

## Preparation, characterization and thermal analysis of rare earth and uranyl hydrazinecarboxylate derivatives

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**Abstract.** Hydrazinecarboxylate derivatives of rare earth elements  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Y}$ ) and  $\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  have been prepared and characterized by chemical analysis and infrared spectra. Simultaneous TG-DTG-DTA of the rare earth complexes show that the thermal decompositions occur through carbonate and oxycarbonate intermediates to the respective oxides. The oxide formation temperatures are lower than the corresponding oxalates and acetates. The uranyl complex decomposes to  $\text{U}_3\text{O}_8$  as the final product of decomposition.

**Keywords.** Hydrazinecarboxylate derivatives; infrared spectra; thermal analysis.

### 1. Introduction

Metal hydrazinecarboxylates are of interest as precursors to fine particle oxide materials (Macek *et al* 1976; Ravindranathan and Patil 1985). In our earlier study we reported the preparation, characterization and thermal analysis of transition metal hydrazinecarboxylate derivatives. In continuation of this study, we now describe the preparation, characterization and thermal analysis of  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Y}$ ) and  $\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ .

### 2. Experimental

Hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) 99–100% BDH was used in all the reactions. Rare earth oxides (99.9% pure) were obtained from Indian Rare Earths Limited.

#### 2.1 Preparation of rare earth hydrazinecarboxylate hydrates

The corresponding rare earth oxide was dissolved in the minimum quantity of dilute HCl required and the solution was then treated with hydrazine hydrate. The precipitate formed dissolved when  $\text{CO}_2$  gas was bubbled through the solution. Crystalline solid products separated from the clear solution in a couple of days and these were washed with alcohol and ether and stored under vacuum. Their composition was shown by chemical analysis to be  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ .

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## 2.2 Preparation of uranyl hydrazinecarboxylate hydrazine hydrate

Hydrazine hydrate was added to a solution of uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (May and Baker). The precipitate initially formed was dissolved by passing  $\text{CO}_2$  gas through the solution and the resulting clear solution was kept open to the atmosphere. Light yellow crystals were formed after 10–15 days, which were washed with alcohol and ether and stored under vacuum. The composition of the crystals was fixed by chemical analysis to be  $\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ .

## 2.3 Analysis

The metal contents in the rare earth complexes were determined by EDTA complexometric titrations. The uranium(VI) in the complex was determined gravimetrically using oxine. The hydrazine content was determined volumetrically using 0.025 M  $\text{KIO}_3$  solution under Andrews' conditions (Vogel 1961).

## 2.4 Physicochemical studies

The infrared spectra of the complexes were recorded as nujol mulls using a Perkin-Elmer 781 spectrophotometer. Simultaneous TG-DTG-DTA of the samples were recorded using an Ulvac Sinku-Riko TA 1500 Instrument. All the experiments were carried out using 3–6 mg samples under ambient conditions. The heating rate employed was  $10^\circ\text{C}/\text{min}$ . The oxides were characterized by the x-ray powder diffraction patterns recorded on a Philips PW 1050/70 diffractometer using  $\text{CuK}_\alpha$  radiation. The BET surface areas of oxides were measured by nitrogen adsorption using a Micromeritics Accusorb 2100E instrument.

## 3. Results and discussion

The reaction of rare earth ions ( $\text{Ln}^{3+}$ ) with  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  in the presence of  $\text{CO}_2$  yields the corresponding hydrazinecarboxylate hydrates,  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$  and  $\text{Y}$ ) as reported (Macek *et al* 1976). Our attempts to obtain any hydrazinium,  $\text{N}_2\text{H}_5\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$  or hydrazine,  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot x\text{N}_2\text{H}_4$  derivatives were not successful. Use of  $\text{N}_2\text{H}_3\text{COON}_2\text{H}_5$  (Ravindranathan and Patil 1985) instead of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  also resulted in the formation of the  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  type of complexes. It is surprising that the corresponding lanthanum derivative  $\text{La}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  could not be obtained under similar experimental conditions.

### 3.1 Infrared spectra

The infrared absorption spectra of  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  type complexes are all identical as is expected. A typical IR spectrum of  $\text{Nd}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  is shown in figure 1. The IR spectra of these complexes show the characteristic N–N stretching frequency of  $\text{N}_2\text{H}_3\text{COO}^-$  in the region  $990\text{--}1000\text{ cm}^{-1}$ . Other IR absorption frequencies of  $\text{N}_2\text{H}_3\text{COO}^-$  are similar to those reported for  $M(\text{N}_2\text{H}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$  type complexes (Patil *et al* 1983). The IR spectrum of  $\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  shows additional bands at  $960\text{ cm}^{-1}$  due to the  $\nu\text{N--N}$  of the bridged hydrazine and at  $900\text{ cm}^{-1}$  due to O–U–O stretching.

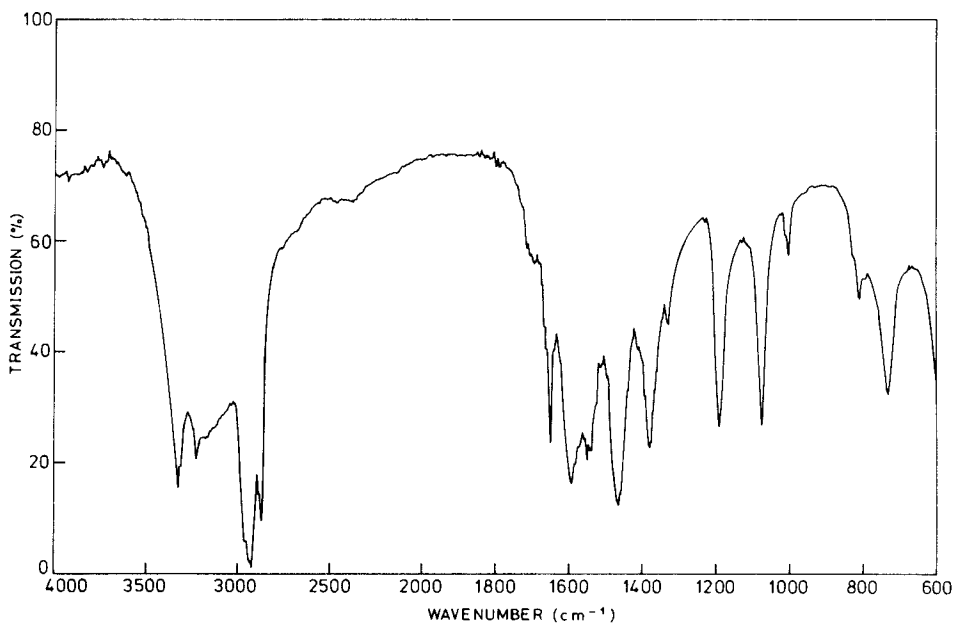


Figure 1. Infrared spectrum of  $\text{Nd}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$

### 3.2 Thermal analysis

The results of TG-DTA of the  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  complexes and  $\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  are summarized in table 1. The thermal analysis curve of  $\text{Nd}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  is shown in figure 2. The composition of the intermediates are those which best fit the observed weight loss in TG.

All the complexes,  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ , lose the water of hydration initially in a single step to yield the corresponding metal hydrazinecarboxylates. The dehydration takes place at fairly high temperatures (120–200°C) indicating the coordination of the water molecules to the metal.

The hydrazinecarboxylates obtained after dehydration decompose exothermically to the respective metal carbonates  $\text{Ln}_2(\text{CO}_3)_3$ . The DTA curve shows two exotherms while the TG curve shows a single step for the decomposition to  $\text{Ln}_2(\text{CO}_3)_3$ . In certain cases, like in Pr, Nd and Gd complexes, the TG shows breaks (~22% weight loss) indicating decomposition through a very unstable intermediate. On the basis of our earlier studies (Patil *et al* 1979; Ravindranathan and Patil 1985), the observed weight loss appears to suggest the formation of an intermediate of the type  $\text{Ln}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{N}_2\text{H}_4$ . This intermediate could not be isolated as the TG curve shows continuous reaction in this region. In the case of lighter rare earths, the respective carbonates decompose through the oxycarbonates ( $\text{Ln}_2\text{O}_3 \cdot \text{CO}_2$ ) (as indicated by TG) which then decompose endothermically to the respective oxides. However, this step is not observed in the heavier rare earth complexes which give the oxide directly. The oxide formation temperatures do not alter significantly in the series.

**Table 1.** Thermal analysis data of rare earth hydrazinecarboxylate hydrates,  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  and  $\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$

Thermogravimetry						
Name of Ln in complex	Step	Temperature range °C	% weight loss		DTA peak temperature °C	Solid product
			Found	Calculated		
Ce	1	100-160	13.00	12.88	145 (endo)	$\text{Ce}(\text{N}_2\text{H}_3\text{COO})_3$
	2	160-280	59.00	58.93	240 (exo)	$\text{CeO}_2$
Pr	1	120-160	13.00	12.86	150 (endo)	$\text{Pr}(\text{N}_2\text{H}_3\text{COO})_3$
	2	160-290	22.00	23.57	275 (exo)	$\text{Pr}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{N}_2\text{H}_4$
	3	290-335	42.00	45.01	310 (exo)	$\text{Pr}_2(\text{CO}_3)_3$
	4	335-450	53.00	55.48		$\text{Pr}_2\text{O}_3 \cdot \text{CO}_2$
Nd	5	450-510	60.00	59.45	475 (endo)	$\text{Pr}_6\text{O}_{11}$
	1	135-170	13.00	12.75	150 (endo)	$\text{Nd}(\text{N}_2\text{H}_3\text{COO})_3$
	2	170-290	23.00	23.39	255 (exo)	$\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{N}_2\text{H}_4$
	3	290-330	39.00	36.56	310 (exo)	$\text{Nd}_2(\text{CO}_3)_3$
	4	330-560	57.00	55.05	380 (endo)	$\text{Nd}_2\text{O}_3 \cdot \text{CO}_2$
Sm	5	560-600	61.00	60.24	560 (endo)	$\text{Nd}_2\text{O}_3$
	1	120-160	13.00	12.57	155 (endo)	$\text{Sm}(\text{N}_2\text{H}_3\text{COO})_3$
	2	160-310	45.00	44.02	260,305 (exo)	$\text{Sm}_2(\text{CO}_3)_3$
	3	310-550	57.00	54.26	455 (endo)	$\text{Sm}_2\text{O}_3 \cdot \text{CO}_2$
	4	550-590	61.00	59.39	575 (endo)	$\text{Sm}_2\text{O}_3$
Eu	1	135-175	13.00	12.53	165 (endo)	$\text{Eu}(\text{N}_2\text{H}_3\text{COO})_3$
	2	175-275	43.00	43.85	245,265 (exo)	$\text{Eu}_2(\text{CO}_3)_3$
	3	275-515	56.00	54.06	420 (endo)	$\text{Eu}_2\text{O}_3 \cdot \text{CO}_2$
	4	515-575	60.00	59.17	560 (endo)	$\text{Eu}_2\text{O}_3$
Gd	1	150-195	13.00	12.37	185 (endo)	$\text{Gd}(\text{N}_2\text{H}_3\text{COO})_3$
	2	195-305	23.00	22.69	280 (exo)	$\text{Gd}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{N}_2\text{H}_4$
	3	305-370	40.00	43.32	335 (exo)	$\text{Gd}_2(\text{CO}_3)_3$
	4	370-670	58.50	58.45	650 (endo)	$\text{Gd}_2\text{O}_3$
Tb	1	130-170	13.00	12.33	160 (endo)	$\text{Tb}(\text{N}_2\text{H}_3\text{COO})_3$
	2	170-310	44.00	43.16	260,300 (exo)	$\text{Tb}_2(\text{CO}_3)_3$
	3	310-480	54.50	53.20	455 (endo)	$\text{Tb}_2\text{O}_3 \cdot \text{CO}_2$
	4	480-610	58.00	57.31	610 (endo)	$\text{Tb}_4\text{O}_7$
Dy	1	130-170	13.00	12.23	165 (endo)	$\text{Dy}(\text{N}_2\text{H}_3\text{COO})_3$
	2	170-310	45.00	42.80	250,305 (exo)	$\text{Dy}_2(\text{CO}_3)_3$
	3	310-575	55.00	52.77	425 (endo)	$\text{Dy}_2\text{O}_3 \cdot \text{CO}_2$
	4	575-610	59.00	57.75	590 (endo)	$\text{Dy}_2\text{O}_3$
Ho	1	130-180	12.50	12.16	175 (endo)	$\text{Ho}(\text{N}_2\text{H}_3\text{COO})_3$
	2	180-315	46.00	42.57	270,310 (exo)	$\text{Ho}_2(\text{CO}_3)_3$
	3	315-655	59.00	57.44	630 (endo)	$\text{Ho}_2\text{O}_3$
Er	1	130-175	13.00	12.10	175 (endo)	$\text{Er}(\text{N}_2\text{H}_3\text{COO})_3$
	2	175-310	45.00	42.35	260,305 (exo)	$\text{Er}_2(\text{CO}_3)_3$
	3	310-620	57.00	57.14	615 (endo)	$\text{Er}_2\text{O}_3$
Yb	1	120-170	12.00	11.94	155 (endo)	$\text{Yb}(\text{N}_2\text{H}_3\text{COO})_3$
	2	170-305	45.00	41.81	245,300 (exo)	$\text{Yb}_2(\text{CO}_3)_3$
	3	305-655	58.00	56.41	455 (endo)	$\text{Yb}_2\text{O}_3$
Y	1	135-175	16.00	14.67	170 (endo)	$\text{Y}(\text{N}_2\text{H}_3\text{COO})_3$
	2	175-315	56.00	51.37	260,310 (exo)	$\text{Y}_2(\text{CO}_3)_3$
	3	315-640	72.00	69.31	415,640 (endo)	$\text{Y}_2\text{O}_3$
$\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	1	140-170	38.00	39.14	165 (exo)	$\text{UO}_3$
	2	170-585	41.00	40.28	575 (exo)	$\text{U}_3\text{O}_8$

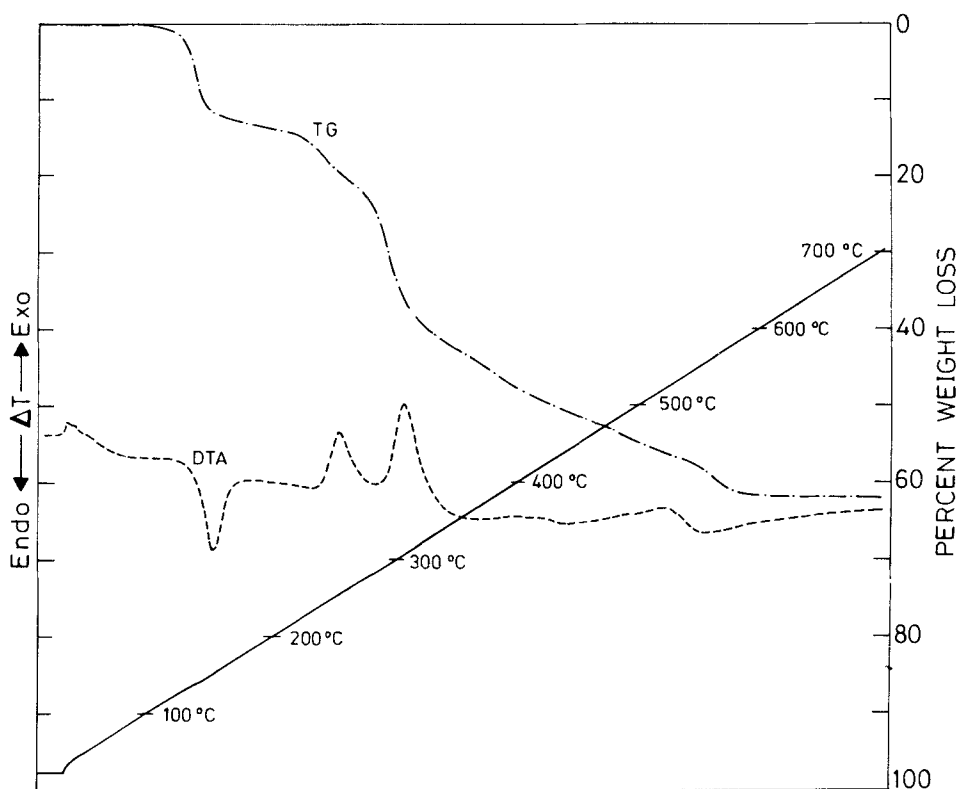
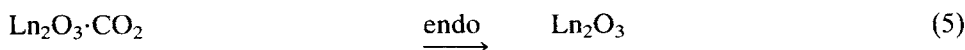
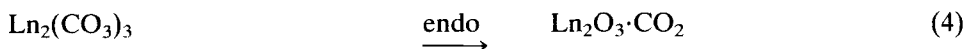
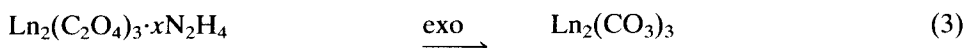
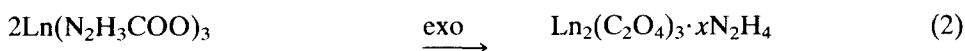
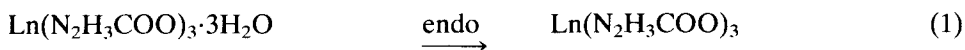


Figure 2. TG-DTA curves of  $\text{Nd}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$

The cerium complex,  $\text{Ce}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ , behaves differently, as compared to the other rare earth complexes. It loses its water of hydration in the region 100–160°C forming  $\text{Ce}(\text{N}_2\text{H}_3\text{COO})_3$ , which then decomposes exothermically in a single step to the oxide,  $\text{CeO}_2$ .

The general decomposition sequence of the rare earth hydrazinecarboxylate hydrates may be represented by the following equations:



The decomposition sequence followed by each complex is indicated in table 1.

The thermal decomposition of  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  is similar to those of rare earth carboxylates, e.g. acetates, oxalates, in that the intermediate stage is the carbonate which then decomposes to the oxide. The oxide formation temperatures are lower than those reported for acetates (Patil *et al* 1968), oxalates (Wendlandt 1959), and chemically prepared carbonates (Sastri *et al* 1966). No carbonate or oxycarbonate stage has been observed during the decomposition of cerium(III) acetate (Edwards and Hayward 1968) or cerium(III) oxalate (Wendlandt 1959).

The uranyl complex  $\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (Slivnik *et al* 1979) decomposes in two steps to give  $\text{U}_3\text{O}_8$  as the final product. Formation of  $\text{U}_3\text{O}_8$  was confirmed by its XRD pattern. The minimum oxide ( $\text{U}_3\text{O}_8$ ) formation temperature is  $\sim 585^\circ\text{C}$ .

### 3.3 BET surface area

The decomposition behaviour of rare earth hydrazinecarboxylates is quite interesting. The decomposition of the cerium complex is autocatalytic and is accompanied by swelling due to the evolution of large volumes of gases like  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$  and  $\text{CO}_2$ . The decomposition product is voluminous fine particle  $\text{CeO}_2$  having a surface area of  $90 \text{ m}^2 \text{ g}^{-1}$ . However, other rare earth complexes do not exhibit autocatalytic decomposition behaviour and yield oxides with lower surface areas e.g.  $\text{Eu}_2\text{O}_3 - 33 \text{ m}^2 \text{ g}^{-1}$ ,  $\text{Sm}_2\text{O}_3 - 27 \text{ m}^2 \text{ g}^{-1}$  and  $\text{Dy}_2\text{O}_3 - 17 \text{ m}^2 \text{ g}^{-1}$ . The observed variation in the surface areas may be attributed to the higher oxide formation temperatures as well as the different decomposition paths followed by the heavier rare earth complexes.

## 4. Conclusions

The following general observations emerge from the present study.

- (i) All the rare earths with the exception of lanthanum form  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  complexes under similar experimental conditions.
- (ii) The decomposition proceeds through carbonates similar to the decomposition of rare earth acetates and oxalates.
- (iii) The oxide formation temperatures of  $\text{Ln}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$  are lower than those of the corresponding rare earth acetates and oxalates.
- (iv) The cerium complex decomposes autocatalytically with swelling to give  $\text{CeO}_2$  with large surface area.

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