

NEW HYDRAZINIUM LANTHANIDE SULPHITE HYDRATES Preparation, spectral and thermal properties

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Abstract

Some new hydrazinium lanthanide sulphite hydrates of the formula $N_2H_5Ln(SO_3)_2(H_2O)_2$ where $Ln=La, Pr, Nd$ or Sm and $N_2H_5Ce(SO_3)_2$ have been prepared and characterized by chemical analyses, magnetic studies and electronic and infrared spectroscopy. Thermal degradation of these complexes has been investigated by simultaneous TG-DTA techniques. These complexes decompose in air after dehydration to give the respective lanthanide sulphate as the final residue. However, cerium complex gives a mixture of cerium sulphate and ceric oxide as the end products. Cerium and neodymium complexes have also been subjected to thermal degradation in nitrogen atmosphere and the dehydration of neodymium complex was observed at a higher temperature than in air. The anhydrous neodymium and cerium complexes decompose in one step to give the respective sulphate in nitrogen atmosphere.

Keywords: hydrazinium metal sulphites, metal oxides, metal sulphates, TG-DTA

Introduction

The monoprotonated hydrazine, the hydrazinium cation still retains a basic site and hence capable of coordination with various metal ions. However, many hydrazinium complexes reported in the literature contain hydrazinium ion as a mere charge neutralizing species [1]. Only a limited number of complexes containing coordinated hydrazinium ion like hydrazinium metal sulphates, $(N_2H_5)_2M(SO_4)_2$ [2–4] where $M=Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd$ or Mg and hydrazinium lanthanide sulphate monohydrates [5, 6], $N_2H_5Ln(SO_4)_2(H_2O)$ where $Ln=La, Ce, Pr, Nd$ or Sm , hydrazine uranyl dicarboxylates [7], hydrazinium oxalato metallates of lanthanide(III) ions [8], hydrazinium metal carboxylates [9–11], $(N_2H_5)_2M(RCOO)_4$ where $M=Co, Ni$ or Zn and $R=H, CH_3$ or NH_2CH_2 have been studied in detail.

During the course of our investigations on hydrazine complexes, we have reported a number of complexes such as metal hydrazinesulphinates and metal

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hydrazinecarboxylates with metal-hydrazine-sulphur dioxide [12–14] and carbon dioxide [15, 16] systems, respectively.

Hydrazinium sulphite monohydrate has been prepared and used as a ligand in the preparation of hydrazine metal complexes [17]. Most of the complexes reported in this case were metal sulphite hydrazinates [18] and their hydrates [19]. The formation of metal sulphite hydrazinates and metal hydrazine sulphinates depends mainly on the pH of the solution. By carefully adjusting the pH, by controlled addition of hydrazine and passing sulphur dioxide gas, different series of complexes have been prepared. However in these cases the solutions were always basic.

By way of further study we have investigated yet another reaction with metal-hydrazine-sulphur dioxide system in ‘acidic medium’ and obtained a different set of complexes, hydrazinium lanthanide sulphite hydrates which are new to the literature. Further, though plenty of hydrazine complexes with transition metal ions have been reported, similar complexes with lanthanides are scarce.

Hence in this paper we report the preparation, characterization, spectral and thermal properties of hydrazinium lanthanide sulphite dihydrates, $N_2H_5Ln(SO_3)_2(H_2O)_2$ where $Ln=La, Pr, Nd$ or Sm and anhydrous hydrazinium cerium sulphite complexes.

Experimental

Anhydrous lanthanide hydrazine carboxylates, $Ln(N_2H_3COO)_3$ where $Ln=La, Ce, Pr, Nd$ or Sm were prepared by adding hydrazinium hydrazine carboxylate to an aqueous solution of the respective lanthanide nitrate hydrate [20]. These complexes were used as precursors for the preparation of hydrazinium lanthanide sulphite hydrates. Hydrazinium sulphite monohydrate was prepared by the method reported in [14].

Preparation of hydrazinium lanthanide sulphite hydrates

About 20 mL of deionised water was saturated with sulphur dioxide gas by passing it into water for about 10 min. To the resultant solution the respective anhydrous lanthanide hydrazine carboxylate was added slowly with constant stirring. During the addition, the complex decomposed with the liberation of carbon dioxide gas. The addition was continued till a little of the lanthanide hydrazine carboxylate remained undissolved at the bottom of the conical flask. Then the solution was filtered and the clear solution was closed and kept aside for about 7–8 days at room temperature. The crystalline complexes deposited at the bottom were filtered, washed with cold water, then with ethanol and dried.

The above complexes were also prepared by adding an aqueous solution containing hydrazinium sulphite monohydrate (3.2 g, 0.02 mol) to an aqueous solution of the respective lanthanide nitrate hydrate (0.01 mol). After the addition, a few drops of dilute nitric acid were added to maintain the pH of the solution between 5 and 6. The resultant solution was kept for crystallization at room temperature. The crystalline complexes settled at the bottom were processed as above.

The complexes were found to be insoluble in water, alcohol and other organic solvents.

Analyses

The metal contents in all the complexes were determined by EDTA complexometric titration [21] after decomposing a known mass of the sample with concentrated nitric acid. The hydrazine content was determined volumetrically using 0.025 M KIO_3 solution under Andrews conditions [21].

Physico-chemical studies

The infrared spectra of the samples were recorded as KBr discs on a Perkin Elmer model 597 spectrophotometer in the range $4000\text{--}400\text{ cm}^{-1}$. Simultaneous TG-DTA experiments in air were carried out using STA 1500 system. Simultaneous TG-DTA for the cerium and neodymium complexes in nitrogen atmosphere were recorded using a DuPont instrument. The heating rate employed was $10^\circ\text{C min}^{-1}$. Aluminium cups were used as sample holders and aluminium oxide was used as the reference material. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. The values were corrected for diamagnetism with the appropriate Pascals constants. The electronic spectra (reflectance) were recorded on a Shimadzu UV-visible 240A double beam spectrophotometer using MgO as the reference material. The spectra were obtained in the solid-state by dispersing the sample in nujol.

Results and discussion

Lanthanide hydrazine carboxylates decomposed in dilute sulphurous acid with the liberation of carbon dioxide to give hydrazinium lanthanide sulphite hydrates. These complexes have also been obtained by the reaction of the respective lanthanide nitrate hydrates with hydrazinium sulphite monohydrate in aqueous medium.

Except cerium which forms anhydrous complex all other lanthanides form dihydrates, $\text{N}_2\text{H}_5\text{Ln}(\text{SO}_3)_2(\text{H}_2\text{O})_2$ where $\text{Ln}=\text{La, Pr, Nd or Sm}$. The composition of all the complexes were assigned on the basis of their metal and hydrazine analyses (Table 1).

Infrared spectra

The infrared spectra of hydrazinium lanthanide sulphite complexes are almost similar to that of hydrazinium lanthanide sulphate complexes [5]. These complexes show a band in the region $990\text{--}100\text{ cm}^{-1}$ for N–N stretching which indicates the coordination of N_2H_5^+ ion to the lanthanide ion. The N–N stretching frequency of free ion is expected to show a band in the region $960\text{--}980\text{ cm}^{-1}$ [1].

The presence of bidentate or bridging sulphite groups are shown by the broadening and splitting of bands in the region $1000\text{--}1200\text{ cm}^{-1}$. NH_2 deformation is shown by the band at 1650 cm^{-1} [22].

All the complexes show three or four sharp bands in the region $3100\text{--}3500\text{ cm}^{-1}$ due to the N–H and O–H stretchings. However, due to the overlap of N–H and O–H stretching frequencies, it is difficult to differentiate these two and also the absence of

Table 1 Analytical and magnetic data

Compound	Color	Metal/% found (calc.)	Hydrazine/% found (calc.)	μ_{eff} (B)
$\text{N}_2\text{H}_5\text{La}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	colorless	36.50 (37.74)	8.40 (8.71)	Diamagnetic
$\text{N}_2\text{H}_5\text{Ce}(\text{SO}_3)_2$	colorless	41.40 (42.04)	9.20 (9.62)	2.35
$\text{N}_2\text{H}_5\text{Pr}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	light green	37.00 (38.07)	8.30 (8.66)	3.42
$\text{N}_2\text{H}_5\text{Nd}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	violet	37.50 (38.62)	8.40 (8.58)	3.47
$\text{N}_2\text{H}_5\text{Sm}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	light yellow	38.60 (39.61)	8.20 (8.44)	1.51

water in the case of cerium complex cannot be confirmed by comparing the infrared spectra of these complexes.

Electronic spectra and magnetic moments

Since La^{3+} and Ce^{3+} are colorless, as expected no absorption bands were observed in the visible region for their complexes. The electronic spectra of the Pr^{3+} , Nd^{3+} and Sm^{3+} complexes show weak but sharp bands in the visible region. These are comparable with the corresponding lanthanide sulphates and hydrazinium lanthanide sulphate monohydrates. Also due to the fact that the 4f-orbitals are effectively shielded from the surroundings by the overlapping 5s and the 5p orbitals, the absorption bands are not much affected by changing the anions. The observed transitions indicate either eight or nine coordination for these complexes.

The room temperature magnetic moments of hydrazinium lanthanide sulphite complexes (Table 1) are similar to those of the respective hydrazinium lanthanide sulphate complexes.

Thermal analysis

All the complexes except cerium complex show similar degradation behaviour when subjected to controlled thermal decomposition. Since these complexes are dihydrated, the first stage of degradation is dehydration as expected to give monohydrates. The TG temperature range is 50–130°C. The observed mass losses are well in accordance with the theoretical losses. The monohydrates again give up a water molecule in the temperature range 130–180°C. These two stages are endothermic as observed from DTA curves.

The anhydrous complexes further decompose exothermically in air to give the respective metal sulphate dihydrazinates which dehydrazinate at higher temperatures to give the respective metal sulphates as the final product. The formation of metal

sulphate as the final residue has been confirmed by removing the product after complete degradation in the temperature range 580–600°C and analyzing the residue for metal and sulphate contents.

The cerium complex however, shows a different thermal behaviour which has also been observed in the case of cerium hydrazinesulphinate and cerium sulphite hydrazinate.

Since cerium forms anhydrous complex, the first stage of degradation of this complex is exothermic and the cerium sulphite hydrazinate, $\text{Ce}_2(\text{SO}_3)_3(\text{N}_2\text{H}_4)$ is formed as an intermediate which again undergoes exothermic decomposition in the temperature range 449–509°C to give a mixture of $\text{Ce}_2(\text{SO}_4)_3$ and CeO_2 in 1:1 ratio as the final product. The assigned final products and their ratios were confirmed by the chemical analyses of the residues after separating the sulphate by dissolving in water. The formation of a mixture of sulphate and oxide has been already observed in various hydrazine complexes.

In nitrogen atmosphere cerium complex decomposes in a single step to give cerium sulphate as the end product in the temperature range 400–500°C. This degradation is exothermic and DTA shows a peak at 470°C.

However, in the case of neodymium complex the first two stages are dehydrations which are similar to that of degradation observed in air. But the anhydrous complex unlike decomposition in air decomposes in nitrogen in one step to give neodymium sulphate as the final residue. This stage is exothermic with a peak at 490°C. The dehydration occurs at a higher temperature in nitrogen atmosphere than in air. However, the final product is formed in the same temperature range in both the atmospheres.

The thermal analysis data of all the complexes are summarized in Table 2. The simultaneous TG-DTA of cerium and neodymium complexes in air and nitrogen atmosphere are shown in Figs 1–4 respectively, as representative examples.

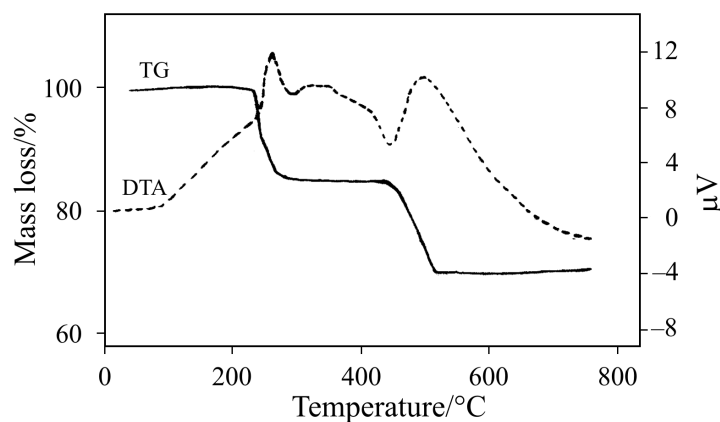


Fig. 1 Simultaneous TG-DTA of $\text{N}_2\text{H}_5\text{Ce}(\text{SO}_3)_2$ in air

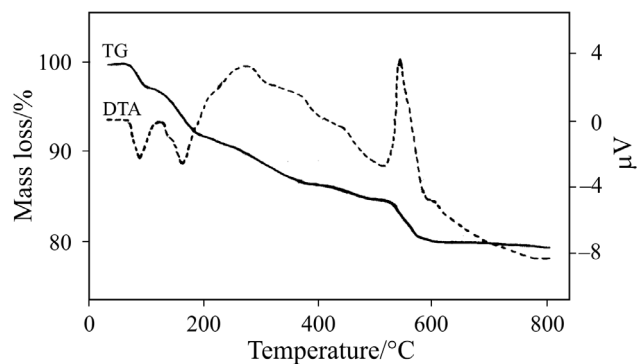


Fig. 2 Simultaneous TG-DTA of $N_2H_5Nd(SO_3)_2(H_2O)_2$ in air

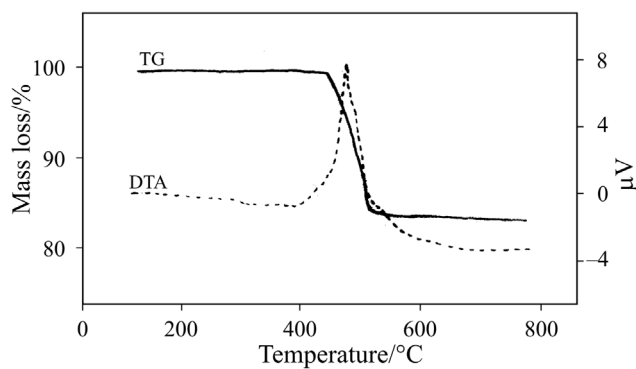


Fig. 3 Simultaneous TG-DTA of $N_2H_5Ce(SO_3)_2$ in nitrogen

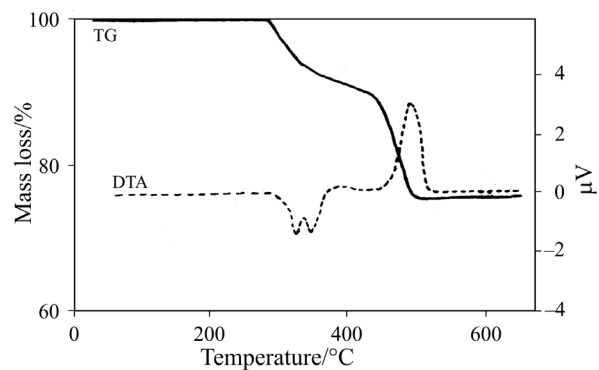


Fig. 4 Simultaneous TG-DTA of $N_2H_5Nd(SO_3)_2(H_2O)_2$ in nitrogen

Table 2 Thermal data

Compound	TG temp. range/°C	DTA peak temp./°C	Mass loss/%		Product
			Found	Calc.	
$N_2H_5La(SO_3)_2(H_2O)_2$	75–130	90(+)	4.10	4.89	$N_2H_5La(SO_3)_2(H_2O)$
	130–170	150(+)	9.00	9.78	$N_2H_5La(SO_3)_2$
	170–510	320(–)	13.20	14.42	$La_2(SO_4)_3(N_2H_4)_2$
	510–600	540(–)	21.50	23.12	$La_2(SO_4)_3$
$N_2H_5Ce(SO_3)_2$	236–281	267(–)	17.00	17.12	$Ce_2(SO_3)_3(N_2H_4)$
	449–509	500(–)	29.00	31.54	$Ce_2(SO_3)_3+CeO_2$
$N_2H_5Pr(SO_3)_2(H_2O)_2$	80–120	100(+)	4.20	4.87	$N_2H_5Pr(SO_3)_2(H_2O)$
	120–190	160(+)	8.70	9.73	$N_2H_5Pr(SO_3)_2$
	190–520	300(–)	15.00	14.34	$Pr_2(SO_4)_3(N_2H_4)_2$
	520–580	560(–)	21.50	23.00	$Pr_2(SO_4)_3$
$N_2H_5Nd(SO_3)_2(H_2O)_2$	68–126	86(+)	4.10	4.82	$N_2H_5Nd(SO_3)_2(H_2O)$
	126–180	161(+)	9.00	9.65	$N_2H_5Nd(SO_3)_2$
	180–521	269(–)	15.30	14.21	$Nd_2(SO_4)_3(N_2H_4)_2$
	521–568	543(–)	21.00	22.79	$Nd_2(SO_4)_3$
$N_2H_5Sm(SO_3)_2(H_2O)_2$	70–120	90(+)	4.00	4.75	$N_2H_5Sm(SO_3)_2(H_2O)$
	120–190	170(+)	8.75	9.48	$N_2H_5Sm(SO_3)_2$
	190–518	275(–)	13.00	13.98	$Sm_2(SO_4)_3(N_2H_4)_2$
	518–580	540(–)	22.00	22.43	$Sm_2(SO_4)_3$
$N_2H_5Ce(SO_3)_2^*$	460–510	470(–)	16.00	14.73	$Ce_2(SO_4)_3$
	280–335	330(+)	5.00	4.82	$N_2H_5Nd(SO_3)_2(H_2O)$
$N_2H_5La(SO_3)_2(H_2O)_2^*$	335–425	350(+)	9.50	9.65	$N_2H_5Nd(SO_3)_2$
	425–500	490(–)	24.50	22.79	$Nd_2(SO_4)_3$

(+) Endotherm; (–) exotherm

*Thermal degradation in nitrogen atmosphere.

Conclusions

Hydrazine lanthanide sulphite hydrates were prepared by the decomposition of the respective lanthanide hydrazine carboxylate in dilute sulfurous acid.

The reaction of lanthanide nitrate hydrates with hydrazinium sulphite monohydrate in acidic medium also resulted in the same set of complexes.

The magnetic moments, electronic and infrared spectra of these complexes suggest the eight or nine coordination around the metal ions. The coordination of hydrazinium ion is also confirmed by their infrared spectra.

When subjected to thermal degradation all the complexes give the respective sulphates as the final residue except cerium complex in air, which gives a mixture of cerium sulphate and cerium oxide as the final residue.

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