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# Preparation and thermal reactivity of some rare earth and uranyl hydrazinesulfinates and sulfite hydrazinates

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**Abstract**

Hydrazinesulfinate and sulfite hydrazinate derivatives of rare earth elements of composition $Ln(N_2H_3SOO)_3(H_2O)$ and $Ln_2(SO_3)_3(N_2H_4)_x(H_2O)_y$, respectively, where Ln = La, Ce, Pr, Nd and Sm, have been prepared and characterized by chemical analysis and infrared spectra. The uranyl complexes of the composition $UO_2(N_2H_3SOO)_2$, $UO_2(N_2H_3SOO)_2(N_2H_4)$ and $UO_2SO_3(N_2H_4)(H_2O)$ have also been prepared under different reaction conditions and studied by different physicochemical techniques. Thermal properties of all these complexes have been studied by thermogravimetry, and differential scanning calorimetry. The hydrazinesulfinate derivatives of rare earth elements undergo thermal decomposition in multisteps to give the respective metal sulfate as the residue. The other series of complexes, viz., rare earth sulfite hydrazinates gave a mixture of metal sulfate and metal oxide as the end products. However, all the uranyl complexes undergo decomposition in air to give $UO_2SO_3$ as the final product.

*Keywords:* Rare earth and uranyl complexes; Metal hydrazinesulfinates; Metal sulfite hydrazinates; Metal sulfites; Metal oxides; TG; DTG; DSC

## 1. Introduction

Hydrazine being a versatile ligand with two basic sites, forms a variety of complexes with alkaline earth metals and also with lanthanides and actinides [1]. The hydrazinecarboxylate ion $N_2H_3COO^-$ which is a derivative of hydrazine, received much attention during the last two decades due to its different modes of coordination towards metal ions [2–6]. It can act as either bidentate chelate or bridging ligand. While studying these hydrazine complexes and their derivatives, more emphasis is laid on their thermal behavior. The thermochemistry of these complexes is attractive since hydrazine is an endothermic compound and it liberates enormous amount of heat energy due to the formation of nitrogen molecule. Hence, metal complexes containing hydrazine and its derivatives have been utilized and are being exploited as precursors to metal oxides by their low temperature decomposition.

The hydrazinesulfinate $N_2H_3SOO^-$ is the sulfur analogue of the hydrazinecarboxylate, which also forms complexes with metal ions [7,8]and has similar coordination behavior. Although the transition metal complexes of hydrazine and its derivatives have been widely studied with various anions such as thiocyanate [9], chloride [10], sulfite [11], sulfate [12], carboxylate [13–17], hydrazinecarboxylate [2–6], hydrazinesulfinate [8], etc., the corresponding complexes of rare earth elements and uranyl ion have not been extensively studied. Only a few reports are available in the literature on these complexes [18–20]. This paper describes the preparation, characterization and thermal reactivity of some lighter lanthanides and uranyl complexes with hydrazinesulfinate and sulfite hydrazinate.

## 2. Experimental

The chemicals used were of AR grade. The rare earth oxides were purchased from Indian Rare Earths Limited. In all the reactions, 99–100% hydrazine hydrate was used as received. The solvents were distilled prior to use.

### 2.1. Preparation of $Ln(N_2H_3SOO)_3(H_2O)$

The respective rare earth oxide, $Ln_2O_3$(0.01 mol) was dissolved in a minimum amount of dilute nitric acid and

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evaporated to dryness. The residue, the nitrate was dissolved in 20 ml of distilled water. To this solution excess of hydrazine hydrate (3 ml, 0.06 mol) was added which resulted in the formation of gelatinous precipitate, the hydroxide. When sulfur dioxide gas was passed through this resultant solution, the precipitate dissolved slowly and the respective lanthanide hydrazinesulfinate monohydrate, $Ln(N_2H_3SOO)_3(H_2O)$, where Ln = La, Ce, Pr, Nd, or Sm was precipitated simultaneously. Excess sulfur dioxide was passed (for about five minutes) and the precipitate was filtered, washed with water then with alcohol and dried in air.

### 2.2. Preparation of $Ln_2(SO_3)_3(N_2H_4)_x(H_2O)_y$

To an aqueous solution (50 ml) of the corresponding rare earth oxide (0.01 mol) dissolved in a minimum quantity of dilute nitric acid, hydrazine hydrate (1.5 ml, 0.03 mol) was added and sulfur dioxide gas passed. The gelatinous precipitate formed initially by the addition of hydrazine hydrate was dissolved slowly on passing sulfur dioxide. The gas was passed continuously (for 10 min) till the solution was clear. Then, the clear solution was left for crystallization. The flake like substance formed after two to 3 days in all the cases was filtered, washed first with water then with alcohol and dried in air.

### 2.3. Preparation of $UO_2(N_2H_3SOO)_2$

It was prepared by passing excess sulfur dioxide gas into an aqueous solution containing uranyl nitrate hexahydrate (5.02 g, 0.01 mol) and hydrazine hydrate (1.5 ml, 0.03 mol). The precipitate formed initially by adding hydrazine hydrate to an aqueous solution of uranyl nitrate first dissolved and the uranyl hydrazinesulfinate precipitated simultaneously during the course of the reaction. The precipitate thus formed was filtered, washed successively with water alcohol and dried in air.

The complex was also prepared by mixing an aqueous solution of uranyl nitrate (0.01 mol) and excess of hydrazinium hydrazinesulfinate, $N_2H_3SOON_2H_5$ (5.12 g, 0.04 mol).

The ligand, $N_2H_3SOON_2H_5$ was prepared by passing sulfur dioxide gas through hydrazine hydrate in absolute alcohol. Initially by mixing the ligand with uranyl nitrate yellow precipitate was formed which dissolved slowly by the addition of excess ligand to give a clear solution. Further addition of ligand to this clear solution resulted in the precipitation of the complex, uranyl hydrazinesulfinate. This precipitate was filtered, washed first with water then with alcohol and dried at room temperature.

### 2.4. Preparation of $UO_2(N_2H_3SOO)_2(N_2H_4)$

This compound was obtained by bubbling the sulfur dioxide gas through a mixture of aqueous solution containing uranyl nitrate hexahydrate (5.02 g, 0.01 mol)and hydrazine hydrate(1.5 ml,0.03 mol). The precipitate formed initially was dissolved slowly by passing sulfur dioxide carefully so as to avoid even a slight excess of sulfur dioxide which otherwise causes the precipitation of uranyl hydrazinesulfinate. The clear solution thus obtained was left aside at room temperature to yield intense yellow spongy crystalline substance after 2–3 days. The complex, uranyl hydrazinesulfinate hydrazinate thus formed was removed, washed with water followed by alcohol and dried.

The above complex was also prepared by adding the ligand $N_2H_3SOON_2H_5$ in water to an aqueous solution of uranyl nitrate hexahydrate as in the case of uranyl hydrazinesulfinate, till the clear solution was obtained. Then, the clear solution was processed as above.

### 2.5. Preparation of $UO_2SO_3(N_2H_4)(H_2O)$

The complex was prepared by mixing the aqueous solutions of uranyl nitrate hexahydrate (5.02 g, 0,01 mol) with either hydrazinium sulfite monohydrate (1.64 g, 0.01 mol) or hydrazinium hydrazinesulfinate (1.28 g, 0.01 mol). In both the cases, the precipitate formed immediately after mixing was dissolved by adding a few drops of concentrated nitric acid. The clear solution thus obtained was allowed to stand at room temperature to give yellow flakes of uranyl sulfite hydrazinate hydrate which was removed, washed with water, then with alcohol and dried.

### 2.6. Physico-chemical techniques

The metal content in the complex was determined by EDTA titration after decomposing a known amount of the complex with nitric acid [21]. The uranium content was determined gravimetrically as $UO_2(C_9H_6ON)_2(C_9H_7ON)$ using oxine. The hydrazine content was determined volumetrically using a standard $KIO_3$ solution (0.025 mol dm$^{-3}$) under Andrew's conditions [21]. The infrared spectra of the complexes were recorded on Perkin-Elmer 597 spectrophotometer using KBr discs in the range 4000–200 cm$^{-1}$. The thermogravimetry and differential thermogravimetry of the complexes were recorded on a Delta series TGA 7 instrument and differential scanning analysis was recorded on a Delta series 7 instrument. The heating rate was 10 °C per minute and all the experiments were carried out in air using platinum cups as sample holders. About 3–8 mg of the sample was used for simultaneous TG, DTG and about 1–5 mg was used for DSC experiment.

## 3. Results and discussion

The rare earth hydrazinesulfinate monohydrates and lanthanide sulfite hydrazinate derivatives were prepared and the compositions of these complexes were assigned on the basis of their metal and hydrazine contents (Table 1). In the case of lanthanide sulfite hydrazinate derivatives lanthanum, cerium and praseodymium form bis-hydrazine complexes

Table 1
Analytical data of the complexes

| Compound | Color | Yield | Hydrazine (%) | | Metal (%) | |
|---|---|---|---|---|---|---|
| | | | Found | Calcd. | Found | Calcd. |
| $La(N_2H_3SOO)_3(H_2O)$ | Colorless | 75 | 21.00 | 21.71 | 30.30 | 30.45 |
| $Ce(N_2H_3SOO)_3(H_2O)$ | Colorless | 75 | 21.00 | 21.65 | 31.70 | 31.60 |
| $Pr(N_2H_3SOO)_3(H_2O)$ | Pale green | 80 | 21.50 | 21.61 | 31.00 | 31.76 |
| $Nd(N_2H_3SOO)_3(H_2O)$ | Rose | 85 | 20.80 | 21.45 | 32.20 | 32.22 |
| $Sm(N_2H_3SOO)_3(H_2O)$ | Light yellow | 70 | 20.60 | 21.16 | 32.50 | 33.11 |
| $La_2(SO_3)_3 \cdot 2N_2H_4$ | Colorless | 80 | 11.20 | 11.00 | 46.90 | 47.77 |
| $Ce_2(SO_3)_3 \cdot 2N_2H_4$ | Colorless | 85 | 11.50 | 10.96 | 46.80 | 47.95 |
| $Pr_2(SO_3)_3 \cdot 2N_2H_4$ | Pale green | 75 | 11.50 | 10.92 | 47.60 | 48.12 |
| $Nd_2(SO_3)_3 \cdot 3N_2H_4 \cdot 3H_2O$ | Rose | 70 | 13.80 | 14.16 | 42.00 | 42.48 |
| $Sm_2(SO_3)_3 \cdot 3N_2H_4 \cdot 3H_2O$ | Light yellow | 75 | 13.25 | 13.91 | 42.70 | 43.48 |
| $UO_2(N_2H_3SOO)_2$ | Light yellow | 90 | 14.30 | 13.91 | 49.90 | 50.74 |
| $UO_2(N_2H_3SOO)_2(N_2H_4)$ | Intense yellow | 70 | 20.00 | 19.79 | 47.60 | 48.37 |
| $UO_2SO_3(N_2H_4)(H_2O)$ | Light yellow | 70 | 8.30 | 8.00 | 58.70 | 59.00 |

while neodymium and samarium tris-hydrazine trihydrate complexes. The formation of different types of complexes in the later case was also observed with transition metal ions [8].

### 3.1. Infrared spectra

All the hydrazinesulfinate monohydrate complexes show three bands in the region 3300–3000 $cm^{-1}$. These bands are assigned to the N–H stretching of $NH_2$ groups. The O–H stretching of the water is seen at 3400 $cm^{-1}$. The N–N stretching of $N_2H_3SOO^-$ ions are observed at 980 $cm^{-1}$. The symmetric and asymmetric stretching of SOO group are observed at 1100 and 880 $cm^{-1}$, respectively, which indicates the oxygen co-ordination rather than sulfur coordination [22].

The band seen at 3450–3400 $cm^{-1}$ for neodymium and samarium sulfite hydrazinate hydrates is due to the O–H stretching of water molecules. All the rare earth sulfite hydrazinates and hydrazinate hydrates show N–H stretching frequency at 3350–3000 $cm^{-1}$. The N–N stretching of the $N_2H_4$ groups are observed at 960 $cm^{-1}$ indicating the bidentate bridging nature of hydrazine moieties [23]. This is expected similar to that of the transition metal complexes.

The uranyl hydrazinesufinate and its hydrazinate show two bands in the region 3300–3200 $cm^{-1}$ due to the N–H stretching frequencies. The N–N stretching of $N_2H_3SOO$ group is observed at 980 $cm^{-1}$ similar to the rare earth complexes. The hydrazinate adduct also shows a band at 960 $cm^{-1}$ which can be attributed to the N–N stretching frequency of bridged hydrazine [23]. The two bands observed at 3300 and 3200 $cm^{-1}$ for the uranyl sulfite hydrazinate hydrate are ascribable for N–H stretchings. The hydrated complex shows a band at 3400 $cm^{-1}$ due to the O–H stretching of water molecule. The N–N stretching for the complexes is observed at 970 $cm^{-1}$. All of the uranyl complexes show S–O asymmetric stretching in the range 1100–1090 $cm^{-1}$ as reported earlier [23]. The characteristic O–U–O stretching of all these compounds is observed at 900 $cm^{-1}$.

### 3.2. Thermal decomposition

The thermal properties of hydrazine complexes are interesting due to their sensitivity towards heat. Besides the final decomposition residues, the degradation scheme is also more interesting which leads to different intermediates and final products. Thus, the decomposition process depends on various factors like rate of heating, surrounding atmosphere etc. are new to the literature the thermal degradation was studied in air with the heating rate of 10 °C $min^{-1}$.

The salient feature of the thermal decomposition studies are summarized as follows. The intermediates and final residue/residues formed during thermal degradation have been proposed on the basis of thermogravimetric weight loss (Table 2). Though the final products have been analyzed for their composition, the intermediates have not been analyzed due to their instability at such temperatures at which they start decomposing as soon as they are formed preventing their isolation.

#### 3.2.1. Rare earth hydrazinesulfinate monohydrates

All the complexes of this type decompose in a similar fashion (Figs. 1 and 2). The first stage is found to be dehydration in the temperature range 60–150 °C. As expected, this step is endothermic as shown by the DSC curve. Also, the removal of water relatively at low temperature is an indication of the presence of this group as non-coordinated species. In the known systems [18] containing coordinated water, the dehydration takes place above 300 °C.

The anhydrous complex thus formed undergoes further decomposition in two steps giving the respective metal sulfate as the final product and the corresponding metal sulfate hydrazinate as the intermediate. The formation of this intermediate has been confirmed by their qualitative and quantitative analyses of metal, sulfate and hydrazine contents. This has been done after the isolation of this intermediate at appropriate temperatures during thermal degradation. The formation of metal sulfate is quite probable since the

Table 2
Thermal analysis data

| Compound | DTG peak temp (°C) | DSC peak temp (°C) | TG temp range (°C) | TG weight loss (%) | | Final products |
|---|---|---|---|---|---|---|
| | | | | Found | Calcd. | |
| $La(N_2H_3SOO)_3(H_2O)$ | 110 | 110 (+, b) | 60–120 | 5.00 | 4.07 | $La(N_2H_3SOO)_3$ |
| | 205 | 210 (+) | 120–250 | 20.00 | 21.51 | $La_2(SO_4)_3\cdot 4N_2H_4$ |
| | 490, 540 (d) | 440, 540 (+, d) | 360–600 | 34.00 | 35.99 | $La_2(SO_4)_3$ |
| $Ce(N_2H_3SOO)_3(H_2O)$ | 95 | 120 (+) | 60–120 | 4.00 | 4.06 | $Ce(N_2H_3SOO)_3$ |
| | 200 | 190 (+) | 160–240 | 19.00 | 21.45 | $Ce_2(SO_4)_3\cdot 4N_2H_4$ |
| | 390, 530 | 485, 520 (+, d) | 300–570 | 23.00 | 25.06 | $CeSO_4$ |
| $Pr(N_2H_3SOO)_3(H_2O)$ | 90, 140 (d) | 90, 130 (+, d) | 60–150 | 4.00 | 4.05 | $Pr(N_2H_3SOO)_3$ |
| | 210 | 210 (+) | 150–250 | 20.00 | 21.41 | $Pr_2(SO_4)_3\cdot 4N_2H_4$ |
| | 470, 535 | 475, 535 (+, d) | 300–595 | 34.70 | 35.83 | $Pr_2(SO_4)_3$ |
| $Nd(N_2H_3SOO)_3(H_2O)$ | 100 | 105 (+) | 60–110 | 5.00 | 4.02 | $Nd(N_2H_3SOO)_3$ |
| | 200 | 220 (+) | 160–240 | 19.50 | 21.26 | $Nd_2(SO_4)_3\cdot 4N_2H_4$ |
| | 550 | 560 (+) | 300–595 | 35.20 | 35.56 | $Nd_2(SO_4)_3$ |
| $Sm(N_2H_3SOO)_3(H_2O)$ | 90 | 100 (+, b) | 60–150 | 3.50 | 3.97 | $Sm(N_2H_3SOO)_3$ |
| | 195, 220, 230 (t) | 220, 240 (+, b) | 150–250 | 22.00 | 20.97 | $Sm_2(SO_4)_3\cdot 4N_2H_4$ |
| | 585 | 590 | 250–600 | 36.80 | 35.08 | $Sm_2(SO_4)_3$ |
| $La_2(SO_3)_3\cdot 2N_2H_4$ | 150 | 170 (−) | 100–180 | 6.00 | 5.50 | $La_2(SO_3)_3(N_2H_4)$ |
| | 320 | 280 (+, ∗) | 180–500 | 12.00 | 11.00 | $La_2(SO_3)_3$ |
| | 550 | 550 (+) | 510–580 | 24.30 | 23.37 | $La_2(SO_4)_3 + La_2O_3$ |
| $Ce_2(SO_3)_3\cdot 2N_2H_4$ | 150 | 150 (−) | 80–200 | 6.00 | 5.48 | $Ce_2(SO_3)_3(N_2H_4)$ |
| | 290 | 290 (+, ∗) | 200–300 | 9.50 | 10.95 | $Ce_2(SO_3)_3$ |
| | 450 | 450 (+) | 300–500 | 12.00 | 13.70 | $Ce(SO_4)_2 + CeO_2$ |
| $Pr_2(SO_3)_3\cdot 2N_2H_4$ | 160 | 160 (−) | 100–180 | 5.60 | 5.46 | $Pr_2(SO_3)_3(N_2H_4)$ |
| | 330 | 330 (+, ∗) | 180–480 | 12.50 | 10.92 | $Pr_2(SO_3)_3$ |
| | 540 | 540 (+) | 510–580 | 26.50 | 23.21 | $Pr_2(SO_4)_3 + Pr_2O_3$ |
| $Nd_2(SO_3)_3\cdot 3N_2H_4\cdot 3H_2O$ | 110 | 90 (+) | 60–130 | 7.00 | 7.96 | $Nd_2(SO_3)_3\cdot 3N_2H_4$ |
| | 220, 460 | 220, 460 (+, ∗) | 130–480 | 22.50 | 22.12 | $Nd_2(SO_3)_3$ |
| | 540 | 540 (+) | 500–580 | 35.78 | 32.74 | $Nd_2(SO_4)_3 + Nd_2O_3$ |
| $Sm_2(SO_3)_3\cdot 3N_2H_4\cdot 3H_2O$ | 80, 110 | 80, 110 (+, d) | 60–130 | 8.00 | 7.82 | $Sm_2(SO_3)_3\cdot 3N_2H_4$ |
| | 210, 460 | 210, 460 (+, ∗) | 150–480 | 22.00 | 21.73 | $Sm_2(SO_3)_3$ |
| | 560 | 560 (+) | 520–580 | 34.00 | 32.17 | $Sm_2(SO_4)_3 + Sm_2O_3$ |
| $UO_2(N_2H_3SOO)_2$ | 185 | 185 (−) | 160–230 | 23.80 | 23.91 | $UO_2SO_3$ |
| $UO_2(N_2H_3SOO)_2(N_2H_4)$ | 145 | 145 (−) | 95–155 | 6.10 | 6.51 | $UO_2(N_2H_3SOO)_2$ |
| | 180 | 180 (−) | 155–280 | 22.30 | 22.35 | $UO_2SO_3$ |
| $UO_2SO_3(N_2H_4)(H_2O)$ | 180 | 180 (+) | 125–210 | 5.00 | 4.50 | $UO_2SO_3(N_2H_4)$ |
| | 240 | 240 (−) | 215–260 | 8.00 | 8.38 | $UO_2SO_3$ |

(+): endotherm; (−): exotherm; d: doublet; t: triplet; b: broad; (∗): broad endotherm with minimum centered at the given temperature.

oxidation of sulfinates to sulfites or sulfates is the normal trend during the decomposition of such complexes in air atmosphere. Though this result is not convincing, since hydrazine chemists and material scientists were always interested to have metal oxide as the final decomposition residue such end products could be achieved through the thermal decomposition of these complexes in inert or reducing atmosphere, which prevents the oxidation of sulfinate group which has been observed in the case of transition metal hydrazinesulfinates and their hydrazinates [8]. Such a trend cannot be expected in the case of well known hydrazinium rare earth sulfate monohydrates.

The TG, DTG and DSC curves of cerium and neodymium complexes given as representative examples show that the DTG curves corresponding to the dehydration are very sharp while the DSC curves show only broad exotherms. Further, the decomposition of the hydrazinate complexes in all the cases is continuous over a wide temperature range to give the mono hydrazinate intermediate, which decompose sharply to give the metal sulfate. The DSC shows a broad endotherm corresponding to the decomposition of hydrazinate complexes and so also the DTG curve. Both DSC and DTG are very sharp for the final step i.e. the degradation of mono hydrazinate to the metal sulfate.

### 3.2.2. Rare earth sulfite hydrazinate derivatives

Since lanthanum, cerium and praseodymium form complexes of the same composition, they are expected to

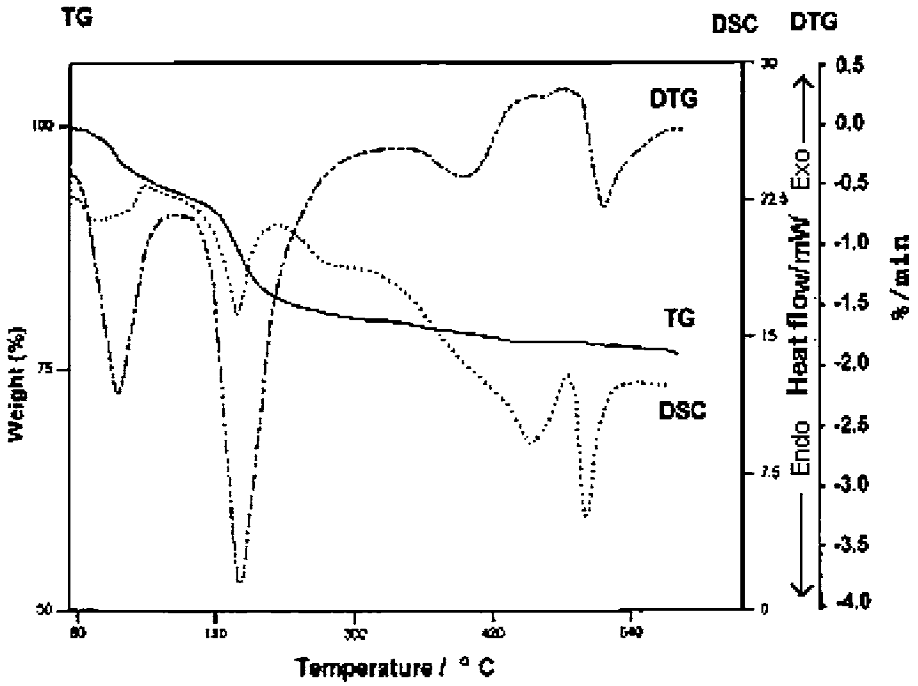

Fig. 1. TG, DTG and DSC curves of $Ce(N_2H_3SOO)_3(H_2O)$.

undergo decomposition in a similar manner. Indeed, all the three complexes decompose in three stages. The first step is the dehydrazination and it is exothermic. The second stage is also dehydrazination which corresponds to a broad endotherm centered at 280, 330 and 290 °C, respectively, for the La, Ce and Pr complexes in the DSC curve and TG (Fig. 3) shows a weight loss for this step in the temperature range 200–550 °C. The final step is the decomposition of lanthanide sulfite at around 600 °C to give the mixture of respective metal sulfate and oxide in 1:1 ratio as the final products and this step is very sharp in DSC and DTG.

In the case of neodymium (Fig. 4) and samarium, since they are hydrated, the complexes first undergo dehydration as expected. The dehydration is endothermic and broad. Then the anhydrous compounds undergo dehydrazination and decomposition as above to give a mixture of metal sulfate and metal oxide in 1:1 ratio. Unlike the above three anhydrous complexes, the neodymium and samarium complexes give up two hydrazine molecules during first step of dehydrazination. The formation of the mixture of metal sulfate and oxide has been previously observed in the thermal degradation of similar transition metal complexes [24].

Again, in this case also the final product is not a pure metal oxide. Of course, the oxide can be separated by dissolving the sulfate in water. However, as mentioned in the transition metal complexes, in this case also it may be possible to get

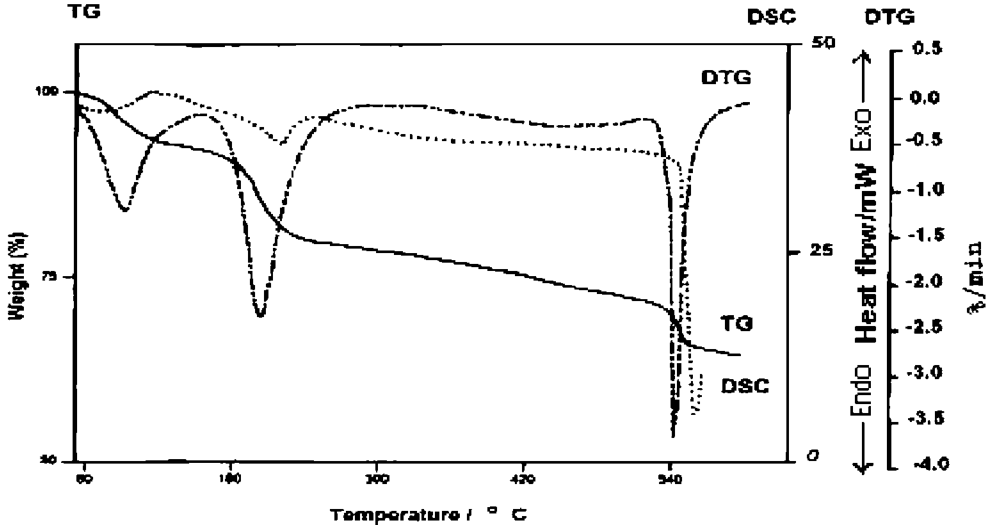

Fig. 2. TG, DTG and DSC curves of $Nd(N_2H_3SOO)_3(H_2O)$.

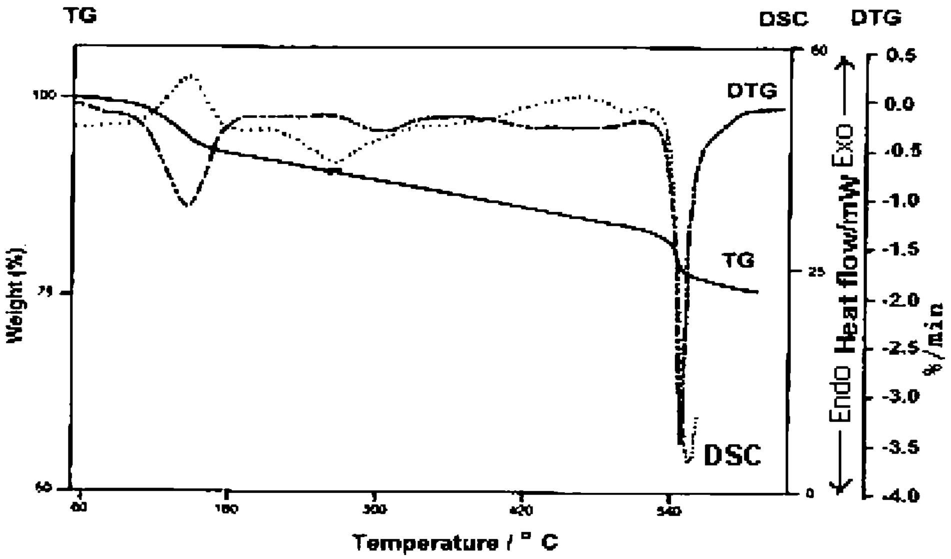

Fig. 3. TG, DTG and DSC curves of $La_2(SO_3)_3{\cdot}2N_2H_4$

metal oxide alone by combustion. The TG, DTG and DSC traces of lanthanum and neodymium complexes are shown in Figs. 3 and 4, respectively, as representative models for anhydrous and hydrated metal sulfite hydrazinates.

### 3.2.3. Uranyl hydrazinesulfinate and its hydrazinate

The DSC of $UO_2(N_2H_3SOO)_2$ shows a single exotherm at 185 °C corresponding to the decomposition of the compound to give $UO_2SO_3$. The uranyl hydrazinesulfinate hydrazinate decomposes in two stages. The first stage is dehydrazination at 145 °C which is exothermic to give the $UO_2(N_2H_3SOO)_2$ as intermediate which further decomposes similar to the above.

### 3.2.4. Uranyl sulfite hydrazinate hydrate

The DSC of $UO_2SO_3(N_2H_4)(H_2O)$ shows two distinct steps. The first endothermic peak is due to dehydration, which occurs at (180 °C), a fairly high temperature, indicating the presence of coordinated water. The anhydrous compound further decomposes exothermically at 240 °C to give $UO_2SO_3$ by the removal of hydrazine. The TG is in accordance with the DSC results. The uranyl sulfite formed in all the above cases have not been further studied since its decomposition at high temperature to give $U_3O_8$ is well known. The TG, DTG and DSC traces of $UO_2(N_2H_3SOO)_2$ are shown in Fig. 5.

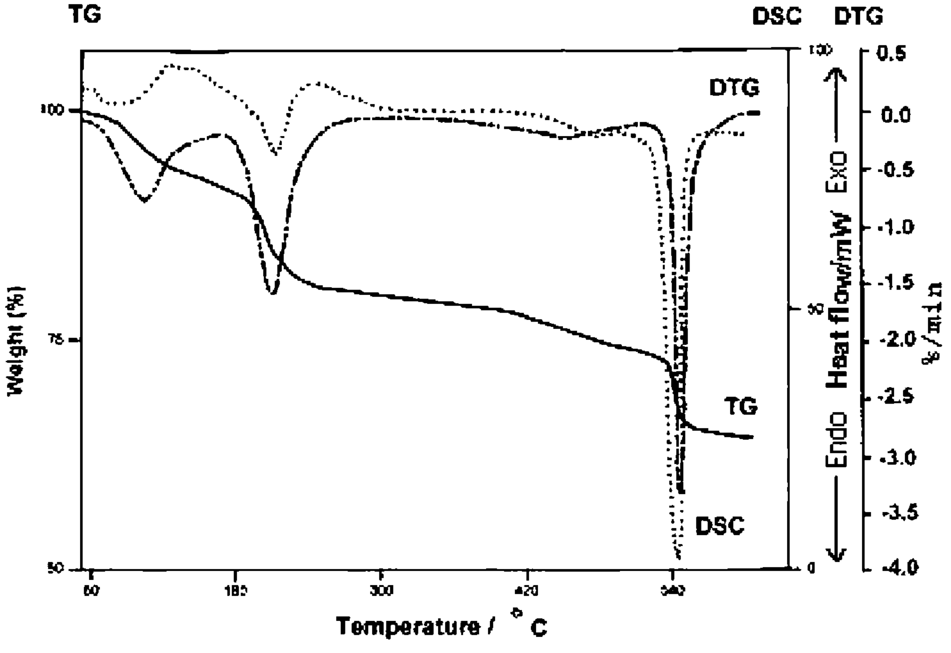

Fig. 4. TG, DTG and DSC curves of $Nd_2(SO_3)_3{\cdot}3N_2H_4{\cdot}3H_2O$.

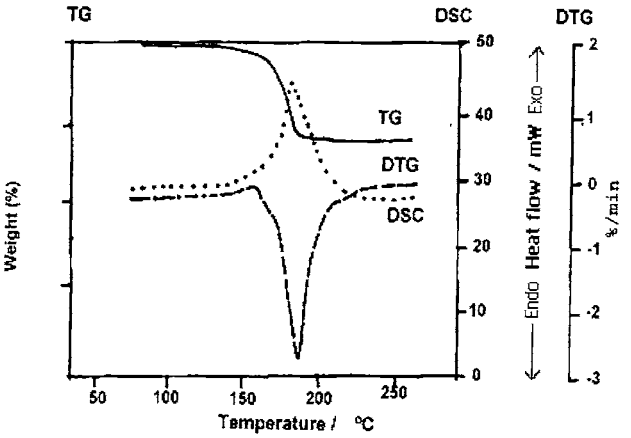

Fig. 5. TG, DTG and DSC curves of $UO_2(N_2H_3SOO)_2$.

## 4. Conclusions

The lanthanide ions such as $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$ and $Sm^{3+}$ react with sulfurdioxide in the presence of hydrazine hydrate to form lanthanide hydrazinesulfinate monohydrate and lanthanide sulfite hydrazinates and their hydrates under different experimental conditions.

Uranyl ion form's three different complexes with sulfurdioxide in the presence of hydrazine hydrate under different conditions.

During thermal degradation in air lanthanide hydrazinesulfinate monohydrates yield the respective lanthanide sulfate as the final residue while lanthanide sulfite hydrazinates and their hydrates give mixture of respective lanthanide sulfate and oxide in 1:1 ratio.

All the uranyl complexes decompose in the temperature range 95–280 °C to give uranyl sulfite as the end residue.

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