

## SPECTRAL AND THERMAL STUDIES ON NEW HYDRAZINIUM METAL SULFITE DIHYDRATES

L. Vikram<sup>1</sup>, D. S. Shanthakumar<sup>1</sup>, R. Ragul<sup>2</sup> and B. N. Sivasankar<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Government Arts College, Udahgamandalam, The Nilgiris 643 002, India

<sup>2</sup>Erode Arts College, Erode, India

Some new hydrazinium transition metal sulfite dihydrate complexes of the formula  $(N_2H_5)_2M(SO_3)_2(H_2O)_2$  where  $M=Fe, Co, Ni, Cu$  and  $Zn$  have been prepared and characterized by hydrazine and metal analyses, magnetic studies, electronic and infrared spectra and thermal analysis. The magnetic studies coupled with electronic spectra of iron, cobalt, nickel and copper complexes indicate their high spin octahedral nature. However the zinc complex is diamagnetic and show only the charge transfer transition. The infrared spectra shows that both the hydrazinium ions are coordinated to the metal ions, the sulfite ions are present as bidentate ligand.

The simultaneous TG-DTA of these complexes were investigated in air and nitrogen atmospheres. In air, cobalt, nickel and zinc complexes give respective metal sulfate as the final residue while iron and copper complexes give the mixture of respective metal oxide and sulfate as the decomposition product. In nitrogen atmosphere respective metal sulfites are formed as the end residue.

**Keywords:** hydrazinium metal sulfite dihydrates, metal oxides, metal sulfates

### Introduction

During the course our studies on hydrazine derivatives, we have reported the preparation, spectral and thermal studies on variety of metal hydrazine sulfinates [1, 2] and metal sulfite hydrazinates [3]. Recently the preparation, spectral and thermal studies on hydrazinium lanthanide sulfite hydrates,  $N_2H_5Ln(SO_3)_2(H_2O)_2$  [4], some transition metal complexes of pyrazinecarboxylate hydrazinates [5] and 3,5-pyrazoledicarboxylate hydrazinates [6] have also been reported. In continuation of these studies, we now report the preparation and properties of  $(N_2H_5)_2M(SO_3)_2(H_2O)_2$  where  $M=Fe, Co, Ni, Cu$  and  $Zn$ .

### Experimental

Anhydrous metal hydrazinecarboxylates of the formula  $M(N_2H_3COO)_2$  where  $M=Fe, Co, Ni, Cu$  and  $Zn$  were prepared by the method already reported in the literature [7]. These complexes were used as precursors for the preparation of hydrazinium metal sulfite dihydrates. Hydrazinium sulfite mono hydrate was also prepared by the literature method [8].

#### Preparation of hydrazinium metal sulfite dihydrates

Anhydrous metal hydrazinecarboxylates,  $M(N_2H_3COO)_2$  where  $M=Fe, Co, Ni, Cu$  and  $Zn$  were added to about 50 mL of distilled water which was pre-

viously saturated with sulfur dioxide gas. The solution was shaken well while adding the respective metal hydrazinecarboxylates which was added in portions. The complex decomposed with the liberation of carbon dioxide. The addition was continued till further dissolution ceased. The resulting solution was filtered and the clear solution was kept at room temperature for about 3–4 days in sulfur dioxide atmosphere. The crystalline complexes deposited at the bottom were filtered, washed several times with cold water and dried in air.

Hydrazinium metal sulfite dihydrates were also prepared by mixing aqueous solutions of respective metal nitrate hydrates (0.01 mol) and hydrazinium sulfite monohydrate (3.2 g, 0.02 mol). To this mixture, a few drops of dilute nitric acid were added to adjust the pH to about 5. This resultant solution when allowed to stand for 2 days, a crystalline complex settled at the bottom, which was filtered, washed with cold water and dried in air.

#### Physico-chemical studies

The metal contents in all the complexes were determined by EDTA complexometric titrations [9] after decomposing a known amount of the complex with concentrated nitric acid for several times. The hydrazine content was determined volumetrically using  $KIO_3$  solution (0.025 M) under Andrews conditions [9].

The infrared spectra of the complexes were recorded on a Perkin-Elmer model 597 spectrophotometer using KBr pellets of the samples in the range

\* Author for correspondence: sivabickol@yahoo.com

4000–400  $\text{cm}^{-1}$ . The room temperature magnetic susceptibility measurements were carried out with a Gouy balance using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant. The solid state electronic absorption spectra of the complexes in Nujol mull were recorded on a Shimadzu UV-vis 240 A spectrophotometer in the range 200–800 nm.

The simultaneous TG-DTA of the complexes in air were carried out using a STA 1500 system. The thermal experiments in nitrogen atmosphere were also carried out for comparison. The heating rate employed was  $10^\circ\text{C min}^{-1}$  and aluminium cups were used to hold about 5–10 mg of the sample.

## Results and discussion

Hydrazinium metal sulfite dihydrates were prepared by either decomposing the respective anhydrous metal hydrazinecarboxylates in aqueous solution containing sulfur dioxide gas or by the aqueous reaction between hydrazinium sulfite monohydrate and respective metal nitrate hydrates. These complexes are insoluble in water, alcohol and other organic solvents and decompose in dilute acids with the liberation of sulfur dioxide which is the characteristic reaction of metal sulfites. The composition of the complexes, on the basis of metal and hydrazine analyses, were assigned as  $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_3)_2(\text{H}_2\text{O})_2$  where  $M = \text{Fe, Co, Ni, Cu}$  and  $\text{Zn}$  (Table 1).

The room temperature magnetic moments of iron, cobalt, nickel and copper complexes are found to be 5.32, 5.02, 3.45 and 1.95, respectively, which indicate the high spin octahedral nature of these metal ions [10–12]. The zinc complex is diamagnetic as expected.

The electronic spectrum of iron(II) complex exhibits a band at  $11200 \text{ cm}^{-1}$  which is assigned to the  $^5\text{E}_g \rightarrow ^5\text{T}_{2g}$  transition. The cobalt complex shows two bands at  $9400 \text{ cm}^{-1}$  and  $19380 \text{ cm}^{-1}$  which are assigned to  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}$  and  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$  transitions, respectively [13]. The nickel complex exhibits three bands characteristic of octahedral geometry at 10210, 17670 and  $27700 \text{ cm}^{-1}$  which are assigned to  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$ ,  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$  and  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$  transitions, respectively [14, 15]. The  $\text{T}_{2g} \rightarrow \text{E}_g$  separation in the regular octahedral copper(II) complex varies from

about  $13000 \text{ cm}^{-1}$  for  $\text{CuO}_6$  to about  $18000 \text{ cm}^{-1}$  for  $\text{CuN}_6$  [13]. The copper(II) complex reported here shows a  $d-d$  transition around  $14200 \text{ cm}^{-1}$  which shows the involvement of nitrogen and oxygen donor sites in coordination.

The infrared spectra of hydrazinium metal sulfite dihydrates are similar to that of sulfite complexes. These complexes show a band in the region  $990\text{--}1000 \text{ cm}^{-1}$  for N–N stretching of coordinated  $\text{N}_2\text{H}_5$  ions [16]. The presence of bidentate and bridging sulfite ions [17] are shown by the broadening and splitting of bands in the region  $1000\text{--}1200 \text{ cm}^{-1}$ . These complexes showed three or four bands in the region  $3200\text{--}3500 \text{ cm}^{-1}$  indicating the presence of both N–H and O–H stretching of  $\text{N}_2\text{H}_5$  or  $\text{H}_2\text{O}$  groups.

### Thermal degradation

The iron complex decomposes in air in a single step in the temperature range  $200\text{--}300^\circ\text{C}$  as shown by the TG curve to give the mixture of ferrous sulfate and ferric oxide as the residues. The DTA shows a doublet at 260 and  $280^\circ\text{C}$ . The TG mass loss corresponds to the product in 1:1 ratio.

The hydrazinium cobalt sulfite dihydrate shows multi-step decomposition. The first stage is dehydration in the temperature range  $30\text{--}80^\circ\text{C}$  showing the non-coordination of water molecules. DTA shows an endotherm at  $52^\circ\text{C}$  corresponding to this dehydration. The mass loss is found to be 12% which is in accordance with the theoretical mass loss. Then the anhydrous complex decomposes in four stages to give cobalt sulfate as the final product below  $300^\circ\text{C}$ . The intermediates proposed for these stages are given in the Table 2. The DTA shows one endotherm and three exotherms at 190, 227, 233 and  $295^\circ\text{C}$ , respectively.

The nickel complex undergoes dehydration in two stages in the temperature range  $50\text{--}165^\circ\text{C}$  as shown by TG curve. The DTA shows two endotherms at 65 and  $150^\circ\text{C}$  for the dehydration. The anhydrous complex undergoes decomposition slowly up to  $525^\circ\text{C}$  and then sharply between 525 and  $570^\circ\text{C}$  to give nickel sulfate as the final residue. The DTA curve shows a broad exotherm from  $200\text{--}500^\circ\text{C}$  and then the sharp exotherm at  $540^\circ\text{C}$ , respectively.

**Table 1** Analytical data

Complex	Colour	Metal/%		Hydrazine/%		$\mu_{\text{eff}}/\text{B.M.}$
		found	calc.	found	calc.	
$(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	light green	17.0	17.56	19.5	20.15	5.32
$(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	pink	17.8	18.35	19.7	19.96	5.02
$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	green	18.0	18.29	19.1	19.97	3.45
$(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	blue	18.9	19.50	19.0	19.67	1.95
$(\text{N}_2\text{H}_5)_2\text{Zn}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	colourless	19.5	19.95	20.1	19.56	diamagnetic

The copper complex after endothermic dehydration undergoes decomposition sharply in the temperature range 220–265°C to give copper sulfite, which undergoes disproportionation in the wide temperature range from 260–750°C to give a mixture of copper sulfate and copper oxide in 1:1 ratio as the residues. Further after the formation of copper sulfite, the TG shows an increase in mass, corresponding to the formation of copper sulfate up to 620°C. Further heating shows decrease in mass. This indicates the partial decomposition of copper sulfate at such a high temperature (620–750°C) to give a mixture of copper sulfate and copper oxide. Though the formation of a mixture of metal sulfite and metal oxide as the end product by the disproportionation of the respective metal sulfites has been observed in many cases, in the present case the increase in mass in TG after the formation of copper sulfite may only be attributed to the formation of copper sulfate in air which then undergoes partial decomposition at higher temperatures.

The zinc complex after endothermic dehydration in the temperature range 100–150°C undergoes multi-step decomposition to give zinc sulfate as the final residue. The decomposition is continuous and no distinct step is observed in TG.

The thermal degradation of cobalt and copper complexes has also been recorded in nitrogen atmosphere for comparison. In both the cases the complexes decompose endothermically followed by exothermic degradation to give respective metal sulfite as the final residue. In nitrogen atmosphere the decomposition was

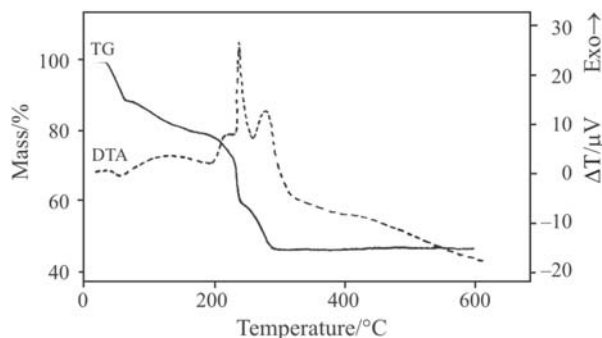


Fig. 1 Simultaneous TG-DTA curves of  $(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_3)_2(\text{H}_2\text{O})_2$  in air

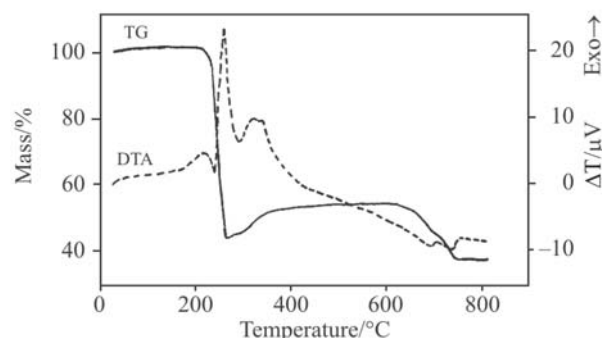


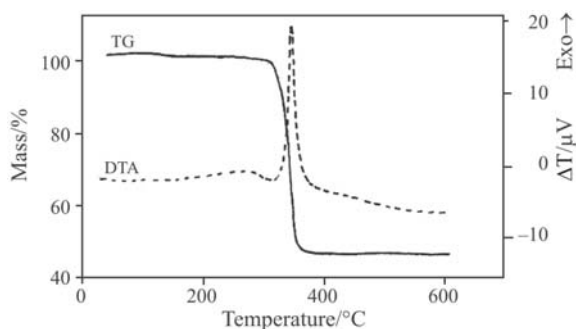
Fig. 2 Simultaneous TG-DTA curves of  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_3)_2(\text{H}_2\text{O})_2$  in air

found to be continuous, hence the intermediate formed is not clearly shown by the TG curve. The final mass loss is found to be 46% in the case of cobalt complex and 45% in the case of copper complex.

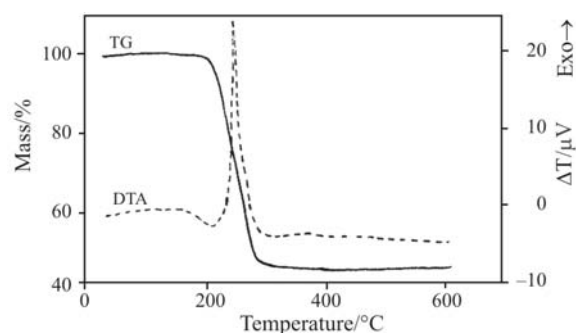
Table 2 Thermal data in air and nitrogen\* atmospheres

Compound	Temperature range/°C	DTA peak/°C	Mass loss/%		Residue
			found	calc.	
$(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	200–300	260, 280 (exo,d)	36.0	36.43	$1/4\text{Fe}_2\text{O}_3 + 1/2\text{FeSO}_4$
	30–80	52 (endo)	12.0	11.22	$(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_3)_2$
	80–185	190 (endo)	20.0	21.20	$\text{N}_2\text{H}_6\text{Co}(\text{SO}_3)_2$
$(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	195–230	227 (exo)	30.0	31.79	$\text{CoSO}_4 \cdot 2\text{N}_2\text{H}_4$
	230–240	233 (exo)	39.5	41.77	$\text{CoSO}_4 \cdot \text{N}_2\text{H}_4$
	240–290	275 (exo)	52.0	51.75	$\text{CoSO}_4$
	50–100	65 (endo)	6.0	5.61	$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_3)_2(\text{H}_2\text{O})$
$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	100–165	150 (endo)	11.5	11.23	$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_3)_2$
	165–525	255 (exo,b)	40.0	41.87	$\text{NiSO}_4 \cdot \text{N}_2\text{H}_4$
	525–570	439 (exo,b)	50.0	51.85	$\text{NiSO}_4$
	220–265	240 (endo)	56.0	55.93	$\text{CuSO}_3$
$(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	260–350	260 (exo)	50.0	51.01	$\text{CuSO}_4$
	340 (exo)	63.0	64.53	$\text{CuO} + \text{CuSO}_4$	
	646–750	693 (endo,b)			
$(\text{N}_2\text{H}_5)_2\text{Zn}(\text{SO}_3)_2(\text{H}_2\text{O})_2$	100–150	160 (endo)	11.0	11.00	$(\text{N}_2\text{H}_5)_2\text{Zn}(\text{SO}_3)_2$
	150–600	350 (exo,b)	54.0	50.73	$\text{ZnSO}_4$
		580 (exo,b)			
$(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_3)_2(\text{H}_2\text{O})_2^*$	310–360	320 (endo)	54.0	56.73	$\text{CoSO}_3$
		347 (exo)			
$(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_3)_2(\text{H}_2\text{O})_2^*$	210–270	230 (endo)	55.0	55.93	$\text{CuSO}_3$
		265 (exo)			

exo – exotherm, endo – endotherm, d – doublet and b – broad



**Fig. 3** Simultaneous TG-DTA curves of  $(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_3)_2(\text{H}_2\text{O})_2$  in nitrogen



**Fig. 4** Simultaneous TG-DTA curves of  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_3)_2(\text{H}_2\text{O})_2$  in nitrogen

TG-DTA data of the complexes are summarized in Table 2. The simultaneous TG-DTA traces of cobalt and copper complexes in air are shown in Figs 1 and 2, respectively. The thermal traces for the above complexes in nitrogen atmosphere are shown in Figs 3 and 4, respectively.

## Conclusions

Hydrazinium metal sulfite dihydrates were prepared by decomposing respective metal hydrazinecarboxylates in aqueous sulfurous acid or aqueous reaction between metal nitrate hydrate and hydrazinium sulfite mono hydrate in acidic condition.

These complexes were characterized by chemical analysis, which shows that the composition of the complexes is  $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_3)_2(\text{H}_2\text{O})_2$ .

The magnetic moment data and electronic spectra of Fe, Co, Ni and Cu complexes are in accordance with the high-spin octahedral variety of these complexes. The zinc complex is diamagnetic as expected.

The thermal analyses indicate that the water molecules are not coordinated to the metal ions and hence evolved at low temperatures. The final residues are respective metal sulfates or a mixture of metal oxide and metal sulfate. In nitrogen atmosphere in all the cases the respective metal sulfites were formed as the residues.

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