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Reactions of heavier lanthanides with hydrazine in the presence of sulphur dioxide

L. Ragunath · B. N. Sivasankar · R. Ragul

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Abstract Hydrazine hydrate reacts with sulphur dioxide in aqueous solution in the presence of heavier lanthanide(III) ions to give variety of complexes. The nature of product formed is highly pH dependent. Several hydrazine complexes of Ln(III) ions of the compositions $Ln(N_2H_3SOO)_3(H_2O)$, $Ln_2(SO_3)_3{\cdot}2N_2H_4$ and $N_2H_5Ln(SO_3)_2(H_2O)_2$ where Ln = Eu, Gd, Tb or Dy and the precursors for the hydrazinium lanthanide sulphite hydrates, the anhydrous lanthanide hydrazinecarboxylates, $Ln(N_2H_3COO)_3$ where Ln = Eu, Gd, Tb or Dy have been prepared and characterized by analytical, spectral, thermal and X-ray powder diffraction techniques. The infrared spectral data are in favour of the coordination of hydrazine and water molecules. These complexes decompose in three stages to yield respective oxides as final residue. The final residues were confirmed by their X-ray powder diffraction patterns and TG mass losses. The SEM photographs of some of the oxides show a lot of cracks indicating that large quantity of gases evolved during decomposition.

Keywords Heavier lanthanide hydrazinesulphite hydrates · Bis hydrazine lanthanide sulphite · Hydrazinium lanthanide sulphite hydrates · Anhydrous lanthanide hydrazinecarboxylates · Lanthanide oxides · TG-DTA · XRD

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Introduction

Sulphur dioxide is known [1] to act as a Lewis acid with amines giving compounds such as R_3NSO_2. Sulphur dioxide behaves also towards hydrazine similarly giving hydrazinesulphinic acid which, in turn, forms hydrazinesulphinate complexes in aqueous solution in the presence of metal ions. On passing into the aqueous medium, sulphur dioxide mostly exists as SO_2 dissolved in water [2] and reacts with hydrazine to form hydrazine sulphinic acid, N_2H_3SOOH. The hydrazinesulphinate complexes with transition metal ions and some lighter lanthanides have been reported, and their thermal properties have been investigated [3, 4]. At lower concentrations of hydrazine, it was observed that both the transition metal ions and lighter lanthanide ions form corresponding rare earth metal sulphite hydrazinates when sulphur dioxide bubbled into an aqueous solution containing metal ion and hydrazine hydrate.

Sulphur dioxide when passed into an alcoholic solution of hydrazine hydrate, has been reported to yield hydrazinium sulphite monohydrate which has been utilized in the preparation of hydrazinium metal sulphite hydrates [5].

Though several hydrazine complexes have been reported with lighter lanthanide ions [6], and transition metal ions [7], similar heavier lanthanide complexes are scarce in the literature except a few [5]. In this article, we report the preparation, characterization and thermal properties of complexes prepared by the reaction of heavier lanthanides with hydrazine hydrate in the presence of sulphur dioxide.

Experimental

Hydrazinium sulphite monohydrate was prepared by the method reported earlier [5]. The hydrazinium hydrazinecarboxylate was prepared by mixing hydrazine hydrate and solid ammonium carbonate in 2:1 molar ratio [8].

Preparation of lanthanide nitrate hydrates

The respective rare earth oxide (0.01 mol) was dissolved in minimum amount of concentrated nitric acid, and the clear solution obtained after heating was evaporated on a water bath to dryness. Then, the residue was dissolved in required quantity of water, and this aqueous solution of rare earth metal nitrate hydrates was used for the preparation of complexes.

Preparation of $Ln(N_2H_3SOO)_3(H_2O)$

The hydrated heavier lanthanide hydrazinesulphinates were prepared by passing excess sulphur dioxide gas through an aqueous solution (20 mL) containing a mixture of respective rare earth metal nitrate (0.01 mol) and excess hydrazine hydrate (3 mL, 0.06 mol). A gelatinous precipitate, the hydroxide formed during the addition of hydrazine hydrate to rare earth metal nitrate solution, was dissolved while passing sulphur dioxide and the complexes, $Ln(N_2H_3SOO)_3(H_2O)$ where Ln = Eu, Gd, Tb or Dy were precipitated simultaneously. The sulphur dioxide gas was passed for about 15 min to ensure the completion of the reaction, and the precipitated complexes were filtered, washed several times with distilled water and then washed with alcohol and dried in air.

Preparation of $Ln_2(SO_3)_3(N_2H_4)_2$

To the respective rare earth nitrate hydrates in 30 mL of distilled water, hydrazine hydrate (1.5 mL, 0.03 mol) was added, and sulphur dioxide gas was passed through the resultant solution. The gelatinous precipitate initially formed by the addition of hydrazine hydrate dissolved slowly on passing sulphur dioxide. On passing the gas continuously for 15 min, a clear solution was obtained. This clear solution was filtered through the Whatman filter paper, and the filtrate was allowed to stand at room temperature for crystallization. Flake-like substances formed after 3 days were filtered, washed with distilled water and then with alcohol and dried in air.

Preparation of $N_2H_5Ln(SO_3)_2(H_2O)_2$

These complexes were prepared using the precursors, the respective anhydrous rare earth hydrazinecarboxylates. The anhydrous complexes, $Ln(N_2H_3COO)_3$ where Ln = Eu, Gd, Tb or Dy were prepared by the addition of hydrazinium hydrazinecarboxylate to the aqueous solution (20 mL) of respective rare earth nitrate hydrates in 1-ml portion. During the addition, first, the precipitate was formed which slowly dissolved with further addition of ligand. The ligand was added till the solution became clear and the clear solution was filtered through the Whatman filter paper and allowed to stand at room temperature. The crystalline powder formed after 24 h was filtered, washed several times with ice cold distilled water and dried in air.

From the above precursors, the hydrazinium lanthanide sulphite hydrates were prepared as follows.

About 20 mL of distilled water was saturated with sulphur dioxide gas. To this solution, the respective anhydrous lanthanide hydrazinecarboxylate was added slowly in portions with constant stirring. During the addition, the decomposition of the complex with the liberation of carbon dioxide was observed. The addition was continued till a little amount of the precursor remained undissolved at the bottom. Then, the solution was filtered and the clear solution was closed and kept aside at room temperature for a week. The crystalline complexes formed and deposited at the bottom of the conical flask were removed, washed with distilled water and dried in air.

All the three sets of complexes were found to be stable in air and insoluble in water, alcohol and other organic solvents.

Physico-chemical techniques

The hydrazine and metal contents of the complexes were determined as described earlier [4, 9]. The infrared spectra of the complexes were recorded with a Perkin Elmer 597 spectrophotometer in the range 4,000–500 cm^{-1} using KBr pellets of the solid samples. Simultaneous TG-DTA of the complexes in air were carried out using a STA 1500 system. The heating rate employed was 10 °C min^{-1}. Aluminium cups were used as sample holders, and aluminium oxide was used as reference material. About 5 mg of the samples were used, and the thermal traces were recorded in the temperature range 30–800 °C.

Results and discussion

The aqueous reaction between rare earth metal nitrate hydrate and hydrazine hydrate in the presence of sulphur dioxide resulted in the formation of two types of complexes viz., rare earth metal hydrazinesulphinate hydrates and rare earth metal sulphite hydrazinates. In the presence of excess hydrazine hydrate (0.06 mol), former series of complexes were obtained, while the latter sets of compounds were formed when the lower ratio (0.03 mol) of hydrazine hydrate was used. Though hydrated lanthanide hydrazinecarboxylates were reported in the literature, corresponding

Table 1 Analytical data of complexes

Compound	Colour	Yield/%	Hydrazine/%		Metal/%	
			Found	Calculated	Found	Calculated
$Eu(N_2H_3SOO)_3(H_2O)$	Colourless	80	21.90	21.11	32.60	33.37
$Gd(N_2H_3SOO)_3(H_2O)$	Colourless	85	20.10	20.87	33.60	34.14
$Tb(N_2H_3SOO)_3(H_2O)$	Pale yellow	85	21.40	20.79	34.00	34.38
$Dy(N_2H_3SOO)_3(H_2O)$	Pale yellow	80	21.60	20.63	34.10	34.88
$Eu_2(SO_3)_3 \cdot 2N_2H_4$	Colourless	70	10.10	10.53	49.10	49.97
$Gd_2(SO_3)_3 \cdot 2N_2H_4$	Colourless	80	10.00	10.35	49.50	50.82
$Tb_2(SO_3)_3 \cdot 2N_2H_4$	Dirty yellow	85	10.90	10.30	49.00	51.09
$Dy_2(SO_3)_3 \cdot 2N_2H_4$	Pale yellow	80	10.80	10.18	50.50	51.64
$N_2H_5Eu(SO_3)_2(H_2O)_2$	Colourless	75	8.90	8.40	39.00	39.86
$N_2H_5Gd(SO_3)_2(H_2O)_2$	Colourless	80	8.80	8.29	39.80	40.68
$N_2H_5Tb(SO_3)_2(H_2O)_2$	Colourless	70	7.90	8.25	39.90	40.94
$N_2H_5Dy(SO_3)_2(H_2O)_2$	Pale yellow	75	7.80	8.18	40.80	41.48
$Eu(N_2H_3COO)_3$	Colourless	90	26.40	25.49	39.50	40.29
$Gd(N_2H_3COO)_3$	Dirty yellow	80	24.90	25.14	39.20	41.12
$Tb(N_2H_3COO)_3$	Pale yellow	85	24.60	25.03	39.40	41.37
$Dy(N_2H_3COO)_3$	Pale yellow	90	24.20	24.80	39.90	41.92

anhydrous complexes of lighter rare earths have not been reported so for. Further, anhydrous complexes of heavier lanthanides are not known. In this study, these anhydrous complexes were also prepared by the method adopted for the anhydrous lighter lanthanide hydrazinecarboxylates, and the complexes were used as precursors to the hydrazinium heavier lanthanide sulphite hydrates. These complexes were prepared by decomposing the precursors in aqueous sulphurous acid, which have been prepared in situ by passing sulphur dioxide gas into distilled water. The lanthanide hydrazine sulphinate hydrates and lanthanide sulphite hydrazinates are amorphous powders, while the hydrazinium complexes are crystalline solids. It is interesting and worthy to note here, however, that due to the precipitation of heavier lanthanide sulphates, the respective hydrazinium heavier lanthanide sulphates monohydrates have not been prepared. During our investigation, we were able to prepare the hydrazinium heavier lanthanide sulphite monohydrates by decomposing hydrazinecarboxylate complexes in sulphurous acid. The composition of the complexes were assigned on the basis of the analytical data, and the data are summarized in Table 1.

Infrared spectra

The infrared spectra of lanthanide hydrzinesulphinate mono hydrates are similar and show three bands between 3,050 and 3,400 cm^{-1}. These bands are assigned to N–H and O–H stretchings. The asymmetric and symmetric SOO stretching were observed at 1,100 and 870 cm^{-1}, respectively indicative of the oxygen coordination [10]. The N–N stretching of $N_2H_3SOO^-$ ions are observed at 980 cm^{-1}. The rare earth sulphite hydrazinates show N–H stretching at 3,000–3,350 cm^{-1}. The band at 960 cm^{-1} in these complexes clearly indicate the bridging bidentate nature of hydrazine which is characteristic of N–N stretching of hydrazine complexes [11].

The infrared spectra of the anhydrous lanthanide hydrazinecarboxylates are also similar and almost superimposable. Besides bands in the region 3,100–3,150 cm^{-1} for N–H stretchings, these complexes show bands at 1,650 and 1,360 cm^{-1} for asymmetric and symmetric stretchings, respectively, of $N_2H_3COO^-$ group. The N–N stretching is seen at 990 cm^{-1} in all the complexes as observed in the case of similar hydrated complexes [5].

The infrared spectra of bis-hydrazine lanthanide sulphites are similar to those of lighter lanthanide complexes and show characteristic bands for N–N of hydrazine at 940 and 960 cm^{-1} along with the band for sulphite moieties. The presence of these two bands are assigned to the presence of one monodentate and one bridged bidentate hydrazine molecules. The infrared spectra of all the hydrazinium heavier lanthanide sulphite hydrates are superimposable and are similar to that of hydrazinium lanthanide sulphate complexes [12]. The N–N stretching observed at 990–1,000 cm^{-1} for $N_2H_5^+$ ion indicates its coordination. The broadening and splitting of bands in the region 1,000–1,200 cm^{-1} indicates bidentate or bridging nature of sulphite ions. As expected, all these complexes show three bands in the region 3,100–3,500 cm^{-1} due to the N–H or O–H stretching frequencies though it is difficult to assign individually.

Thermal analysis

The salient features of the thermal degradation are summarized for different sets of complexes as follows. The intermediates formed during thermal degradation have been proposed on the basis of TG-mass loss. The final products have been analysed for their composition and confirmed by X-ray powder diffraction. However, due to the continuous decomposition and instability, we were not able to isolate the intermediates for further study.

$Ln(N_2H_3SOO)_3(H_2O)$

These complexes where Ln = Eu, Gd, Tb or Dy decompose in a similar fashion by dehydration, formation of respective lanthanide sulphate dihydrazinate as intermediate and finally dehydrazination of the above to give lanthanide sulphate as residue. All the above three stages are endothermic as shown by DTA curves. The general scheme of decomposition is given below along with the temperature range.

(1)

$$Ln(N_2H_3SOO)_3(H_2O) \xrightarrow{50-130\ ^\circ C} Ln(N_2H_3SOO)_3$$

(2)

$$2Ln(N_2H_3SOO)_3 \xrightarrow{130-240\ ^\circ C} Ln_2(SO_4)_3 \cdot 2N_2H_4$$

(3)

$$Ln_2(SO_4)_3 \cdot 2N_2H_4 \xrightarrow{230-600\ ^\circ C} Ln_2(SO_4)_3$$

$Ln_2(SO_3)_3 \cdot 2N_2H_4$ where Ln = Eu, Gd, Tb or Dy

The bis-hydrazine lanthanide sulphite complexes also show three-step decomposition. In the first stage, one hydrazine molecule is evolved in the temperature range 80–180 °C to give respective mono hydrazine lanthanide sulphite which loses another hydrazine molecule slowly at higher temperature up to 500 °C to give the respective lanthanide sulphites. These sulphites formed undergo disproportionation around 500–550 °C to give a mixture of lanthanide sulphate and oxide in 1:1 ratio. Formation of the above mixture was confirmed by TG-mass loss, analytical and XRD techniques. The DTA curves show an exotherm for the first stage and endotherms for other two stages. The removal of hydrazine molecules in two stages also indicates their different modes of coordination. The degradation trend for these complexes are given below.

(1)

$$Ln_2(SO_3)_3 \cdot 2N_2H_4 \xrightarrow{80-190\ ^\circ C} Ln_2(SO_3)_3 \cdot N_2H_4$$

(2)

$$Ln_2(SO_3)_3 \cdot N_2H_4 \xrightarrow{180-500\ ^\circ C} Ln_2(SO_3)_3$$

(3)

$$2Ln_2(SO_3)_3 \xrightarrow{490-550\ ^\circ C} Ln_2(SO_4)_3 + Ln_2O_3$$

$Ln(N_2H_3COO)_3$ where Ln = Eu, Gd, Tb or Dy

Though hydrated complexes of lanthanide hydrazinecarboxylates have been reported and their thermal degradations were investigated, the anhydrous complexes are new to the literature. The anhydrous complexes undergo two- or three-step decomposition. In the first step, these complexes decompose in the temperature range 140–250 °C to give respective lanthanide carbonates which at higher temperature decompose to give respective oxycarbonates which then decompose endothermally to the respective oxides below 600 °C. The first stage is exothermic and the other two stages are endothermic as observed from the DTA traces. The general thermal equations are represented as follows. Europium and Terbium complexes do not give the oxycarbonate intermediates.

(1)

$$Ln(N_2H_3COO)_3 \xrightarrow{120-280\ ^\circ C} {}^1\!/_2 Ln_2(CO_3)_3$$

(2)

$${}^1\!/_2 Ln_2(CO_3)_3 \xrightarrow{250-420\ ^\circ C} {}^1\!/_2 Ln_2O_3CO_2$$

(3)

$${}^1\!/_2 Ln_2O_3CO_2 \xrightarrow{400-640\ ^\circ C} {}^1\!/_2 Ln_2O_3$$

These anhydrous complexes decompose at lower temperatures than the respective hydrated complexes reported earlier. The formation of oxycarbonates have been observed both with similar hydrated complexes and degradation of many simple lanthanide carboxylates. The final residues were confirmed by X-ray powder diffractions.

$N_2H_5Ln(SO_3)_2(H_2O)_2$ where Ln = Eu, Gd, Tb or Dy

These complexes undergo dehydration in two stages between 60–120 and 120–180 °C indicating the presence of one lattice water and one coordinated water molecule. These two stages are endothermic. The anhydrous complex decompose exothermically to give respective bis-hydrazine lanthanide sulphate which undergoes dehydrazination exothermically to give the respective sulphates below 550 °C. The scheme of decomposition is given below.

Table 2 Thermal decomposition data

Compound	DTA peak temperature/°C	TG temperature range/°C	TG mass loss/%		Residue
			Found	Calculated	
$Eu(N_2H_3SOO)_3(H_2O)$	100(+)	60–120	3.89	3.95	$Eu(N_2H_3SOO)_3$
	190(+)	120–230	27.12	27.93	$Eu_2(SO_4)_3{\cdot}2N_2H_4$
	570(+)	230–590	33.91	34.97	$Eu_2(SO_4)_3$
$Gd(N_2H_3SOO)_3(H_2O)$	120(+)	50–130	3.80	3.91	$Gd(N_2H_3SOO)_3$
	220(+)	130–240	26.72	27.61	$Gd_2(SO_4)_3{\cdot}2N_2H_4$
	560(+)	240–600	33.91	34.57	$Gd_2(SO_4)_3$
$Tb(N_2H_3SOO)_3(H_2O)$	120(+)	70–130	3.21	3.89	$Tb(N_2H_3SOO)_3$
	200(+)	130–220	7.09	7.51	$Tb_2(SO_4)_3{\cdot}2N_2H_4$
	490, 570(+,d)	240–590	33.62	34.44	$Tb_2(SO_4)_3$
$Dy(N_2H_3SOO)_3(H_2O)$	180(+), 100(+)	50–130	3.17	3.86	$Dy(N_2H_3SOO)_3$
	–, 205(+)	130–230	26.89	27.30	$Dy_2(SO_4)_3{\cdot}2N_2H_4$
	550(+)	230–600	33.65	34.18	$Dy_2(SO_4)_3$
$Eu_2(SO_3)_3{\cdot}2N_2H_4$	150(−)	100-180	4.92	5.26	$Eu_2(SO_3)_3{\cdot}2N_2H_4$
	350(+,*)	180–510	9.81	10.53	$Eu_2(SO_3)_3$
	520(+)	510–550	21.92	22.39	$Eu_2(SO_4)_3 + Eu_2O_3$
$Gd_2(SO_3)_3{\cdot}2N_2H_4$	165(−)	90–180	4.86	5.17	$Gd_2(SO_3)_3{\cdot}N_2H_4$
	240(+,*)	180–500	9.88	10.35	$Gd_2(SO_3)_3$
	530(+)	500–540	21.76	22.00	$Gd_2(SO_4)_3 + Gd_2O_3$
$Tb_2(SO_3)_3{\cdot}2N_2H_4$	170(−)	100–190	4.91	5.15	$Tb_2(SO_3)_3{\cdot}N_2H_4$
	280(+,*)	190–490	10.02	10.30	$Tb_2(SO_3)_3$
	530(+)	490–550	20.65	21.24	$Tb_2(SO_4)_3 + Tb_4O_7$
$Dy_2(SO_3)_3{\cdot}2N_2H_4$	160(−)	80–180	4.82	5.09	$Dy_2(SO_3)_3{\cdot}N_2H_4$
	295(+,*)	180–500	9.89	10.18	$Dy_2(SO_3)_3$
	535(+)	500–550	21.17	21.64	$Dy_2(SO_4)_3 + Dy_2O_3$
$Eu(N_2H_3COO)_3$	220(−)	150–240	35.24	35.83	$Eu_2(CO_3)_3$
	520(+)	400–540	53.01	53.33	Eu_2O_3
$Gd(N_2H_3COO)_3$	230(−)	140–250	34.98	35.33	$Gd_2(CO_3)_3$
	300(+)	250–400	46.32	46.84	$Gd_2O_3CO_2$
	580(+)	400–600	52.09	52.60	Gd_2O_3
$Tb(N_2H_3COO)_3$	270(−)	120–280	34.76	35.18	$Tb_2(CO_3)_3$
	390(+)	280–420	46.12	46.64	$Tb_2O_3CO_2$
	560(+)	420–600	50.99	51.33	Tb_4O_7
$Dy(N_2H_3COO)_3$	740(−)	160–260	34.35	34.85	$Dy_2(CO_3)_3$
	280(+)	260–300	45.88	46.21	$Dy_2O_3CO_2$
	620(+)	300–640	51.42	51.88	Dy_2O_3
$N_2H_5Eu(SO_3)_2(H_2O)_2$	110(+)	70–120	3.91	4.34	$N_2H_5Eu(SO_3)_2(H_2O)$
	150(+)	120–170	8.21	8.69	$N_2H_5Eu(SO_3)_2$
	380(−)	170–480	20.25	20.79	$Eu_2(SO_4)_3{\cdot}2N_2H_4$
	510(−)	480–550	28.09	28.52	$Eu_2(SO_4)_3$
$N_2H_5Gd(SO_3)_2(H_2O)_2$	90(+)	60–110	3.89	4.29	$N_2H_5Gd(SO_3)_2(H_2O)$
	160(+)	110–180	8.12	8.58	$N_2H_5Gd(SO_3)_2$
	400(−)	180–500	20.08	20.52	$Gd_2(SO_4)_3{\cdot}2N_2H_4$
	530(−)	500–550	27.69	28.16	$Gd_2(SO_4)_3$
$N_2H_5Tb(SO_3)_2(H_2O)_2$	105(+)	80–120	3.85	4.27	$N_2H_5Tb(SO_3)_2(H_2O)$
	165(+)	120–170	8.11	8.55	$N_2H_5Tb(SO_3)_2$
	420(−)	170–490	19.88	20.44	$Tb_2(SO_4)_3{\cdot}2N_2H_4$
	535(−)	490–550	27.62	28.01	$Tb_2(SO_4)_3$

Table 2 continued

Compound	DTA peak temperature/°C	TG temperature range/°C	TG mass loss/%		Residue
			Found	Calculated	
$N_2H_5Dy(SO_3)_2(H_2O)_2$	90(+)	60–120	3.82	4.24	$N_2H_5Dy(SO_3)_2(H_2O)$
	165(+)	120–180	8.10	8.48	$N_2H_5Dy(SO_3)_2$
	430(−)	180–500	19.65	20.27	$Dy_2(SO_4)_3 \cdot 2N_2H_4$
	520(−)	500–550	27.34	27.81	$Dy_2(SO_4)_3$

(+), endotherm; (−), exotherm; d, doubled; b, broad; w, weak; *, broad endotherm with minimum centered at the given temperature

$$N_2H_5Ln(SO_3)_2(H_2O)_2 \xrightarrow{60-120\ ^\circ C} N_2H_5Ln(SO_3)_2(H_2O)$$

$$N_2H_5Ln(SO_3)_2(H_2O) \xrightarrow{110-180\ ^\circ C} N_2H_5Ln(SO_3)_2$$

$$2N_2H_5Ln(SO_3)_2 \xrightarrow{180-500\ ^\circ C} {}^1\!/\!{}_2Ln_2(SO_4)_3 \cdot 2N_2H_4$$

$${}^1\!/\!{}_2Ln_2(SO_4)_3 \cdot 2N_2H_4 \xrightarrow{480-550\ ^\circ C} {}^1\!/\!{}_2Ln_2(SO_4)_3$$

The thermal degradation data of the complexes are summarized in Table 2 and the simultaneous TG-DTA traces of dysprosium complexes are shown in Figs. 1, 2, 3 and 4 as representative examples. The SEM photographs of the oxides formed by the thermal decomposition of the complexes show a lot of cracks and voids indicating that large quantity of gaseous products evolved during the decomposition. The SEM photographs of Eu_2O_3 and Dy_2O_3 are shown in the Figs. 5 and 6, respectively.

Coordination nature of Ln(III) ions

The coordination number of Ln(III) ions varies from 6 to 12, which depends on the nature of ligand and extent of hydration. Among the four types of complexes reported in this study, in rare earth metal hydrazinesulphinate mono hydrates, the metal ions, are expected to be seven coordinated with three bidentate hydrazinecarboxylate ions and a coordinated water molecule. In rare earth metal sulphite hydrazinates, the sulphite ions act as a tridentate bridged ligands, and among two hydrazine molecule, one acts as a monodentate ligand while the other as a bidentate bridged ligand. This provides an octahedral environment around each metal ion.

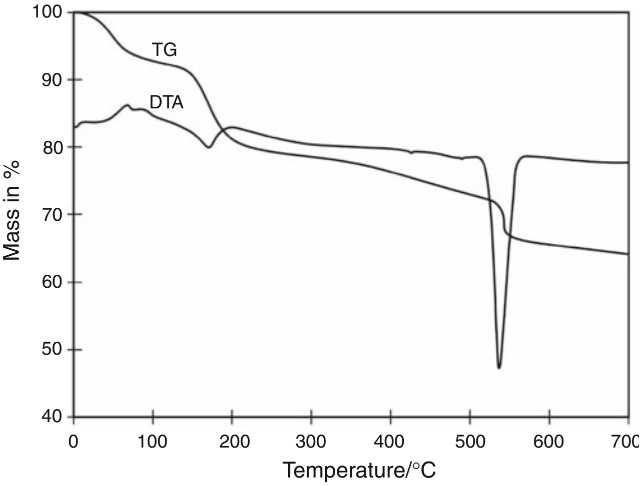

Fig. 1 Simultaneous TG-DTA of $Dy(N_2H_3SOO)_3 \cdot H_2O$

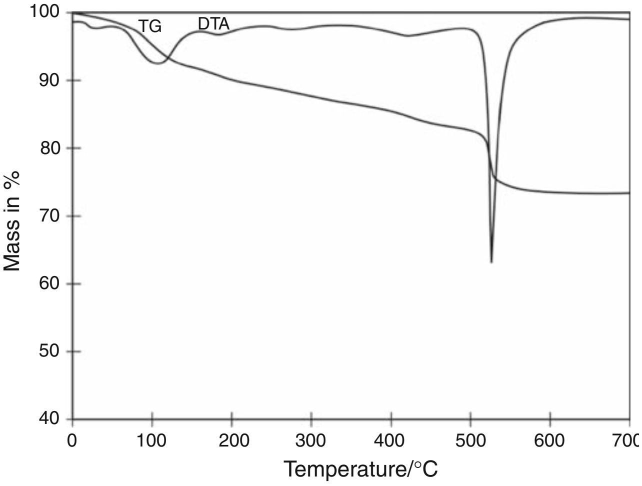

Fig. 2 Simultaneous TG-DTA of $Dy_2(SO_3)_3 \cdot 2N_2H_4$

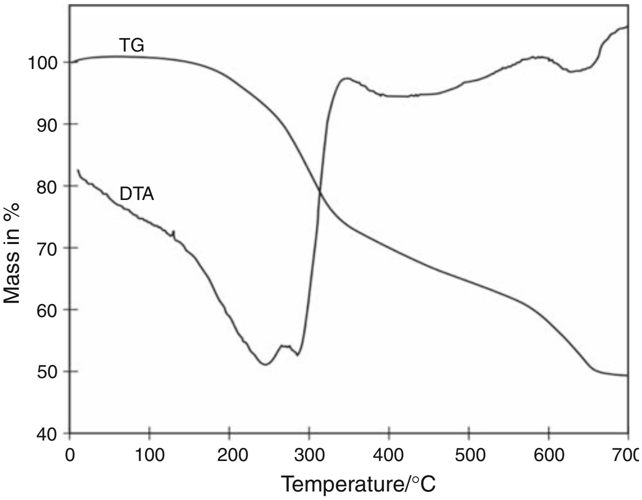

Fig. 3 Simultaneous TG-DTA of $Dy(N_2H_3COO)_3$

The hydrazinium complexes are assigned to have nine coordinated structure similar to the respective sulphate

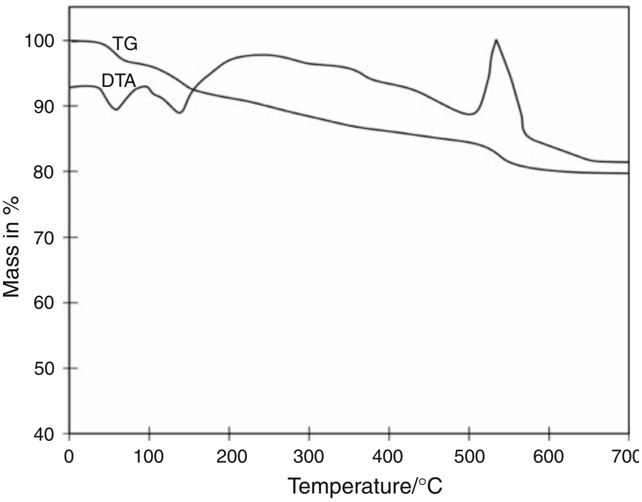

Fig. 4 Simultaneous TG-DTA of $N_2H_5Dy(SO_3)_2{\cdot}(H_2O)_2$

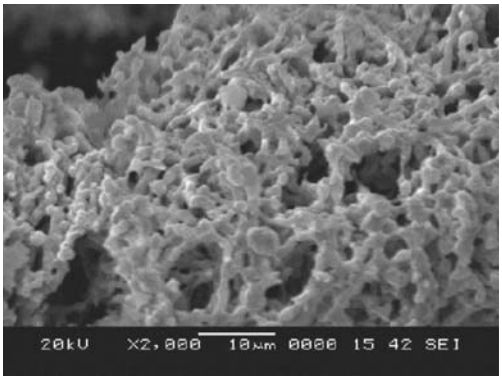

Fig. 5 SEM photograph of Eu_2O_3

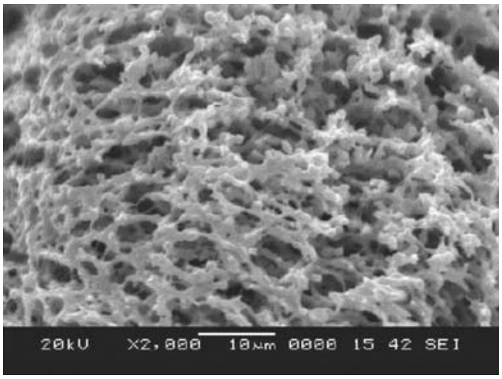

Fig. 6 SEM photograph of Dy_2O_3

complexes [12]. The sulphite ions are coordinated to the metal ions by bridged fashion. The metal ions coordinated to seven oxygen atoms from six sulphite groups, one water, oxygen and one nitrogen atom of hydrazinium cation. In rare earth metal hydrazinecarboxylates, the octahedral geometry is proposed around the three Ln(III) ions considering the N, O chelation of three hydrazinecarboxylate ions. The assignments have been made on the basis of infrared spectra and thermal analysis.

Conclusions

Hydrazine hydrate reacts with heavier lanthanide ions in the presence of sulphur dioxide under different conditions to give different series of complexes such as lanthanide hydrazinesulphinate monohydrates, bis-hydrazine lanthanide sulphites and hydrazinium lanthanidesulphite dihydrates.

These complexes undergo multi-step thermal degradation to yield lanthanide sulphate, lanthanide oxide or a mixture of the above two as the final residue and the degradation completes below 650 °C in all the cases.

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