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# SPECTRAL, THERMAL AND X-RAY STUDIES ON SOME NEW *BIS*-HYDRAZINE LANTHANIDE(III) GLYOXYLATES

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Some new and *bis*-hydrazine lanthanide glyoxylates $Ln[OOC–CHO]_3(N_2H_4)_2$ where *Ln*=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy have been prepared and the compositions of the complexes have been determined by chemical analysis and elemental analysis. The magnetic moment and electronic spectra suggest except $Ln^{3+}$ which is diamagnetic and all the other complexes are paramagnetic. Infrared spectral data indicate the bidentate coordination of carboxylates group is coordinate to lanthanide ion in a monodentate fashion. However, as a whole, glyoxylate ion acts as a bidentate ligand. The curves of all the complexes show multi-step degradation and the final products are found to be the respective metal oxides. The final residues were identified by their metal analysis, infrared spectra and the X-ray powder diffraction patterns. X-ray powder patterns of the complexes are almost super-imposable as expected which is in favour of isomorphism among the series.

***Keywords:*** *isomorphism, lanthanide(III) glyoxylates, metal oxides, simultaneous TG-DTA, X-ray powder diffraction*

## Introduction

Hydrazine, with two lone pairs over nitrogen atoms is capable of forming variety of complexes with metal salts. The bidentate coordination mode of hydrazine is common with transition metal ions containing inorganic and organic anions. Several *bis*-hydrazine metal complexes containing inorganic ions such as $Cl^-$, $Br^-$, $I^-$, $F^-$, $NO_3^-$, $SO_4^{2-}$, $SO_3^{2-}$, $CN^-$ etc. have been prepared and well characterized [1–3]. During the course of our research work we have reported several hydrazine metal complexes with transition metal ions [4–10]. Recently we have also reported *bis*-hydrazine transition metal glyoxylates and their mixed metal complexes as precursors to metal oxides and mixed metal oxides [9].

Lanthanides, including heavier ones also form complexes with neutral hydrazine in the presence of halides, carbonates, sulphites and other inorganic anions as charge neutralizing species [1, 11]. However, such complexes with carboxylate ions are scarce in the literature due to the following two reasons. In the presence of carboxylic acids, lanthanides form stable lanthanide(III) carboxylates which are highly insoluble and hence precipitated from aqueous solutions. Furthermore in the presence of hydrazine which usually added in excess to precipitate the *bis*-hydrazine carboxylates leads to the increase in pH of the solution. As it is well known under such conditions lanthanides form insoluble hydroxides and hence complex formation is very difficult.

Lanthanide ions in aqueous solution form aquated complexes and hence in aqueous media, any ligand added is in competition with the water molecules that are present in large quantities. Furthermore, displacement of coordinated water molecule by another ligand is commonly difficult. Thus, only strong ligands are which chelating, form lanthanide complexes of sufficient stability. The net result is that in comparison with the transition metal ions the lanthanide ions as a whole form far fewer complexes and yield complexes with significantly different properties.

We made many attempts with several carboxylic acids under different pH to isolate hydrazine complexes of lanthanide carboxylates. During these studies we were able to isolate *bis*-hydrazine lanthanide(III) glyoxylates as only series of complexes in the monocarboxylic acid series. As we are aware of the literature this is the first report on the *bis*-hydrazine lanthanide(III) carboxylates. Though some hydrazinium lanthanide sulphites and carboxylates are reported in the literature [12–15], the hydrazine adducts are not known except a few complexes of lanthanide oxalates with hydrazine were mentioned in the literature [16–19] for which also the composition have not been well understood and those complexes have not been thoroughly investigated. In this paper, we report the preparation, characterization and thermal properties of some new *bis*-hydrazine rare earth glyoxylates. We have also established the isomorphism among the series of complexes by their powder X-ray diffraction patterns.

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## Experimental

The chemicals used where of analytical reagents grade. All the preparations and estimation were carried out using double distilled water and the solvents were distilled before use. The hydrazine hydrate and glyoxylic acid were as their monohydrate. lanthanide(III) oxides and cerium(III) nitrate were received from Indian rare earth limited.

### *Preparation of Ln(OOCCHO)$_3$(N$_2$H$_4$)$_2$ where* Ln=*La, Ce, Pr, Nd or Sm*

To an aqueous solution (50 mL) of respective lanthanide nitrate hydrate (0.01 mol), an aqueous mixture (30 mL) containing glyoxylic acid monohydrate (2.76 g, 0.03 mol) and hydrazine hydrate (1.5 mL, 0.03 mol) was added slowly in drops with constant stirring. After the addition, the clear solution thus obtained was filtered through a Whatmann filter paper to remove any impurities present in minute quantities and dust particles. Now the resultant solution was allowed to stand at room temperature. After 24 h, the complexes settled as powder at the bottom of the beaker was filtered through a pump and washed several times with distilled water to remove any hydrazine adsorbed over the surface of the complex and finally washed with alcohol and dried in air.

Alternatively after the addition of the hydrazinium glyoxylate to respective lanthanide nitrate, the resultant solution was filtered and vigorously stirred with a glass rod for about 30 min yielded the complex as the precipitate, which was allowed to settle and processed as above.

### *Preparation of Ln(OOCCHO)$_3$(N$_2$H$_4$)$_2$ where* Ln=*Eu, Gd, Tb or Dy*

The method described and the stoichiometry of lanthanide nitrate hydrate, glyoxyalic acid monohydrate and hydrazine hydrate used for the preparation of lighter lanthanide complexes were also followed for the heavier lanthanides also. However, in contrast to the former case, even after allowing the resultant solution for about a month or prolonged stirring the mixture for several hours, complexes were not precipitated. Hence, the clear solutions were evaporated on a water bath to reduce the volume to one-half of the original volume. These concentrated solutions when allowed to stand at room temperature the complexes formed as crystalline powders within 30 min were filtered, washed with cold distilled water, then with alcohol and dried in air.

### *Preparation of lanthanide nitrate hydrates*

The respective rare earth oxides were accurately weighed, dissolved in 4N nitric acid, and evaporated on a water bath to dryness. To this about 50 mL of distilled water was added and these residues, the rare

**Table 1** Analytical data

| Compound | Amount of lanthanide oxide used/g | Colour | Yield/% | Hydrazine/% | Metal/% | C/% | H/% | N/% |
|---|---|---|---|---|---|---|---|---|
| | | | | Found (Calc.) | | | | |
| La(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.6291 | Colourless | 90 | 14.90<br>(15.19) | 31.25<br>(32.91) | 17.04<br>(17.08) | 2.67<br>(2.62) | 13.81<br>(13.28) |
| Ce(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 4.3423* | Colourless | 80 | 15.00<br>(15.14) | 32.30<br>(33.11) | 16.80<br>(17.03) | 2.68<br>(2.62) | 12.82<br>(13.24) |
| Pr(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.7024 | Light green | 90 | 15.20<br>(15.12) | 33.05<br>(33.23) | 16.96<br>(17.00) | 2.58<br>(2.62) | 13.66<br>(13.21) |
| Nd(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.6824 | Violet | 90 | 14.80<br>(15.00) | 33.10<br>(33.75) | 16.66<br>(16.86) | 2.54<br>(2.59) | 13.42<br>(13.11) |
| Sm(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.7435 | Light yellow | 85 | 15.10<br>(14.79) | 34.05<br>(34.69) | 16.52<br>(16.63) | 2.52<br>(2.56) | 12.67<br>(12.93) |
| Eu(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.7596 | Colourless | 75 | 15.20<br>(14.73) | 34.30<br>(34.93) | 16.49<br>(16.56) | 2.50<br>(2.55) | 12.39<br>(12.88) |
| Gd(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.8125 | Dirty white | 90 | 14.70<br>(14.55) | 35.25<br>(35.70) | 16.45<br>(16.36) | 2.48<br>(2.52) | 12.35<br>(12.72) |
| Tb(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.8692 | Dirty white | 80 | 14.20<br>(14.50) | 35.40<br>(35.95) | 16.40<br>(16.30) | 2.54<br>(2.51) | 12.46<br>(12.68) |
| Dy(OOCCHO)$_3$(N$_2$H$_4$)$_2$ | 1.8650 | Pale yellow | 90 | 14.10<br>(14.38) | 36.15<br>(36.47) | 16.40<br>(16.17) | 2.56<br>(2.49) | 12.12<br>(12.57) |

Amount of cerium nitrate hexahydrate used earth nitrate hydrates were dissolved. The resultant solutions were filtered and used for the preparation of the complexes. The amounts of oxides used are given in Table 1.

### *Physico-chemical techniques*

To determine the metal contents, a known quantity of the complex was decomposed with concentrated nitric acid for three or four times to destroy the hydrazine and organic matter. Thus the complexes after decomposition were converted to respective metal nitrate hydrates which were dissolved in water and titrated *vs.* disodium salt of ethylenediaminetetraacetic acid using xylenol orange indicator and hexammine powder as buffer [20]. The hydrazine content in the complexes was determined volumetrically under Andrew's conditions [20] using a standard potassium iodate solution (0.025 mol $dm^{-3}$).

The magnetic susceptibility measurements at room temperatures were carried out in a Gouy's balance using $Hg[Co(SCN)_4]$ as the calibrant. Using Pascal's constants for various elements the diamagnetic corrections were applied to get resultant magnetic moments. Since the complexes are insoluble in water and most of the organic solvents, the solid-state absorption spectra of the complexes in nujol mull were recorded on a Shimadzu UV-visible 240 Å spectrophotometer. The infrared spectra of the complexes were recorded on a Perkin-Elmer 597 spectrophotometer in the range 4000–400 $cm^{-1}$ using KBr discs of the samples. The simultaneous TG-DTA of the samples in air was recorded on a SDT Q 600V8.2 Build 100, universal V4.2E TA instruments using 4–5 mg of samples with platinum cups as sample holders. The heating rate employed was 10°C $min^{-1}$. The X-ray powder diffraction patterns of the dry powdered complexes were recorded using Philips X-ray diffractometer model PW 1050/70 employing $CuK_\alpha$ radiation ($\lambda$=1.5406 Å) between $2\theta$=10 to 70° at a scan rate of 2° $min^{-1}$ with scintillation counter as detector.

## Results and discussion

In aqueous solution hydrazine hydrate reacts with glyoxalic acid monohydrate to give hydrazinium glyoxylate ($OHCCOON_2H_5$). However, the above aqueous mixture when evaporated did not yield the solid ligand, instead, a dark brown liquid was formed. When the reaction was carried out in alcoholic medium light yellow crystals were formed, which were found to be low melting and highly hygroscopic, hence we were not able to isolate the ligand. Hence, in the present investigation an aqueous mixture containing hydrazine hydrate and glyoxylic acid monohydrate in 1:1 ratio was used as ligand in the preparation of complexes.

The *bis*-hydrazine lanthanide glyoxylates were prepared by the aqueous reaction between the respective lanthanide nitrate hydrates and ligand in 1:3 molar ratios. The resultant clear solution was stirred well to precipitate the desired complexes. The chemical reaction is represented as follows.

$$Ln(NO_3)_3.xH_2O+3HOOCCHO{\cdot}H_2O+N_2H_4{\cdot}H_2O\rightarrow$$
$$Ln(OOCCHO)_3(N_2H_4)_2+N_2H_5NO_3+$$
$$2HNO_3+(x+6)H_2O$$

where *Ln*: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy.

Lanthanide carboxylate complexes containing hydrazine either in the form of neutral molecule or hydrazinium cations is scarce in the literature due to the formation and precipitation of soluble hydrated lanthanide carboxylates from the aqueous solution containing lanthanide ion and carboxylic acids. Due to the presence of water molecules inside the coordination sphere, weak ligands like hydrazine or its cation cannot easily enter into the coordination sphere, even inclusion of these entities in the complex itself found difficult. However few cases are known [13], where the hydrazinium cation present, along with a strong chelating ligand and water in the lanthanide complexes, outside the coordination sphere. Furthermore, it is observed that the hydrazine should be present in excess than required on the basis of the molecular formula for the formation of hydrazinium or hydrazine complexes, keeping the medium still acidic.

However, in the preparation of *bis*-hydrazine complexes or so-called hydrazine adducts, usually especially in the case of transition metal ions excess hydrazine hydrate was added, so that the medium will be basic and the complexes are thrown out from the solution. In the case of lanthanides when excess hydrazine is added, the respective hydroxides are precipitated even the pH is just above 7. Hence, besides hydrazinium rare earth carboxylates which are scarce, *bis*-hydrazine rare earth carboxylates could not be prepared under normal conditions. However, it is surprising to note that in the present case, addition of ligand (mixture of hydrazine hydrate and glyoxylic acid monohydrate) to metal in 3:1 ratio resulted in the precipitation of the *bis*-hydrazine lanthanide glyoxylate, though the medium is slightly acidic (pH=6.8).

The compositions of the complexes were assigned based on metal, hydrazine and CHN analyses (Table 1). These complexes are stable in air, insoluble in water and alcohol and they undergo decomposition without melting.

### *Magnetic moments*

Due to the lack of unpaired electrons, among the lanthanide complexes prepared, $La^{3+}$ ions are diamagnetic. Since in other lanthanide ions the unpaired f- electrons are quite deeply placed and well shielded by outer S and P electrons the effect due to the ligand field on these 4f-electrons is not appreciable. Consequently the effective magnetic moment of $Ln^{3+}$ ions are given by $\mu_{eff}=\mu_J g\sqrt{J(J+1)}$ BM. In these cases the energy different between J levels of a multiplet is large compared to KT, there is strong L-S coupling. Exceptions are $Sm^{3+}$ and $Eu^{3+}$ ions where the energy difference between the successive J levels is comparable to KT and the higher J levels are also populated to some extent. In the present case the $\mu_{eff}$ observed are in good agreement with the calculated values (Table 2).

### *Electronic spectra*

Usually the electronic spectral profile for lanthanide(III) complexes consists of number of weak but sharp bands due to the Laporte forbidden f-f transitions. Mostly the ions with no unpaired electrons, half filled or completely filled 4f-orbitals are colourless. Hence, the 4f orbitals are the source of colour of Ln(III) ions and the numbers of unpaired electrons in these 4f-orbitals decide the colour, though strictly speaking, even the ions with same number of unpaired electrons show different colour.

**Table 2** Magnetic and Felectronic spectral data

| Complex | Magnetic moment $\mu_{eff}$ (BM) | Absorption maximum/ $cm^{-1}$ | Assignment |
|---|---|---|---|
| $Pr^{3+}$ | 3.56 | 22 300<br>21 000<br>20 560<br>16 760 | $^3H_4\rightarrow{}^3P_2$<br>$\rightarrow{}^3P_1$<br>$\rightarrow{}^3P_0$<br>$\rightarrow{}^1D_2$ |
| $Nd^{3+}$ | 3.60 | 23 600<br>20 700<br>19 300<br>17 220 | $^4I_{9/2}\rightarrow{}^2P_{1/2}$, $^4G_{9/2}$<br>$\rightarrow{}^2K_{5/2}$<br>$\rightarrow{}^4G_{7/2}$<br>$\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$ |
| $Sm^{3+}$ | 1.55 | 24 800<br>23 810<br>21 540<br>20 530 | $^6H_{5/2}\rightarrow{}^6P_{3/2}$, $^4I_{13/2}$<br>$\rightarrow{}^6P_{5/2}$<br>$\rightarrow{}^4I_{13/2}$<br>$\rightarrow{}^4I_{9/2}$ |
| $Dy^{3+}$ | 10.35 | 24 620<br>23 720<br>22 000<br>20 710 | $^5H_{15/2}\rightarrow{}^5P$ |
| $Ce^{3+}$ | 2.42 | – | – |
| $Eu^{3+}$ | 3.58 | – | – |
| $Gd^{3+}$ | 7.80 | – | – |
| $Tb^{3+}$ | 9.40 | – | – |

In the present case, since the complexes are insoluble in water and organic solvents the absorption spectra were recorded in solid-state. The Pr(III) complex exhibits band at 22330, 21000, 20560 and 16760 $cm^{-1}$ while the Nd(III) complex shows four bands at 23600, 20700, 19300 and 17220 $cm^{-1}$. The electronic spectra of Sm(III) and Dy(III) complexes also show four bands each in the same regions. This is quite expected because these two ions are whole equivalent of each other. Other complexes are colourless or almost colourless and do not show any characteristic absorption in the visible region. The electronic spectra data and their assignments are summarized in Table 2.

### *Infrared spectra*

The infrared spectra of *bis*-hydrazine rare earth glyoxylates are almost identical indicating the similarity in their structure which is also evidenced by their composition assigned on the basis of analytical data. Two broad bands centered at 3450 and 3270 $cm^{-1}$ are assigned to the N–H stretching of hydrazine molecules. However, in the case of similar transition metal complexes, two sharp bands are observed in this region. These broad bands are the characteristic of lanthanide complexes, and in the absence of water molecule in the complexes it is also an indication of different mode of coordination of two hydrazine molecules. The asymmetric stretching of carboxylate ion and the carbonyl stretching are expected to show two sharp bands in the region of 1660–1670 and 1580–1590 $cm^{-1}$, respectively, if the glyoxylate ion is coordinated to lanthanide ion in a monodentate fashion through carboxylate oxygen. This is indeed observed with *bis*-hydrazine transition metal glyoxylate complexes. However, in the present case the above two carbonyl stretching for the asymmetric mode merge together and a broad band in the region 1570–1650 $cm^{-1}$. This shifting of aldehydic carbonyl stretching towards lower frequency region and the observed band broadening could be attributed to the bidentate coordination of glyoxylate ion through carboxylate and carbonyl oxygen atoms. However, the carboxylate group is coordinated to lanthanide ion in a monodentate fashion [23] as evidenced by the difference in $\nu_{asy}$ and $\nu_{sym}$ stretching vibrations which is found to be between 220–230 $cm^{-1}$.

The N–N stretching in hydrazine complexes are much important in assigning the nature of its coordination. Braibanti *et al.* [24] have given a thumb rule on the basis of earlier studies to distinguish the different modes of coordination of hydrazine molecules by carefully examining the N–N stretching frequencies. On this basis the infrared frequency region between

900–1000 $cm^{-1}$ was closely observed in the present series of complexes. In the case of transition metal complexes in this region the only one sharp band at 985–990 $cm^{-1}$ was observed which was attributed to the bidentate bridged nature of $N_2H_4$ moieties without any ambiguity which excludes any absorption due to glyoxylate ions in this region. However, lanthanide complexes show three sharp bands exactly at 1000, 970 and 920–925 $cm^{-1}$ for the complexes. Hence, it is very difficult to justify anyone mode of coordination of hydrazine molecules. Since, hydrazine complexes of lanthanides reported with nine coordinations [13, 15, 25] here it is expected that one $N_2H_4$ molecule might be coordinated as bridged bidentate ligand while the other acting as monodentate ligand to result in familiar nine coordination assuming six other coordination sites are occupied by three bidentate glyoxylate ions. The infrared spectra of praseodymium and neodymium complexes are shown in Figs 1a–b as representative examples.

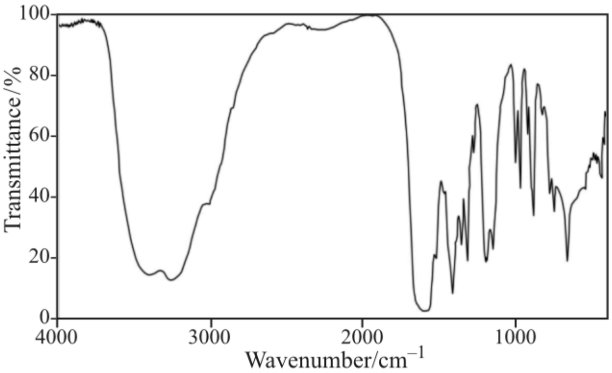

**Fig. 1a** IR-spectrum of $Pr(OOCCHO)_3(N_2H_4)_2$

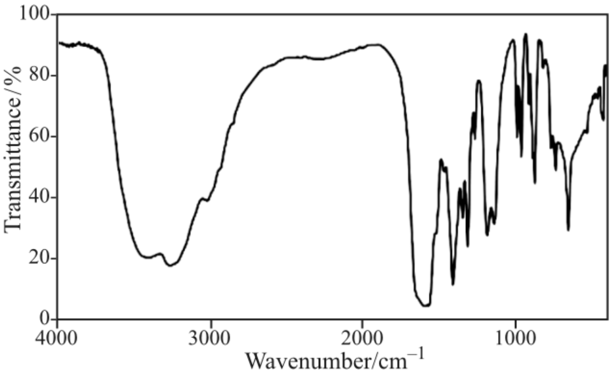

**Fig. 1b** IR-spectrum of $Nd(OOCCHO)_3(N_2H_4)_2$

### *Thermal degradation*

### $Pr(OOCCHO)_3(N_2H_4)_2$

This complex shows multi-step degradation. Initially at lower temperatures between 50–150°C a monodentate hydrazine molecule was eliminated. At higher temperatures between 150–195°C bridged hydrazine is lost. Both these stages are exothermic at 170 and 280°C. Then the praseodymium glyoxylate decomposes in the temperature range 240–385°C, to give praseodymium oxalate as intermediate. This intermediate further undergoes two-stage decomposition, which continues to give $Pr_6O_{11}$ as the end residue. The final degradation temperature is found to be 530°C. The DTA shows exotherms for the formation of praseodymium oxalate at 278°C and its decomposition to the oxide as doublet at 435 and 485°C, respectively.

### $Nd(OOCCHO)_3(N_2H_4)_2$

The neodymium complex also initially loses a monodentate hydrazine molecule in the temperature range 50–145°C. Another bridged bidentate hydrazine was eliminated in the temperature range 145–240°C. Both these stages are exothermic at 170 and 290°C. After the elimination of two hydrazine molecules, neodymium glyoxylate undergo exothermic decomposition in the temperature range 240–395°C to give neodymium oxalate. That further decomposes in the temperature range 395–500°C, to give neodymium oxy-carbonate and finally neodymium oxide at 650°C. DTA shows exotherms at 425 and 530°C for the formation of neodymium oxy-carbonate and finally the neodymium oxide, respectively.

### $Sm(OOCCHO)_3(N_2H_4)_2$

The continous decomposition of this samarium complex in two stages takes place in the temperature ranges 50–130 and 130–200°C. DTA shows a broad exotherm for the dehydrazination. Then the samarium glyoxylate undergo decomposition to give samarium oxalate at 385°C. which gives the samarium oxy carbonate at 540°C by exothermic decomposition. At higher temperatures between 540–655°C the above compound gives the $Sm_2O_3$ as final residue. The DTA shows an exotherm at 280°C for the formation of samarium oxalate, a sharp exotherm at 410°C for the formation of samarium oxycarbonate and a broad exotherm at 530°C for the formation of the oxide.

### $Gd(OOCCHO)_3(N_2H_4)_2$

TG of this complex shows similar decomposition trend as shown by samarium complex. Elimination of both the monodentate and bridged bidentate molecules takes place in the temperature range 50–235°C. The DTA shows a broad exotherm for these stages, this intermediate decomposes to give gadolinium oxalate, gadolinium oxy-carbonate and finally the gadolinium oxide as the end residues.

$Tb(OOCCHO)_3(N_2H_4)_2$

This complex initially shows a weak exotherm for the liberation of a hydrazine molecule and then two broad exotherms for the formation of terbium glyoxylate and its decomposition to terbium oxalate below 415°C. This terbium oxalate undergoes continous decomposition in a single stage to give the terbium oxide as the final residue.

The DTA shows three exotherms at 60°C and a doublet at 180 and 285°C, respectively for the first three stages. Other two exotherms, one broad signal at 325°C and another strong and sharp exotherm at 460°C are due to the formation and decomposition of terbium oxalate.

Since the TG curves of the complexes show continuous degradation, we were not able to isolate the intermediates. Hence, the compositions of the intermediates were proposed on the basis of TG-mass loss. However, the final products, the respective lanthanide oxides have been assigned on the basis of TG-mass loss and confirmed by X-ray powder diffraction.

The simultaneous TG-DTA curves of the complexes are shown in Figs 2a–e.

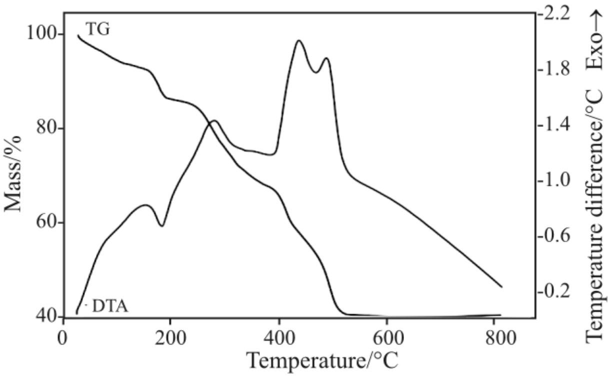

**Fig. 2a** Simultaneous TG-DTA of $Pr(OOCCHO)_3(N_2H_4)_2$

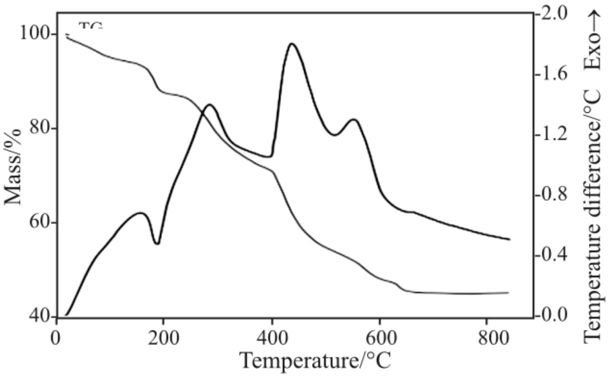

**Fig. 2b** Simultaneous TG-DTA of $Nd(OOCCHO)_3(N_2H_4)_2$

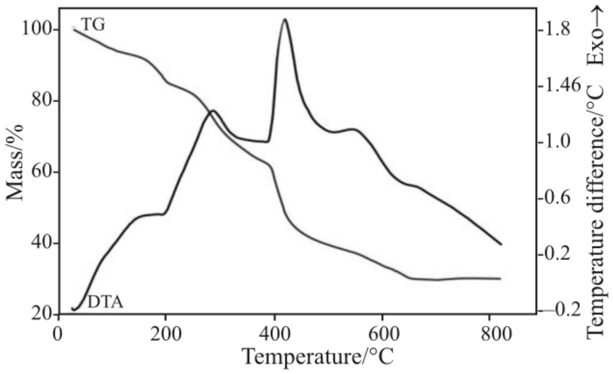

**Fig. 2c** Simultaneous TG-DTA of $Sm(OOCCHO)_3(N_2H_4)_2$

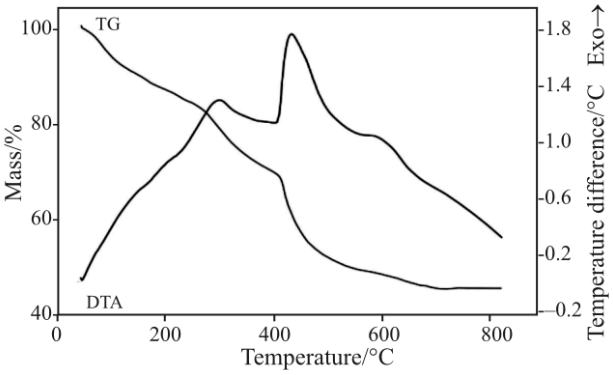

**Fig. 2d** Simultaneous TG-DTA of $Gd(OOCCHO)_3(N_2H_4)_2$

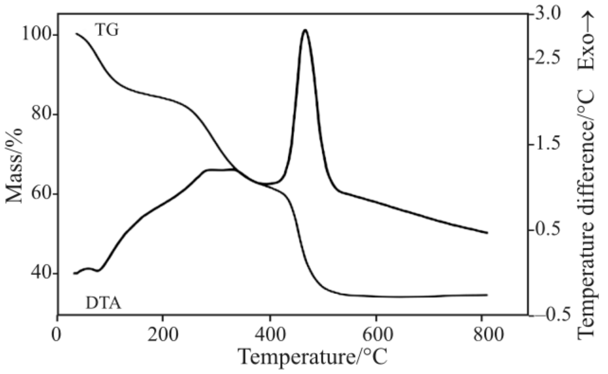

**Fig. 2e** Simultaneous TG-DTA of $Tb(OOCCHO)_3(N_2H_4)_2$

### *X-ray powder diffraction*

Though the infrared spectra of the complexes are almost similar, the X-ray powder diffraction patterns of the lanthanide complexes were recorded to support the similarity in the structure of these complexes. The powder patterns are almost superimposable as expected which is in favour of isomorphism among the series. The lines are very sharp indicating the purity of the samples. At the lower 2θ values several sharp lines are found at same positions for all the complexes. The X-ray powder

**Table 3** Thermal degradation data

| S.No. | Complex | M.Wt | Mass loss/% | | | | |
|---|---|---|---|---|---|---|---|
| | | | $-N_2H_4$ | $-2N_2H_4$ | Formation of $Ln_2(C_2O_4)_3$ | Formation of $Ln_2O_3CO_2$ | Formation of oxides |
| | | | Found (Calc.) | | | | |
| 1 | $La(OOCCHO)_3(N_2H_4)_2$ | 422.08 | 7.00 (7.59) | 15.00 (15.18) | 35.00 (35.81) | 55.70 (56.19) | 61.00 (61.40) |
| 2 | $Ce(OOCCHO)_3(N_2H_4)_2$ | 423.29 | 7.00 (7.57) | 14.50 (15.14) | 35.50 (35.71) | 56.00 (56.03) | 61.00 (61.23) |
| 3 | $Pr(OOCCHO)_3(N_2H_4)_2$ | 424.02 | 7.00 (7.56) | 15.00 (15.12) | 34.00 (35.63) | – | 59.00 (59.85) |
| 4 | $Nd(OOCCHO)_3(N_2H_4)_2$ | 427.36 | 6.50 (7.50) | 15.00 (15.00) | 34.50 (35.35) | 53.50 (55.48) | 61.00 (60.63) |
| 5 | $Sm(OOCCHO)_3(N_2H_4)_2$ | 433.48 | 6.50 (7.39) | 14.00 (14.79) | 35.50 (34.86) | 55.00 (54.70) | 62.00 (59.78) |
| 6 | $Eu(OOCCHO)_3(N_2H_4)_2$ | 435.14 | 7.00 (7.36) | 14.50 (14.73) | 34.20 (34.73) | 54.00 (54.50) | 59.10 (59.56) |
| 7 | $Gd(OOCCHO)_3(N_2H_4)_2$ | 440.37 | 7.00 (7.28) | 16.00 (14.55) | 32.50 (34.31) | 54.00 (53.84) | 57.50 (58.84) |
| 8 | $Tb(OOCCHO)_3(N_2H_4)_2$ | 442.04 | 8.50 (7.25) | 15.50 (14.50) | 36.00 (34.64) | – | 60.00 (58.62) |
| 9 | $Dy(OOCCHO)_3(N_2H_4)_2$ | 445.68 | 6.60 (7.19) | 13.80 (14.38) | 33.20 (33.91) | 53.00 (53.22) | 57.50 (58.15) |

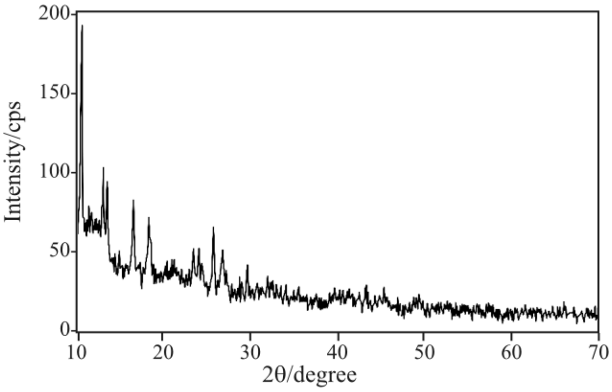

**Fig. 3a** X-ray powder diffraction pattern of $Pr(OOCCHO)_3(N_2H_4)_2$

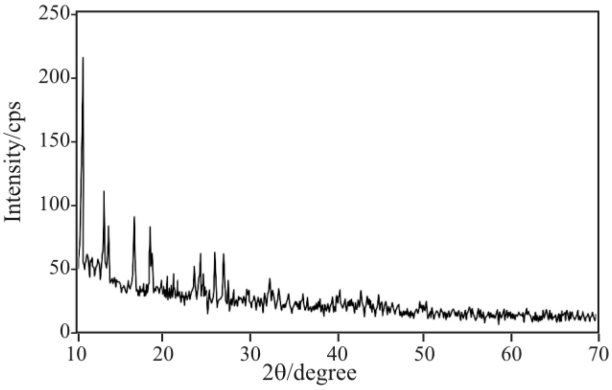

**Fig. 3b** X-ray powder diffraction pattern of $Nd(OOCCHO)_3(N_2H_4)_2$

diffraction patterns of Pr and Gd complexes are given in Figs 3a and b, respectively.

Based on the analytical, magnetic, spectral, thermal and XRD studies nine coordinated around $Ln^{3+}$ ions is assigned. Each lanthanide ion is surrounding by three bidentate glyoxylate ions, satisfying six of the nine coordinated sites and the remaining three are occupied by one bridged bidentate hydrazine and a monodentate hydrazine molecule. Hence, two dimensioned polymeric structure with hydrazine bridge is expected for the complexes, which is also expected from their insoluble nature and precipitation in aqueous solutions.

## Conclusions

Some new lighter and heavier lanthanides glyoxylate complexes containing neutral bridged hydrazine with the molecular formula $Ln(OOCCHO)_3(N_2H_4)_2$ where *Ln*=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy have been prepared, in slightly acidic aqueous medium (pH 6.8), by the aqueous reaction between respective lanthanide nitrate hydrates and hydrazinium glyoxylate.

These compounds were characterized by hydrazine, metal and CHN analyses, magnetic susceptibility measurement, spectral (UV-visible and infrared), thermal and X-ray powder diffraction techniques.

The infrared spectra of the complexes indicates that the one molecule coordinated to the metal as bridged bidentate ligands while the other as unidentate and the glyoxylate ions are coordinated only through both carbonyl and carboxylate oxygen atoms.

All the complexes undergo multi-step degradation as shown by their thermal profile to yield invariably the respective lanthanide oxide as the end residue. The dehydrazination takes place in two stages also supports the difference in the nature of hydrazine molecules.

The X-ray powder diffraction patterns of the present series of complexes are almost superimposable, indicating the isomorphism among the series. The lines are sharp and distinct.

Considering the stable coordination numbers observed for several lanthanide complexes and spectral, thermal and XRD studies nine-coordination around the lanthanide ions is proposed.

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