

## **THERMAL AND SPECTRAL PROPERTIES OF SOME ANHYDROUS AND HYDRATED RARE EARTH HYDRAZINECARBOXYLATES**

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### **Abstract**

The anhydrous rare earth hydrazinecarboxylates,  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3$  where  $\text{Ln}=\text{La, Ce, Pr, Nd or Sm}$  and hydrated rare earth hydrazinecarboxylates,  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3(\text{H}_2\text{O})_3$  where  $\text{Ln}=\text{La or Nd}$  have been prepared and characterized by chemical analyses, infrared spectroscopy and thermal analyses (TG/DTA/DTG). The infrared spectra indicate that the hydrazinecarboxylate group in both the sets of complexes is coordinated in a bidentate (chelate) fashion with the N–N stretching frequency at  $980\text{--}1000\text{ cm}^{-1}$ . The thermal analyses of all the complexes show multi-step decomposition. The final product in all the cases is invariably the respective metal oxide carbide,  $\text{Ln}_2\text{O}_2\text{C}_2$ , though there are some variations in the decomposition pattern.

**Keywords:** metal oxalate hydrazinates, metal oxide carbides, rare earth hydrazinecarboxylates

### **Introduction**

The hydrazinecarboxylate ion,  $\text{N}_2\text{H}_3\text{COO}^-$  is a versatile ligand which provides a wide opportunity for inorganic chemists interested in structure, bonding and thermal reactivity of metal complexes and synthesis of fine metal oxides, metal powders and mixed metal oxides at low temperatures. This ligand is highly reactive both chemically and thermally. The chemical reactivity or coordinating ability is due to the presence of four donor atoms while the thermal reactivity is due to the presence of N–N bond, which is endothermic in nature, which results in the liberation of large amount of heat energy during its thermal cleavage.

The hydrazinecarboxylate ion has been exploited by several groups of researchers for the past three decades and tremendous outcome has been registered in the areas of inorganic chemistry and material science. Despite its exhaustive utilization, this ligand still has sufficient scope for further research and development.

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Among the various metal hydrazinecarboxylates known so far [1–10], the rare earth complexes have been studied to a limited extent [11–14]. We have been interested in preparing hydrazine complexes of rare earth elements using hydrazinium hydrazinecarboxylate as ligand. To ensure the required purity, the complexes have been prepared by mixing respective metal nitrate and the ligand in appropriate ratio [7]. Our literature survey reveals that the anhydrous metal hydrazinecarboxylate complexes have been isolated only with transition metal ions and the corresponding rare earth complexes are unknown in spite of many reports available on hydrated rare earth hydrazinecarboxylates. Further, though the lanthanum hydrazinecarboxylate trihydrate has been mentioned in the literature [14], no further studies have been carried out with this complex.

Hence we were interested in studying these new anhydrous rare earth hydrazinecarboxylates of some lighter rare earth elements such as La, Ce, Pr, Nd and Sm with respect to their spectral and thermal properties. In this paper, we report the preparation, spectral and thermal properties of anhydrous rare earth hydrazinecarboxylates and lanthanum and neodymium hydrazinecarboxylate trihydrates. These hydrated complexes have been studied for comparison.

## Experimental

### *Preparation of hydrazinium hydrazinecarboxylate*

The ligand was prepared by mixing 100 mL of hydrazine hydrate (2 mol) and 192 g of solid ammonium carbonate (1 mol) in a dry beaker. The ammonium carbonate dissolved in hydrazine hydrate with the liberation of ammonia. The mixture was kept aside at room temperature for about 24 h for the completion of the reaction. The clear viscous liquid thus obtained was filtered and used as the ligand.

### *Preparation of the anhydrous complexes*

The corresponding rare earth oxide (0.01 mol) was dissolved in minimum amount of concentrated nitric acid and the clear solution obtained after filtration was evaporated on a water bath to dryness. Then the residue, the metal nitrate hydrate was dissolved in 20 mL of distilled water. To this solution the ligand was added in 1 mL portion. During the addition, initially the precipitate was formed which slowly dissolved by the addition of more ligand. The ligand was added till the solution became clear and all the precipitate just dissolved. Then the resultant solution was kept at room temperature. The crystalline complex formed after two days was filtered, washed with small amount of cold water and dried in air. The complexes thus obtained were crystalline in nature and stable in air. The complexes are insoluble in water and organic solvents while they undergo decomposition in hydrochloric acid with the liberation of carbon dioxide.

*Preparation of hydrated complexes*

The lanthanum oxide (0.01 mol) was dissolved in a minimum quantity of concentrated nitric acid and the clear solution was evaporated on a water bath to dryness. Then the residue was dissolved in 20 mL of distilled water. To this solution hydrazine hydrate was added in excess (0.06 mol). A gelatinous white precipitate was formed. Carbon dioxide gas was passed through the precipitate. The precipitate was slowly dissolved and the lanthanum hydrazinecarboxylate trihydrate was simultaneously precipitated. Carbon dioxide gas was passed continuously for about fifteen minutes. The powdery white precipitate, which settled down was filtered, washed with water and dried in air.

The above procedure was repeated for the preparation of trihydrated neodymium complex by replacing lanthanum oxide by neodymium oxide.

*Physico-chemical techniques*

The hydrazine content of the complexes was determined volumetrically using a standard  $\text{KIO}_3$  solution (0.025 mol) under Andrews condition [15]. The metal contents were determined by EDTA titration after decomposing a known amount of the complex with concentrated nitric acid [15].

The infrared spectra of the complexes were recorded with a Perkin Elmer 597 spectrophotometer in the range  $4000\text{--}200\text{ cm}^{-1}$  using KBr pellets of the solid samples. Simultaneous TG-DTG-DTA of the complexes were carried out using a Netzsch STA 409 instrument in argon atmosphere with a heating rate of  $20\text{ K min}^{-1}$  in the temperature range  $30\text{--}1000^\circ\text{C}$ . Aluminium cups were used as sample holders and aluminium oxide was used as reference material. Almost equal masses of the aluminium oxide and complex were used in thermal experiments.

**Results and discussion**

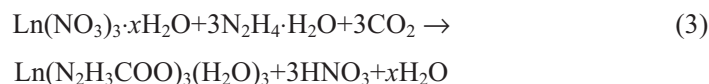
The anhydrous rare earth hydrazinecarboxylate were prepared by mixing the respective metal nitrate hydrate and the ligand, hydrazinium hydrazinecarboxylate in an appropriate ratio. The ligand was prepared by mixing hydrazine hydrate and ammonium carbonate. The hydrated complexes of lanthanum and neodymium were prepared by passing carbondioxide gas through an aqueous solution containing the respective metal nitrate hydrate and hydrazine hydrate. The chemical reaction for preparation of ligand, anhydrous complexes and hydrated complexes are given below in Eqs (1), (2) and (3), respectively.



where  $\text{Ln} = \text{La, Ce, Pr, Nd or Sm}$ .

**Table 1** Analytical data

Compound	Colour	Yield/%	Metal/%		Hydrazine/%	
			found	calcd.	found	calcd.
La(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	colourless	80	37.50	38.16	26.00	26.41
Ce(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	colourless	85	38.00	38.36	26.70	26.33
Pr(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	light green	85	39.00	38.49	25.80	26.27
Nd(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	rose	90	38.20	39.05	25.40	26.03
Sm(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	pale yellow	80	39.10	40.04	25.00	25.61
La(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub> ·(H <sub>2</sub> O) <sub>3</sub>	colourless	90	35.10	36.07	24.00	24.97
Nd(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub> ·(H <sub>2</sub> O) <sub>3</sub>	rose	85	35.20	36.94	23.90	24.63



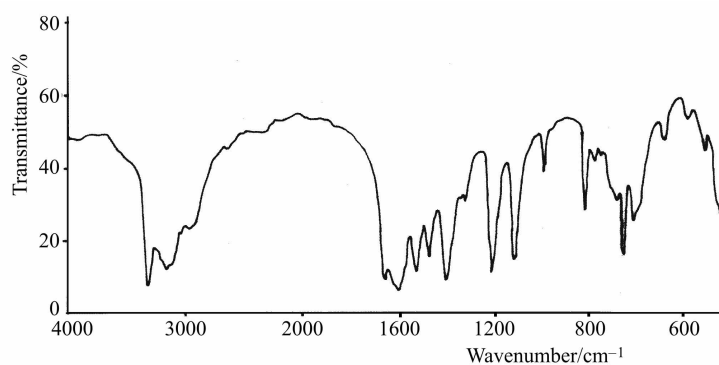
where  $\text{Ln}=\text{La}$  or  $\text{Nd}$ .

The formulae proposed for the ligand and complexes are in good agreement with the analytical data presented in Table 1.

It is interesting to note that the earlier workers reported the preparation of trihydrated complexes by the reaction of rare earth chlorides and carbon dioxide in the presence of hydrazine hydrate, where the hydrazinecarboxylate ion formed in situ reacts with the metal salt. However the formation of anhydrous complexes cannot be ruled out because the same procedure with transition metal nitrates gave the anhydrous complexes, though in many aspects transition metal complexes differ considerably from rare earth complexes.

#### *Infrared spectra*

The infrared spectra of all the anhydrous complexes are similar and superimposable as expected. The hydrated complexes also show similarity among themselves. But there is a slight difference between the spectra of anhydrous and hydrated complexes. The infrared spectra of  $\text{La}(\text{N}_2\text{H}_3\text{COO})_3$  and  $\text{La}(\text{N}_2\text{H}_3\text{COO})_3(\text{H}_2\text{O})_3$  are shown in Figs 1 and 2 as representative examples. The spectra of both the series of complexes show three bands in the region  $3100\text{--}3350\text{ cm}^{-1}$  due to the N–H stretching of  $\text{NH}_2\text{--NH}$  group. The asymmetric and symmetric COO stretching are observed at  $1650$  and  $1380\text{ cm}^{-1}$  respectively in the case of anhydrous complexes and for hydrated complexes these are observed at  $1650$  and  $1360\text{ cm}^{-1}$  respectively. The  $\Delta\nu$  separation of  $270$  and  $290\text{ cm}^{-1}$  for the two sets of complexes clearly shows the monodentate coordination of carboxylate ions. As reported earlier [16], the  $\text{N}_2\text{H}_3\text{COO}$  group acts as a bidentate (chelate) ligand and coordinates to the metal through nitrogen and oxygen atoms forming a stable five-membered ring. The characteristic N–N stretching frequency of such bidentate ligand is seen in the region



**Fig. 1** Infrared spectrum of  $\text{La}(\text{N}_2\text{H}_3\text{COO})_3$

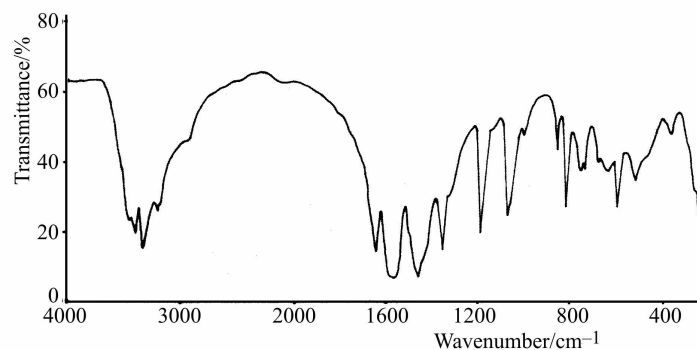


Fig. 2 Infrared spectrum of  $\text{La}(\text{N}_2\text{H}_3\text{COO})_3 \cdot (\text{H}_2\text{O})_3$

990–1000  $\text{cm}^{-1}$  in all the complexes. In the case of hydrated complexes an additional band is observed at 3450  $\text{cm}^{-1}$  for O–H stretching of coordinated water molecules. Though in the case of trihydrated complexes metal ions are expected to be nine coordinated by three bidentate  $\text{N}_2\text{H}_3\text{COO}$  groups and three water molecules, for anhydrous complexes, the octahedral geometry is assigned. Also in infrared spectra of anhydrous complexes there is no evidence for the bridging nature of carboxylate ion which excludes the possibility of higher coordination number. For bridged carboxylate group the  $\Delta\nu$  is expected to be 150–180  $\text{cm}^{-1}$  as observed in the case of barium complex and in oxalate complexes [10, 17]. Bridging mode of  $\text{N}_2\text{H}_3\text{COO}^-$  is rare. The infrared spectral data of the complexes are summarised in Table 2.

Table 2 Infrared spectral data of  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3$  and  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot (\text{H}_2\text{O})_3$ \* ( $\text{cm}^{-1}$ )

La	Ce	Pr	Nd	Sm	La*	Nd*	Assignments
–	–	–	–	–	3400	3400	O–H stretching
3300	3300	3300	3360	3300	3340	3340	N–H stretching
3250	3250	3250	3250	3250	3250	3220	N–H stretching
3150	3140	3150	3140	3140	3120	3120	N–H stretching
1650	1650	1650	1650	1650	1650	1650	C–O asymmetric stretching
1380	1380	1380	1380	1380	1360	1360	C–O symmetric stretching
1100	1100	1000	1000	1100	1070	1070	$\text{NH}_2$ wagging
990	990	990	990	990	1000	1000	N–N stretching
800	800	800	800	800	810	810	C–O bending
730	730	730	730	730	740	740	C–O bending
530	530	530	530	530	520	520	$\text{NH}_2$ rocking
480	480	480	480	478	470	470	M–O stretching

### Thermal studies

The hydrazinecarboxylate group is sensitive to heat due to the endothermic nature of N–N bond. Hence, the complexes containing this ligand are expected to decompose at low temperature. The thermal degradation was carried out in an inert argon atmosphere, because we expect that in air these complexes decompose similar to hydrated complexes except dehydration.

All the complexes undergo decomposition in the temperature range (100–720°C) to give the respective rare earth oxide carbide as the final residue. The intermediates formed were assigned on the basis of TG mass loss and on the basis of earlier studies [12]. The intermediates could not be isolated due to the continuous decomposition. The thermal traces are given in Figs 3–9.

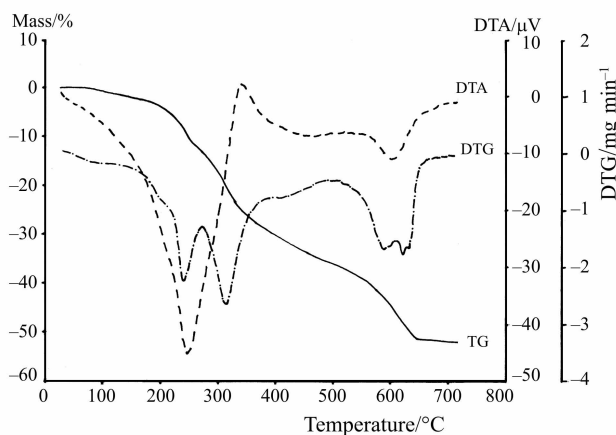


Fig. 3 TG/DTA/DTG of  $\text{La}(\text{N}_2\text{H}_3\text{COO})_3$

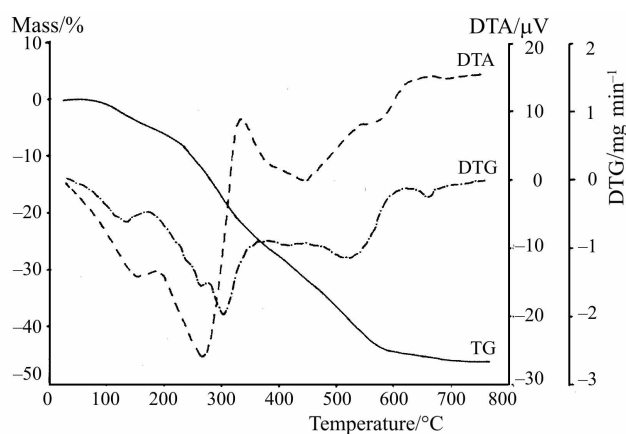
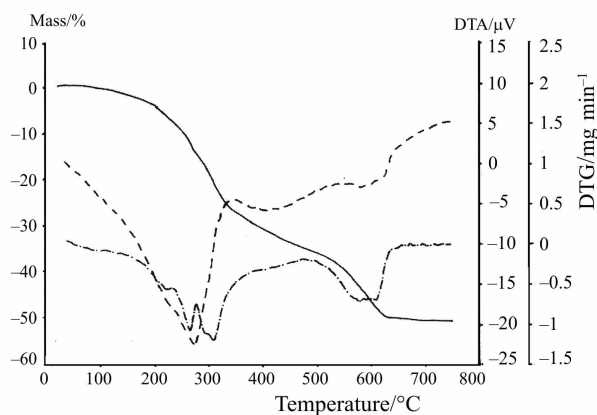
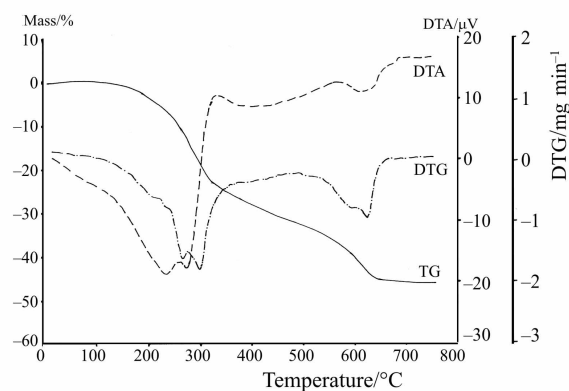
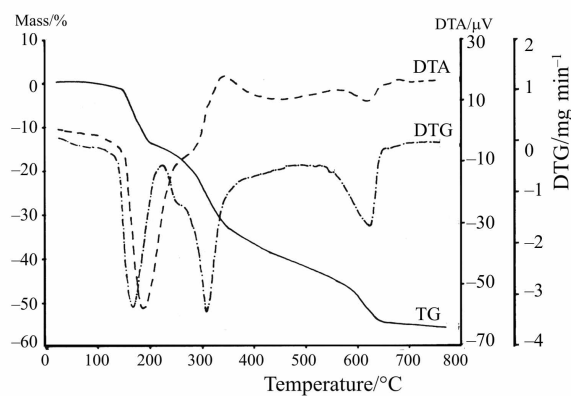


Fig. 4 TG/DTA/DTG of  $\text{Ce}(\text{N}_2\text{H}_3\text{COO})_3$

**Fig. 5** TG/DTA/DTG of Pr(N<sub>2</sub>H<sub>3</sub>COO)<sub>3</sub>**Fig. 6** TG/DTA/DTG of Nd(N<sub>2</sub>H<sub>3</sub>COO)<sub>3</sub>**Fig. 7** TG/DTA/DTG of Sm(N<sub>2</sub>H<sub>3</sub>COO)<sub>3</sub>



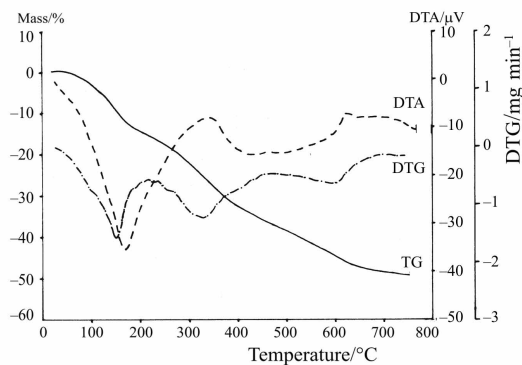


Fig. 8 TG/DTA/DTG of  $\text{La}(\text{N}_2\text{H}_3\text{COO})_3 \cdot (\text{H}_2\text{O})_3$

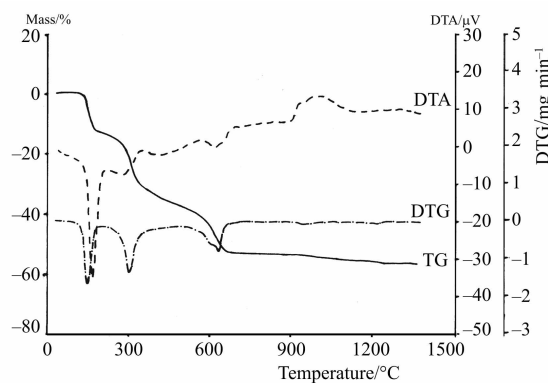


Fig. 9 TG/DTA/DTG of  $\text{Nd}(\text{N}_2\text{H}_3\text{COO})_3 \cdot (\text{H}_2\text{O})_3$

### $\text{La}(\text{N}_2\text{H}_3\text{COO})_3$

This complex undergoes five step decomposition. The first stage is the degradation of the complex to the tris(hydrazine) lanthanum oxalate in the temperature range 150–300°C. The DTA shows an exotherm effect at 247°C. This intermediate at higher temperature, between 300–405°C gives lanthanum cyanamide. This on further degradation results in the overall mass loss of about 36%. This may be due to the partial decomposition of the cyanamide intermediate to give a mixture of lanthanum oxide and amorphous carbon. The DTA corresponding to this step shows a broad endotherm in the temperature range 420–480°C. The DTG shows only a very little effect in the region 400–440°C for the above step. At about 600°C all the cyanamide intermediate is likely to be converted into a mixture of lanthanum oxide amorphous carbon with the TG mass loss of 46.72% as a whole. The DTA shows an endotherm at

**Table 3** Thermal data

Compounds	DTA peak temp./°C	DTG peak temp./°C	TG temp. range/°C	Mass loss/%		Residue
				found	calcd.	
La(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	247(+)	242	150–300	13.56	12.37	La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>3</sub>
	340(+)	316	300–405	30.49	28.85	La(CN <sub>2</sub> ) <sub>3</sub>
	420–480(+,b)	400–440	405–500	35.69	36.56	La(CN <sub>2</sub> )(CN) <sub>2</sub>
	599(+,b)	588	500–600	46.72	45.36	La <sub>2</sub> O <sub>3</sub> +3C
	620(+,b)	622	600–650	51.98	54.15	La <sub>2</sub> O <sub>2</sub> C <sub>2</sub>
Ce(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	265(+)	269	175–283	13.53	12.33	Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>3</sub>
	332(+)	309	285–400	25.69	28.49	Ce <sub>2</sub> (CN <sub>2</sub> ) <sub>3</sub>
	440(+,d)	420d	400–625	44.52	45.21	Ce <sub>2</sub> O <sub>3</sub> +3C
	580(+,d)	514d	–	–	–	–
	700(+)	665	625–720	48.00	50.46	CeOC <sub>2</sub>
Pr(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	274(+,b)	227d	100–280	15.18	16.68	Pr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>3</sub>
	–	275d	–	–	–	–
	–	318	280–340	30.24	28.70	Pr(CN <sub>2</sub> ) <sub>3</sub>
	408(+,b)	410	340–475	34.95	36.36	Pr(CN <sub>2</sub> )(CN) <sub>2</sub>
	583(+,b)	588d	475–620	50.81	53.85	Pr <sub>2</sub> O <sub>2</sub> C <sub>2</sub>
Nd(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	–	617d	–	–	–	–
	248(+d)	234t	140–270	9.48	–	Nd <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>3</sub>
	286(+d)	287t	–	–	12.19	–
	–	319t	270–320	29.61	–	Nd(CN <sub>2</sub> ) <sub>3</sub>
	400–500(+,b)	330–440(b)	320–500	35.83	28.44	Nd(CN <sub>2</sub> )(CN) <sub>2</sub>
Sm(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>	615(+,b)	594d	500–680	50.97	36.03	Nd <sub>2</sub> O <sub>2</sub> C <sub>2</sub>
	–	634d	–	–	53.37	–
	187(+,s)	176	120–240	15.18	16.27	Sm(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>
	320(+)	317	250–355	32.66	35.44	Sm <sub>2</sub> (CN <sub>2</sub> ) <sub>3</sub>
	450(+,b)	422	355–550	44.39	43.98	Sm <sub>2</sub> O <sub>3</sub> +3C
La(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub>	617(+,s)	632	550–670	55.36	52.50	Sm <sub>2</sub> O <sub>2</sub> C <sub>2</sub>
	170(+)	159	50–223	15.57	14.03	La(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>
	423(+,b)	336	223–466	36.56	32.75	La(CN <sub>2</sub> ) <sub>3</sub>
Nd(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub>	520(+,b)	601	466–693	52.98	56.66	La <sub>2</sub> O <sub>2</sub> C <sub>2</sub>
	155(+)	150	111–203	13.50	13.84	Nd(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub>
	331(+)	305	203–452	36.39	32.30	Nd(CN <sub>2</sub> ) <sub>3</sub>
	602(+)	636	452–683	53.14	55.88	Nd <sub>2</sub> O <sub>2</sub> C <sub>2</sub>

+: endotherm; b: broad; d: doublet; t: triplet; s: sharp; c: continuous

599°C and DTG at 588°C. Finally the lanthanum oxide and amorphous carbon combine to give the lanthanum oxide carbide as the final product. The DTA and DTG show an endotherm at 620 and 622°C, respectively, with the overall mass loss of 51.98% in TG curve.

#### *Ce(N<sub>2</sub>H<sub>3</sub>COO)<sub>3</sub>*

The first two stages are similar to the lanthanum complex. The oxalate and cyanamide derivatives are formed as the intermediates in the temperature range 175–283 and 285–400°C respectively. The DTA shows endotherms at 265 and 332°C respectively, for the first and second stages, for which the DTG was observed at 269 and 309°C. The third stage is the partial decomposition and then the complete decomposition of the cyanamide intermediate to the mixture of oxide and amorphous carbon in the temperature range 400–625°C. The TG shows only a continuous decomposition corresponding to this stage. However, the DTA and DTG show two endotherms and two minima respectively indicating the partial decomposition and complete decomposition. Then finally the cerium oxide carbide is formed at 720°C.

#### *Pr(N<sub>2</sub>H<sub>3</sub>COO)<sub>3</sub>*

This complex shows four-step decomposition. The first endotherm is broad, for which there appears a DTG minimum, which splits into three sharp lines. The TG temperature range is between 100 and 340°C. In the TG also two distinct steps are observed in this temperature range in which one corresponds to the formation of bis(hydrazine) praseodymium oxalate and the other to cyanamide. The praseodymium cyanamide decomposes partially to the oxide and carbon in the range 340–475°C with broad DTA endotherm at 408°C and DTG peak at 410°C. However, the final step is the simultaneous decomposition of the remaining cyanamide intermediate and the formation of praseodymium oxide carbide. For this step the DTA shows a broad endotherm with minimum at 583°C and a splitting in the DTG signal as a doublet was observed at 588 and 617°C.

#### *Nd(N<sub>2</sub>H<sub>3</sub>COO)<sub>3</sub>*

The formation of oxalate hydrazinate and cyanamide are observed in the temperature ranges 140–280 and 280–340°C respectively. There is no marked difference in the TG curve. A break is seen after the mass loss of about 9.5% which is attributed to the formation of trihydrazine neodymium oxalate. The DTA shows a doublet as endotherms at 248 and 286°C while the DTG shows a triplet at 234, 287 and 319°C. The remaining steps are similar to the praseodymium complex and give Nd<sub>2</sub>O<sub>2</sub>C<sub>2</sub> as the final product. The DTA shows two broad endotherms while DTG shows one broad singlet and a doublet respectively for the partial decomposition of the cyanamide intermediate and simultaneous decomposition and oxide carbide formation.

$Sm(N_2H_3COO)_3$ 

The samarium complex decomposes similar to that of cerium complex. The DTA shows four endotherms at 187, 320, 450 and 617°C. The corresponding minima observed in DTG are at 176, 317, 422 and 632°C. The complex finally gives samarium oxide carbide through tris(hydrazine) samarium oxalate, samarium cyanamide and oxide-carbon intermediates. The final temperature is 670°C.

 $La(N_2H_3COO)_3 \cdot (H_2O)_3$ 

In this hydrated complex three-step decomposition is observed. The complex first undergoes dehydration in the temperature range 50–223°C, followed by the decomposition to lanthanum cyanamide at 466°C and finally yields lanthanum oxide carbide as the end product. The final TG temperature is 693°C. The DTA shows three endotherms at 170, 423 and 520°C and three minima are observed at 159, 336 and 601°C in DTG curve.

 $Nd(N_2H_3COO)_3 \cdot (H_2O)_3$ 

This complex decomposes similar to the above complex to give neodymium oxide carbide as the final residue. Dehydration is common for most of the hydrated complexes. The final decomposition temperature is 683°C.

In the present case of the anhydrous complexes the TG mass loss in the first step corresponds to the formation of rare earth oxalate trihydrazinates as intermediate which is more common and has been already proposed in the decomposition of trihydrate complexes [12]. However, it is surprising to note that the trihydrate complexes of lanthanum and neodymium in the present case do not form such intermediate in argon atmosphere. This may be due to the fact that, after dehydration the temperature is so high that the direct decomposition to the cyanamide intermediate takes place.

Since all the lanthanide hydrazinecarboxylate so far isolated are their trihydrates, the first step of decomposition of such complexes is always expected to be dehydration; indeed it is observed. However, attempts to isolate the anhydrous complexes to study their geometry were unsuccessful due to the continuous decomposition of these anhydrous complexes after dehydration.

Now we have achieved the preparation of such anhydrous complexes by chemical reactions. In these complexes due to the absence of three water molecules, the endothermic dehydration is not observed and due to the absence of water six coordination around the metal is expected. In all the complexes the oxide carbide formation temperatures do not alter significantly in the series.

## Conclusions

The hitherto unknown anhydrous rare earth hydrazinecarboxylates have been prepared by the reaction of metal nitrate and the hydrazinum hydrazinecarboxylate prepared by mixing ammonium carbonate and hydrazine hydrate in appropriate ratio.

As expected all the complexes decompose at lower temperature than the trihydrated neodymium complex in inert argon atmosphere.

All the complexes undergo thermal degradation in the temperatures range 100–720°C to give the respective metal oxide carbide as the end product. The respective tris(hydrazine) metal oxalate, metal cyanide, metal oxide and amorphous carbon have been proposed as the intermediates.

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