{D}_2\text{O})_9]^{3+}$  ion but greater than those [16] for  $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$  ion, indicating relatively little covalent character. Furthermore, the observed changes in the shape and intensity of 'hypersensitive' transitions for  $\text{Nd}^{3+}$ ,  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$ ,  ${}^2\text{G}_{7/2}$ , indicate a coordination number of nine [16–18].

Table 2  
Electronic spectral data

Complex	Band max./cm <sup>-1</sup>	Assignment	Parameters
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> [Pr(C <sub>6</sub> H <sub>4</sub> (COO) <sub>2</sub> ) <sub>2.5</sub> ]	17,007	<sup>3</sup> H <sub>4</sub> → <sup>1</sup> D <sub>2</sub>	β = 1.006
	20,747	<sup>3</sup> P <sub>0</sub>	%δ = -0.5964
	21,368	<sup>3</sup> P <sub>1</sub>	
	22,522	<sup>3</sup> P <sub>2</sub>	
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> [Nd(C <sub>6</sub> H <sub>4</sub> (COO) <sub>2</sub> ) <sub>2.5</sub> ]	17,241	<sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> G <sub>7/2</sub>	β = 1.0008
	19,231	<sup>4</sup> G <sub>7/2</sub>	%δ = -0.0767
	20,833	<sup>2</sup> K <sub>15/2</sub> , <sup>4</sup> G <sub>9/2</sub>	
	21,552	<sup>2</sup> D <sub>3/2</sub> , <sup>2</sup> P <sub>3/2</sub>	
	23,148 } 23,585 }	<sup>2</sup> P <sub>1/2</sub>	
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> [Sm(C <sub>6</sub> H <sub>4</sub> (COO) <sub>2</sub> ) <sub>2.5</sub> ]	20,833	<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> I <sub>9/2</sub>	β = 1.0045
	21,552	<sup>4</sup> I <sub>13/2</sub>	%δ = -0.4480
	23,810	<sup>6</sup> P <sub>5/2</sub>	
	24,876	<sup>6</sup> P <sub>3/2</sub> , <sup>4</sup> I <sub>13/2</sub>	
	26,880	<sup>6</sup> P <sub>7/2</sub> , <sup>4</sup> D <sub>1/2</sub> , <sup>4</sup> F <sub>9/2</sub>	
	27,777	-	

### 3.4. Infrared spectra

The infrared spectral data of the complexes are given in Table 3. The complexes **A** have identical infrared spectra and compounds **B** have similar spectra. The N–N stretching frequency in the range 960–965 cm<sup>-1</sup> corresponds to non-coordination of N<sub>2</sub>H<sub>5</sub><sup>+</sup> ions. A similar IR spectral evidence for non-coordinated N<sub>2</sub>H<sub>5</sub><sup>+</sup> in dihydrazinium uranyl phthalate has already been reported [19]. The asymmetric and symmetric stretching frequencies of the carboxylate group in the complexes show negative shifts (10–50 cm<sup>-1</sup>) and positive shifts (5–40 cm<sup>-1</sup>), respectively, from those of the ligand. This supports the coordination of phthalate in the complex. The separation, Δν (ν<sub>asym</sub> – ν<sub>sym</sub> = 200 and 140 cm<sup>-1</sup>), between the asymmetric and symmetric stretching frequencies is indicative of the fact that OCO<sup>-</sup> groups from phthalate have bridging oxygens leading to both mono- and bidentate coordination. This has literature support from the IR data and X-ray single-crystal structure of cobalt phthalate complexes reported elsewhere [20].

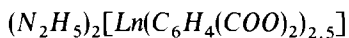
The IR spectra of complexes **B** show broad absorption bands with maxima at 3500 cm<sup>-1</sup>; sharp bands at 1620–1600 cm<sup>-1</sup> (overlapped with asymmetric stretching of COO<sup>-</sup>) confirm the presence of coordinated water molecules [21, 22]. Due to the overlapping of the stretching frequencies of coordinated and lattice water molecules, they are not distinctly identified in the IR spectra. However, they are distinguished by the thermal results.

The absence of carbonyl stretching around 1700 cm<sup>-1</sup> confirms that the carboxylic acid group is not present in the complexes. This rules out the presence of phthalic acid in the complexes of La and Ce, reported earlier by Brzyska and Goral [5].

Table 3  
IR data

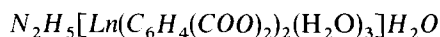
La	$(N_2H_5)_2[Ln(C_6H_4(COO)_2)_{2.5}]$					$N_2H_5[Ln(C_6H_4(COO)_2)_2(H_2O)_3] \cdot H_2O$					Band assignments/cm <sup>-1</sup>
	Ce	Pr	Nd	Sm	Eu	Eu	Gd	Tb	Dy		
—	—	—	—	—	—	3480	3490	3490	3490	3500	O–H str. of H <sub>2</sub> O
3350	3345	3350	3350	3340	3350	3355	3335	3340	3340	3340	N–H stretching
3150	3150	3140	3140	3145	3140	3200	3200	3190	3200	3200	COO <sup>-</sup> asym. stretching
3070	3075	3070	3075	3075	3075	3080	3070	3080	3070	3070	COO <sup>-</sup> sym. stretching
1540	1610	1600	1590	1620	1620	1535	1590	1600	1540	1550	$\Delta\nu(v_{\text{asym}} - \nu_{\text{sym}})$
1390	1550	1540	1550	1550	1540	1415	1540	1540	1420	1400	N–N stretching
—	1420	1420	1385	1400	1400	1415	1415	1420	1390	1400	
150	190	180	205	220	220	—	175	180	175	180	
960	150	140	165	150	140	120	150	150	150	150	
—	962	965	960	962	960	965	960	960	960	965	

### 3.5. Thermal studies



The thermal data of the complexes are presented in Table 4. The simultaneous TG–DTA results of the complexes are similar and undergo two major stages of weight loss upon heating. The DTA curves of the complexes show an endothermic peak between 225 and 260°C. The decomposition with loss in mass started at around 200°C in the corresponding thermograms. All the complexes decompose to give hydrazinium metal phthalates as intermediates, whereas the Nd complex forms neodymium phthalate only. This is the reason why this stage of weight loss in the Nd complex shows an additional peak as an exotherm in DTA at 250°C.

The second major weight loss begins at about 300°C. The DTA curves show two or three exotherms between 400 and 560°C. The residual weight in all the complexes corresponds to the respective metal oxides. The decomposition is completed before 600°C. This temperature range is significantly less than the metal oxide formation temperature of simple lanthanide salts and other hydrazine lanthanide complexes [6–8]. Close observation of the TG results shows that lanthanide oxycarbonates are formed as intermediates but that the decomposition is continuous so that this cannot be quantified. The simultaneous TG–DTA thermograms of the Eu complex are given in Fig. 1 as a representative example.



These compounds undergo three stages of weight loss. The first stage, which occurs in the range 70–150°C, is attributed to the loss of one H<sub>2</sub>O molecule. The corresponding DTA peaks are endotherms. Such a low temperature of dehydration supports the presence of one lattice H<sub>2</sub>O in the compounds. TG shows a weight loss corresponding to this. The second-stage mass loss also takes place endothermically as shown by DTA. In the Eu complex, the mass loss is in accordance with the loss of a molecule of hydrazine and three H<sub>2</sub>O molecules at 230°C. The other complexes show a weight loss equal to three water molecules above 270°C. The dehydration occurs at a fairly high temperature (230°C) confirming the coordinated [6] nature of the water molecules. The presence of lattice and coordinated water molecules in Gd and Dy acetate hydrates have been reported by Patil et al. [23].

The third-stage major weight loss corresponds to the decomposition of the intermediates to metal oxides. The DTA curves show both endothermic and exothermic peaks. Here again the metal oxide formation temperature is significantly low. The simultaneous TG–DTA curves of the Dy complex are given in Fig. 2 as a representative example.

Because of the close similarity of the rare-earth-metal complexes, the observed decomposition temperatures are in almost the same range.

### 3.6. X-ray powder pattern studies

The values of the *d*-spacings and the relative intensities are given in Table 5. The **A** complexes have identical and the same number of peaks, proving isomorphism and hence similar properties among them. Similarly, the set of **B** complexes are isomorphs and were found to possess almost the same properties.

Table 4  
Thermal data

Compound	DTA peak temp/ $^{\circ}\text{C}$	Thermogravimetry		Decomposition product	
		Temperature range/ $^{\circ}\text{C}$	Weight loss %		
			Found		Calcd.
$(\text{N}_2\text{H}_5)_2[\text{La}(\text{C}_6\text{H}_4(\text{COO})_2)_2 \cdot 5\text{H}_2\text{O}]$	260(+)	230–280	18.0	18.71	$\text{N}_2\text{H}_5[\text{La}(\text{C}_6\text{H}_4(\text{COO})_2)_2]$ $\text{La}_2\text{O}_3$
	450(-)	350–600	73.0	73.52	
	500(-)				
$(\text{N}_2\text{H}_5)_2[\text{Ce}(\text{C}_6\text{H}_4(\text{COO})_2)_2 \cdot 5\text{H}_2\text{O}]$	260(+)	220–300	18.5	18.67	$\text{N}_2\text{H}_5[\text{Ce}(\text{C}_6\text{H}_4(\text{COO})_2)_2]$ $\text{CeO}_2$
	405(-)	325–460	71.2	72.08	
	435(-)				
$(\text{N}_2\text{H}_5)_2[\text{Pr}(\text{C}_6\text{H}_4(\text{COO})_2)_2 \cdot 5\text{H}_2\text{O}]$	225(+)	220–270	18.3	18.65	$\text{N}_2\text{H}_5[\text{Pr}(\text{C}_6\text{H}_4(\text{COO})_2)_2]$ $\text{Pr}_6\text{O}_{11}$
	440(-)	330–590	71.5	72.42	
	490(-)				
$(\text{N}_2\text{H}_5)_2[\text{Nd}(\text{C}_6\text{H}_4(\text{COO})_2)_2 \cdot 5\text{H}_2\text{O}]$	240(+)	200–270	31.5	31.93	$\text{Nd}(\text{C}_6\text{H}_4(\text{COO})_2)_2$ $\text{Nd}_2\text{O}_3$
	250(-)	300–580	72.0	72.89	
	440(-)				
	480(-)				
$(\text{N}_2\text{H}_5)_2[\text{Sm}(\text{C}_6\text{H}_4(\text{COO})_2)_2 \cdot 5\text{H}_2\text{O}]$	240(+)	200–300	19.0	18.37	$\text{N}_2\text{H}_5[\text{Sm}(\text{C}_6\text{H}_4(\text{COO})_2)_2]$ $\text{Sm}_2\text{O}_3$
	400(-)	340–550	73.0	72.18	
	525(-)				
$(\text{N}_2\text{H}_5)_2[\text{Eu}(\text{C}_6\text{H}_4(\text{COO})_2)_2 \cdot 5\text{H}_2\text{O}]$	225(+)	160–280	18.0	18.32	$\text{N}_2\text{H}_5[\text{Eu}(\text{C}_6\text{H}_4(\text{COO})_2)_2]$ $\text{Eu}_2\text{O}_3$
	260(+)	400–720	72.5	72.00	
	460(-)				
	510(-)				
560(-)					



$N_2H_5[Eu(C_6H_4(COO)_2(H_2O)_3)] \cdot H_2O$	100(+)	70–150	3.1	3.08	$N_2H_5[Eu(C_6H_4(COO)_2)(H_2O)_3]$
	230(+)	150–245	17.5	17.79	$Eu(C_6H_4(COO)_2)(C_6H_4(COOHCOO))$
	350(+)				
$N_2H_5[Gd(C_6H_4(COO)_2(H_2O)_3)] \cdot H_2O$	410(-)	245–650	70.0	69.94	$Eu_2O_3$
	500(-)				
	90(+)	70–110	3.0	3.05	$N_2H_5[Gd(C_6H_4(COO)_2)(H_2O)_3]$
	285(+)	250–310	12.0	12.20	$N_2H_5[Gd(C_6H_4(COO)_2)_2]$
	450(+)	380–600	68.5	69.31	$Ga_2O_3$
$N_2H_5[Tb(C_6H_4(COO)_2(H_2O)_3)] \cdot H_2O$	510(-)				
	105(+)	90–120	3.0	3.04	$N_2H_5[Tb(C_6H_4(COO)_2)(H_2O)_3]$
	275(+)	230–320	12.0	12.17	$N_2H_5[Tb(C_6H_4(COO)_2)_2]$
	540(+)				
	580(-)	320–700	68.0	68.44	$Tb_4O_7$
$N_2H_5[Dy(C_6H_4(COO)_2(H_2O)_3)] \cdot H_2O$	110(+)	90–120	3.0	3.02	$N_2H_5[Dy(C_6H_4(COO)_2)(H_2O)_3]$
	270(+)	230–300	12.0	12.09	$N_2H_5[Dy(C_6H_4(COO)_2)_2]$
	500(+)				
	550(+)	300–670	68.0	68.70	$Dy_2O_3$
	575(-)				

Key: (+), endotherm; (-), exotherm; d, doublet; m, multiplet.

Table 5  
X-ray powder diffraction data  $d$  (in Å) and  $I$  (%)

$(N_2H_5)_2[Ln(C_6H_4(COO)_2)_2 \cdot s]$										$N_2H_5[Ln(C_6H_4(COO)_2)_2(H_2O)_3] \cdot H_2O$									
La	Ce	Pr	Nd	Sm	Eu	Eu	Gd	Tb	Dy	La	Ce	Pr	Nd	Sm	Eu	Eu	Gd	Tb	Dy
7.70(90)	7.63(80)	7.70(80)	7.70(100)	7.60(50)	7.65(80)	7.65(80)	7.70(100)	7.60(100)	7.42(90)	7.70(100)	7.60(100)	7.60(100)	7.60(100)	7.60(100)	7.42(90)	7.42(90)	7.70(100)	7.60(100)	7.50(100)
6.51(15)	6.51(20)	6.53(20)	6.81(40)	6.81(20)	6.60(30)	6.60(30)	6.81(40)	6.81(20)	6.58(50)	6.55(50)	6.55(50)	6.55(50)	6.55(50)	6.58(50)	6.58(50)	6.58(50)	6.55(50)	6.55(50)	6.55(50)
5.98(40)	5.98(50)	6.00(50)	6.00(25)	6.00(40)	6.00(50)	6.00(50)	6.00(25)	6.00(40)	6.08(100)	6.28(30)	6.28(30)	6.28(30)	6.28(30)	6.08(100)	6.08(100)	6.28(30)	6.20(40)	6.30(50)	6.30(50)
5.68(60)	5.64(100)	5.68(90)	—	5.61(100)	5.65(100)	5.65(100)	—	5.61(100)	5.52(40)	—	—	—	—	5.52(40)	5.52(40)	—	5.50(50)	5.55(40)	5.55(40)
5.28(10)	5.37(20)	—	5.44(25)	—	5.38(20)	5.38(20)	5.44(25)	—	—	5.10(25)	5.10(25)	5.10(25)	5.10(25)	—	—	5.10(25)	—	—	5.15(25)
5.04(80)	4.98(80)	5.01(70)	5.06(70)	4.93(45)	4.96(60)	4.96(60)	5.06(70)	4.93(45)	4.86(30)	4.92(20)	4.92(20)	4.92(20)	4.92(20)	4.86(30)	4.86(30)	4.92(20)	4.90(25)	4.85(30)	4.85(30)
4.75(80)	4.72(60)	4.77(80)	4.82(50)	4.75(45)	4.75(40)	4.75(40)	4.82(50)	4.75(45)	4.64(50)	4.80(20)	4.80(20)	4.80(20)	4.80(20)	4.64(50)	4.64(50)	4.80(20)	4.70(50)	4.75(40)	4.75(40)
4.70(60)	4.70(50)	4.67(60)	—	4.65(45)	—	—	—	4.65(45)	4.30(40)	4.30(25)	4.30(25)	4.30(25)	4.30(25)	4.30(40)	4.30(40)	4.30(25)	4.30(25)	4.30(30)	4.30(30)
—	4.60(40)	4.60(50)	4.53(40)	4.53(45)	4.55(40)	4.55(40)	4.53(40)	4.53(45)	4.10(25)	4.10(40)	4.10(40)	4.10(40)	4.10(40)	4.10(25)	4.10(25)	4.10(40)	4.10(30)	4.10(20)	4.10(20)
4.31(80)	4.31(100)	4.29(90)	4.27(40)	4.25(60)	4.27(90)	4.27(90)	4.27(40)	4.25(60)	3.82(40)	3.80(20)	3.80(20)	3.80(20)	3.80(20)	3.82(40)	3.82(40)	3.80(20)	3.80(20)	3.80(30)	3.80(30)
4.11(10)	4.13(20)	4.11(10)	4.04(50)	—	4.10(50)	4.10(50)	4.04(50)	—	3.56(35)	3.56(30)	3.56(30)	3.56(30)	3.56(30)	3.56(35)	3.56(35)	3.56(30)	3.56(40)	3.56(50)	3.56(50)
3.80(50)	3.79(60)	3.79(50)	3.78(30)	3.77(35)	3.80(60)	3.80(60)	3.78(30)	3.77(35)	3.36(10)	—	—	—	—	3.36(10)	3.36(10)	—	3.40(20)	3.35(15)	3.35(15)
3.71(25)	—	3.70(70)	—	—	—	—	—	—	3.28(20)	—	—	—	—	3.28(20)	3.28(20)	—	3.30(25)	—	—
3.66(25)	3.68(30)	3.68(20)	3.65(30)	3.66(30)	3.68(30)	3.68(30)	3.65(30)	3.66(30)	3.12(90)	3.16(50)	3.16(50)	3.16(50)	3.16(50)	3.12(90)	3.12(90)	3.16(50)	3.15(90)	3.15(80)	3.15(80)
3.60(50)	3.60(70)	3.58(100)	3.55(30)	3.56(50)	3.55(40)	3.55(40)	3.55(30)	3.56(50)	2.94(80)	2.94(50)	2.94(50)	2.94(50)	2.94(50)	2.94(80)	2.94(80)	2.94(50)	2.94(60)	2.94(60)	2.94(60)
3.55(60)	3.55(70)	3.48(10)	3.48(30)	—	—	—	3.48(30)	—	2.66(80)	2.66(50)	2.66(50)	2.66(50)	2.66(50)	2.66(80)	2.66(80)	2.66(50)	2.66(70)	2.66(90)	2.66(90)
3.35(50)	3.34(60)	3.34(80)	3.28(40)	3.37(20)	3.35(30)	3.35(30)	3.28(40)	3.37(20)	2.50(60)	2.46(20)	2.46(20)	2.46(20)	2.46(20)	2.50(60)	2.50(60)	2.46(20)	2.50(50)	2.48(40)	2.48(40)
3.22(100)	3.20(75)	3.20(90)	3.19(40)	3.19(40)	3.20(40)	3.20(40)	3.19(40)	3.19(40)	2.20(30)	2.24(20)	2.24(20)	2.24(20)	2.24(20)	2.20(30)	2.20(30)	2.24(20)	2.22(20)	2.25(25)	2.25(25)
3.10(40)	3.10(40)	3.11(40)	3.08(20)	3.10(35)	3.10(25)	3.10(25)	3.08(20)	3.10(35)	2.14(40)	2.20(20)	2.20(20)	2.20(20)	2.20(20)	2.14(40)	2.14(40)	2.20(20)	2.15(30)	2.18(20)	2.18(20)
3.03(20)	3.02(30)	3.05(10)	3.03(15)	3.00(25)	3.05(20)	3.05(20)	3.03(15)	3.00(25)	2.02(40)	2.06(90)	2.06(90)	2.06(90)	2.06(90)	2.02(40)	2.02(40)	2.06(90)	2.05(80)	2.06(70)	2.06(70)
2.98(25)	2.98(40)	2.98(30)	2.98(20)	2.98(20)	2.98(20)	2.98(20)	2.98(20)	2.98(20)	1.98(30)	2.00(15)	2.00(15)	2.00(15)	2.00(15)	1.98(30)	1.98(30)	2.00(15)	2.00(20)	2.00(15)	2.00(15)
2.95(40)	2.93(50)	2.93(30)	2.90(25)	2.94(20)	2.90(15)	2.90(15)	2.90(25)	2.94(20)	1.86(30)	1.92(20)	1.92(20)	1.92(20)	1.92(20)	1.86(30)	1.86(30)	1.92(20)	1.90(15)	1.90(20)	1.90(20)
2.89(20)	2.88(20)	2.88(20)	—	2.88(25)	—	—	—	2.88(25)	1.82(20)	1.80(20)	1.80(20)	1.80(20)	1.80(20)	1.82(20)	1.82(20)	1.80(20)	1.82(20)	1.80(25)	1.80(25)
2.80(20)	2.80(20)	2.80(20)	2.82(20)	2.83(20)	2.80(30)	2.80(30)	2.82(20)	2.83(20)	—	1.76(15)	1.76(15)	1.76(15)	1.76(15)	—	—	1.76(15)	1.75(15)	—	—

–	2.71(20)	2.71(25)	2.70(20)	2.71(20)	2.70(25)	–	1.60(20)	1.60(20)	1.60(20)
–	2.66(25)	2.65(20)	2.66(40)	–	–	–	1.54(20)	1.54(20)	1.54(25)
2.58(30)	2.58(40)	2.58(50)	2.60(25)	2.56(30)	2.58(30)	–	–	–	–
2.51(40)	2.52(20)	2.53(20)	2.54(20)	2.53(25)	2.52(40)	–	–	–	–
2.46(40)	2.49(30)	2.49(40)	2.49(30)	2.45(20)	2.46(20)	–	–	–	–
–	2.44(25)	2.45(40)	2.43(25)	2.42(20)	2.44(30)	–	–	–	–
2.40(20)	2.40(25)	2.41(15)	2.40(20)	2.39(20)	2.40(20)	–	–	–	–
2.34(20)	–	2.37(30)	2.35(25)	2.30(30)	2.35(10)	–	–	–	–
2.25(50)	2.25(30)	2.26(25)	2.28(20)	2.26(20)	2.25(20)	–	–	–	–
–	–	2.23(40)	2.22(50)	2.20(40)	–	–	–	–	–
2.15(20)	2.15(45)	2.15(20)	2.13(25)	2.15(25)	2.15(20)	–	–	–	–
–	–	2.12(20)	2.11(50)	2.12(20)	2.12(30)	–	–	–	–
–	–	2.09(20)	2.07(25)	–	2.05(10)	–	–	–	–

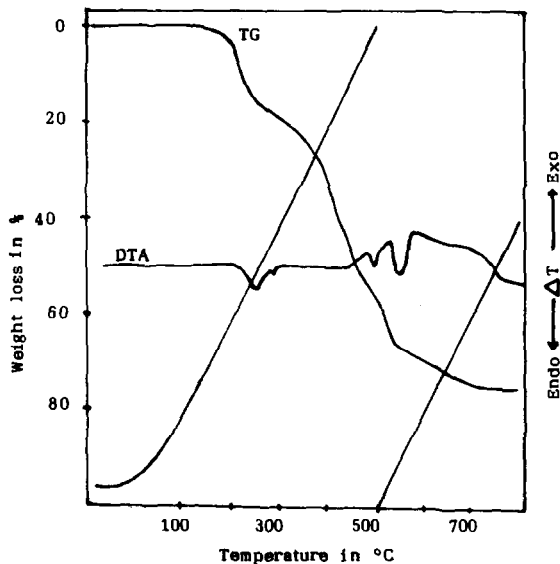


Fig. 1. TG and DTA curves of  $(\text{N}_2\text{H}_5)_2[\text{Eu}(\text{C}_6\text{H}_4(\text{COO})_2)_{2.5}]$ .

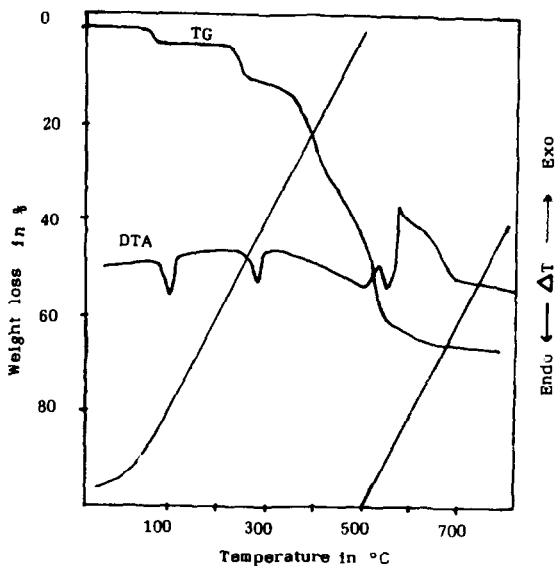


Fig. 2. TG and DTA curves of  $\text{N}_2\text{H}_5[\text{Dy}(\text{C}_6\text{H}_4(\text{COO})_2)(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ .

#### 4. Conclusion

Based on the evidence drawn from solubility, molar conductance, and spectral and thermal properties, it is reasonable to propose a structure for the complexes in which  $\text{N}_2\text{H}_5^+$  ions, as with  $\text{NH}_4^+$ ,  $\text{K}^+$  or  $\text{Na}^+$ , are the charge-compensating cations outside the

anionic complex coordination sphere. Such types of complexes of hydrazinium uranyl with a number of carboxylates, including phthalate, have been reported by the authors [19]. Govindarajan et al. have established crystallographically the non-coordination of  $N_2H_5^+$  in  $(N_2H_5)_6(UO_2)_2(C_2O_4)_5(H_2O)_2$  [24]

The metal ions (both in **A** and **B**) are nine-coordinated, probably with a coordination geometry of a tricapped trigonal prism. The phthalate ligand has two  $OCO^-$  groups and every carboxylate group can be mono- or bidentate, which accounts for the nine co-ordination. The exact carboxylate coordination and the possible dimeric form of the **A** complexes could be determined by single-crystal X-ray studies which, however, could not be carried out as the compounds do not form crystals suitable for such studies.

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