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SYNTHESIS, INFRARED SPECTRA AND THERMOANALYTICAL PROPERTIES OF TRANSITION METAL SULFITE HYDRAZINE HYDRATES

Jayant S. Budkuley and *K. C. Patil**

DEPARTMENT OF CHEMISTRY GOA UNIVERSITY BAMBOLIM, GOA 403 005, INDIA
*DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY INDIAN INSTITUTE OF SCIENCE, BANGALORE 560 012, INDIA

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Transition metal sulfite hydrazine hydrates, $MSO_3 \cdot xN_2H_4 \cdot yH_2O$ where M = Mn, Fe, Co, Ni and Zn have been prepared and characterized by chemical analysis, infrared spectra, thermoanalytical and combustion studies. The colours, x and y parameters of the complexes varied depending upon the preparation conditions. Thermal decomposition characteristics differ from metal to metal yielding metal oxides at relatively low temperatures.

Hydrazine is well known [1] to form various complexes with transition metals. The nature of these complexes is greatly influenced by the type of anions such as sulfates, oxalates, hydrazidocarbonate etc., associated with the metal ions. These complexes are important as precursors to obtain simple and/or mixed oxides which can have interesting semiconducting and catalytic properties. Ray and Goswami [2] in 1928 reported sulfite based metal hydrazinate hydrate complexes having the composition $MSO_3 \cdot xN_2H_4 \cdot yH_2O$. Their preparation involves varying degree of saturation of a solution of metal hydroxide and hydrazine with SO_2 gas. The present investigation was aimed at synthesizing such complexes under definite preparative conditions and study their infrared spectra, magnetic properties and thermal behaviour.

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Experimental

The synthesis of these hydrazine complexes $MSO_3 \cdot xN_2H_4 \cdot yH_2O$, involved two steps. Hydrazine hydrate (99-100%) was at first saturated with SO_2 gas and the resulting product-hydrazinium sulfite monohydrate, $(N_2H_5)_2SO_3 \cdot H_2O$ was precipitated out by the addition of alcohol. Subsequently hydrazinates were obtained by treatment of $(N_2H_5)_2SO_3 \cdot H_2O$ with divalent metal ions, M^{2+} = Fe, Mn, Co, Ni or Zn under different preparative conditions as mentioned below:

Method I: Reaction in presence of $N_2H_4 \cdot H_2O$*

Calculated quantity of $(N_2H_5)_2SO_3 \cdot H_2O$ was dissolved in $N_2H_4 \cdot H_2O$. To the alkaline solution (pH~9) thus obtained, stoichiometric quantity (M: SO_3 equal to 1:1) of metal salt solution was added with constant stirring. The compound formed was initially washed with alcohol and then dried in a vacuum desiccator over P_2O_5. (Method I is indicated by single asterisk (*) in the ensuing discussion.)

*Method II**: Reaction in the absence of $N_2H_4 \cdot H_2O$*

To an aqueous solution of $(N_2H_5)_2SO_3 \cdot H_2O$ (pH 4), stoichiometric quantity M: SO_3 (1:1) of metal salt solution was added with constant stirring. To the resulting solution alcohol was added to the product precipitate which was filtered and washed with alcohol and then filtered. It was then washed with alcohol and dried in a vacuum desiccator over P_2O_5.

$$(N_2H_5)_2SO_3 \cdot H_2O + \text{aq.} \rightarrow (N_2H_5)_2SO_3 \cdot H_2O \ \text{aq.}$$

$$(N_2H_5)_2SO_3 \cdot H_2O \ \text{aq.} \rightleftarrows (N_2H_4)_2 \cdot H_2SO_3 \cdot H_2O \ \text{aq.}$$

$$MCl_2 + (N_2H_4)_2H_2SO_3 \cdot H_2O \ \text{aq} + nH_2O \rightarrow$$

$$\rightarrow MSO_3 \cdot xN_2H_2 \cdot yH_2O + 2HCl + (2-x)N_2H_4 + (n+1-y)H_2O$$

(Method II is indicated by two asterisks (**) in the ensuing discussion.)

The compositions of metal sulfite hydrazine hydrate complexes were established by chemical analysis. The metal content was fixed by EDTA titrations [3]. The usual volumetric method of determining hydrazine using

0.025 M KIO_3 solution under Andrews [3] conditions could not be used for these complexes as sulfite also reacts with KIO_3. Therefore, a modified procedure [4] (method of difference) for determination of hydrazine and sulfur (in sulfite) was used.

Thermogravimetry (TG) experiments were carried out using a Stanton-Redcroft TG - 750 thermobalance with 6-8 mg samples. Differential Thermal Analysis (DTA) was carried out using an instrument described elsewhere [5] with 50-100 mg sample. The heating rate employed was 5 deg·min^{-1} both in TG and DTA experiments which were carried out in air. Pt sample holders were used. Infrared spectra of the samples were recorded as Nujol mull using Perkin-Elmer 599 spectrophotometer. X-ray powder diffraction patterns of the samples were recorded on a Philips PW 1050/70 diffractometers using CoKα and CuKα radiations.

Results and discussions

Ray and Goswami [2] reported the synthesis of various metal sulfite hydrazinate hydrates $MSO_3 \cdot xN_2H_4 \cdot yH_2O$ by passing SO_2 gas for different duration in solution of metal salt containing hydrazine. In the present investigation it was noted that irrespective of the method of preparation, hydrazine hydrate represented by the formula given above was formed. The value of x and y representing the number of molecules of N_2H_4 and H_2O respectively varied depending upon the method of preparation. It is interesting to note that while Fe, Mn and Zn formed those complexes only by Method I, Co and Ni could form these complexes by both the methods viz. Method I and Method II.

The results of chemical analysis (Table 1) show that there is a good agreement between observed and calculated values of metal, sulfur and N_2H_4 contents for proposed formula mentioned therein.

Infrared absorption spectra (Fig. 1) of the compounds are identical and show characteristic absorption of N_2H_4 and sulfite. The assignments of the i.r. absorptions have been made on the basis of earlier studies and summarized in Table 2. The absorption ~960 cm^{-1} is characteristic of N-N stretching frequency of bridged hydrazine. Sulfite absorptions are observed around 1000, 620 and 495 cm^{-1} in comformity with those reported [7] in the literature. Infrared absorptions of H_2O molecule are also observed (Table 2).

Thermoanalytical (TG and DTA) data of the complexes are presented in Table 3. Discussion of the individual complex is as follows:

$FeSO_4 \cdot 2N_2H_4 \cdot H_2O$*

This complex is pale green in colour, highly susceptible to atmospheric oxidation and exhibits autocombustion. TG and DTA curves of this complex are shown in Fig. 2. Thermogravimetry of this complex shows 38% weight loss in the temperature range 130-142° due to the loss of H_2O and N_2H_4. Complementary peak is observed in the DTA at 135°. $FeSO_3$ thus formed decomposes disproportionately into oxide and sulfate in the temperature range 190-198° showing 50% loss in the TG and sharp exotherm at 190°. Qualitative tests of the decomposition residue in the TG and DTA confirm the presence of oxide and sulfate. However combustion residue of this complex contains a mixture of α and γ-Fe_2O_3 (mostly γ-Fe_2O_3). This is confirmed [8] by its X-ray (Fig. 3). This can be ascribed to the highly exothermic decomposition of the complex.

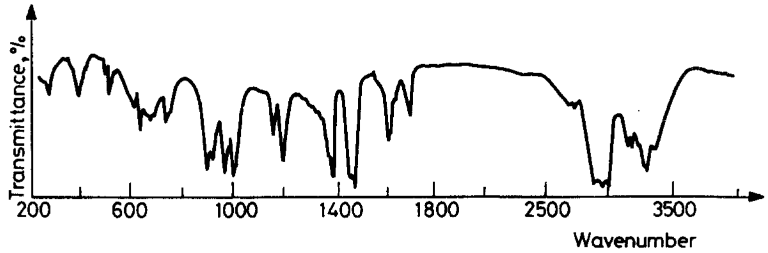

Fig. 1 Infrared spectra of $MnSO_3 \cdot 2N_2H_4 \cdot 2H_2O$ in Nujol Mull

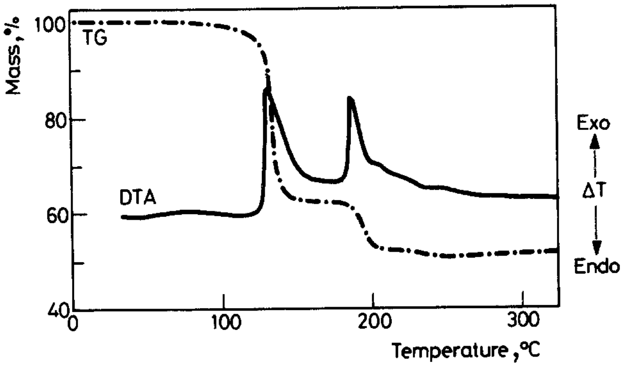

Fig. 2 TG and DTA $FeSO_3 \cdot 2N_2H_4 \cdot H_2O$

Table 1 Chemical analysis data of metal sulfite hydrazine hydrate complexes

$MSO_3 \cdot xN_2H_4 \cdot yH_2O$ *M* =	% Metal obsd.	Content theor.	% Sulfur obsd.	Content theor.	% Hydrazine obsd.	Content theor.	Formula assigned
Fe*	25.51	25.68	14.82	14.09	29.1	29.38	$FeSO_3 \cdot 2N_2H_4 \cdot H_2O$ (pale green)
Mn*	24.00	23.38	13.79	13.62	27.1	27.24	$MnSO_3 \cdot 2N_2H_4 \cdot 2H_2O$ (colourless)
Co*	26.70	26.67	14.32	14.48	29.0	28.96	$CoSO_3 \cdot 2N_2H_4 \cdot H_2O$ (flesh)
Ni*	23.16	23.23	12.7	12.66	37.81	37.98	$NiSO_3 \cdot 3N_2H_4 \cdot H_2O$ (rose)
Zn*	28.04	27.65	13.50	13.53	27.68	27.08	$ZnSO_3 \cdot 2N_2H_4 \cdot 1\frac{1}{2}H_2O$ (colourless)
Co**	26.22	26.43	14.30	14.35	21.62	21.53	$CoSO_3 \cdot 1\frac{1}{2}N_2H_4 \cdot 2H_2O$ (yellow)
Ni**	26.58	26.6	15.02	14.49	28.8	28.99	$NiSO_3 \cdot 2N_2H_4 \cdot H_2O$ (blue)

* Method I, ** Method II

Table 2 Infrared absorption frequencies of $MSO_3 \cdot xN_2H_4 \cdot yH_2O$ and their assignments

M = Mn	Fe	Co	Ni	Zn	Assignment
3510 (w)	3530 (w)	3540 (w)	3530 (w)	3560 (w)	O–H stretching
3280 (sp)	3300 (sp)	3300 (sp)	3340 (sp)	3300 (sp)	N–H stretching
3180 (w)	3170 (w)	3260 (w)	3180 (s)	3280 (sp)	
	3140 (w)	3130 (w)			
1620 (m)	1630 (m)	1640 (m)	1650 (m)	1670 (m)	H_2O bending
1600 (sp)	1605 (sp)	1595 (sp)	1620 (sp)	1600 (s, sp)	NH_2 bending
1195 (s, sp)	1200 (s)	1188 (s, sp)	1215 (s, sp)	1190 (s, sp)	NH_2 bending wagging
1150 (sp)	1150 (sp)	1150 (sp)	1165 (sp)	1152 (sp)	NH_2 twisting
1000 (sp)	1000 (sp)	1000 (sp)	980 (sp)	1000 (m)	S–O stretching
960 (sp)	900 (sp)	900 (b)	900 (sp)	960 (sp)	N–N stretching
900 (sp)	900 (sp)	900 (b)	900 (b)	900 (b)	S–O asym. stretching
640 (s)	660 (s)	642 (s)	660 (s)	665 (m)	NH_2 rocking
630 (m)	623 (w)	600 (w)	620 (m)	605 (m)	S–O sym. bending
495 (sp)	500 (sp)	495 (sp)	485 (s)	500 (sp)	S–O asym.bending
355 (sp)	370 (sp)	370 (sp)	370 (sp)	370 (sp)	M–N stretching

s - strong, m - medium, w - weak, sp - sharp, b - broad

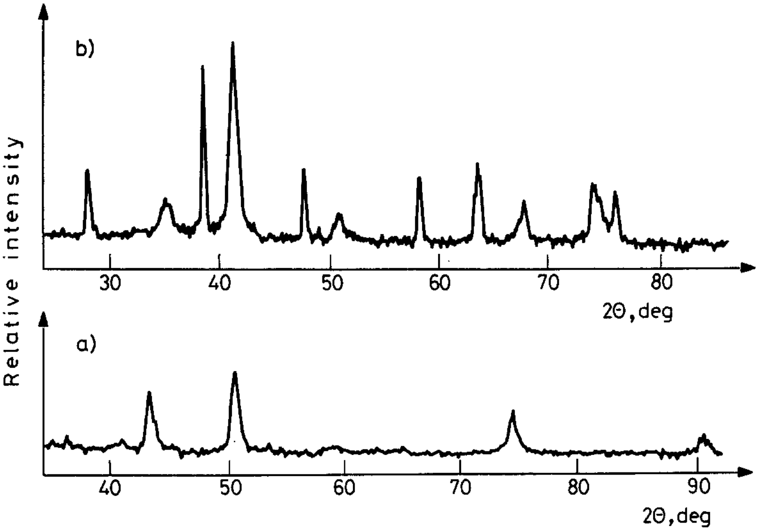

Fig. 3 X-ray diffraction pattern of a) $\gamma - Fe_2O_3$ (CoKα) b) NiO(CuKα)

$MnSO_3 \cdot 2N_2H_4 \cdot H_2O$*

This colourless complex shows a comparatively high thermal stability. TG shows 17.0% weight loss in the range 120-158° and 42% weight loss in the range 202-245°. The former is due to the removal of H_2O and the later due to the loss of N_2H_4 through decomposition. Complementary peaks are seen in the DTA - an endotherm at 152° and an exotherm at 232.8° beyond 360° $MnSO_3$ disproportionates [9] into sulfate (major) and oxide/sulfide.

$CoSO_3 \cdot 2N_2H_4 \cdot H_2O$*

It is a flesh coloured complex found stable upto 88°. Beyond this temperature, it gradually loses H_2O as is evident from the thermogram which shows 8% loss in the range 88-121°. The exothermic loss of N_2H_4 and decomposition of $CoSO_3$ is continuous in the TG. Weight loss of 50% and analysis of the residue suggest the decomposition to oxide and sulfate. Complementary peaks are seen in the DTA. X-ray diffraction data [8] of the TG residue shows the presence of Co_3O_4 as a major component.

Table 3 Thermal analysis data of $MSO_3 \cdot xN_2H_4 \cdot yH_2O$ where M = Mn, Fe, Co, Ni, Zn

	Thermogravimetry				DTA	
Compound	Step No.	Temp. range, °C	weight loss, % obsd.	weight loss, % reqd.	Peak temp. °C	Reaction***
$MnSO_3 \cdot 2N_2H_4 \cdot 2H_2O$	1	120-158	15.00	15.32	158 (Endo)	$MnSO_3 \cdot 2N_2H_4 \cdot 2H_2O \rightarrow MnSO_3 \cdot 2N_2H_4$
	2	202-245	42.00	42.56	232.8 (Exo)	$MnSO_3 \cdot 2N_2H_4 \rightarrow MnSO_3$
$FeSO_3 \cdot 2N_2H_4 \cdot H_2O$*	1	130-142	38.00	37.60	135 (Exo)	$FeSO_3 \cdot 2N_2H_4 \cdot H_2O \rightarrow FeSO_3$
	2	190-198	50.00	46.80	190 (Exo)	$3FeSO_3 \rightarrow Fe_2O_3 + FeSO_4$
$CoSO_3 \cdot 2N_2H_4 \cdot H_2O$*	1	88-121	8.00	8.15	105 (Endo)	$CoSO_3 \cdot 2N_2H_4 \cdot H_2O \rightarrow CoSO_3 \cdot 2N_2H_4$
	2	150-156	39.00	37.11	151 (Exo)	$CoSO_3 \cdot 2N_2H_4 \rightarrow CoSO_3$
	3	156-220	56.00	55.22	190 (Exo)	$4CoSO_3 \rightarrow CoS_3O_4 + CoSO_4$
$NiSO_3 \cdot 3N_2H_4 \cdot H_2O$*	1	72-140	8.00	7.12	98 (Endo)	$NiSO_3 \cdot 3N_2H_4 \cdot H_2O^* \rightarrow NiSO_3 \cdot 3N_2H_4$
	2	164-215	45.00	45.11	182 (Exo)	$NiSO_3 \cdot 3N_2H_4 \rightarrow NiSO_3$
	3	365-325	55.00	54.76	276 (Exo)	$2NiSO_3 \rightarrow NiO + NiSO_4$
$ZnSO_3 \cdot 2N_2H_4 \cdot 1.5H_2O$*	1	115-155	23.5	24.95	145 (Endo)	$ZnSO_3 \cdot 2N_2H_4 \cdot 1.5H_2O \rightarrow ZnSO_3 \cdot N_2H_4$
	2	200-236	40.00	38.5	215 (Exo)	$ZnSO_3 \cdot N_2H_4 \rightarrow ZnSO_3$
	3	370-400	49.00	48.65	400 (Exo)	$2ZnSO_3 \rightarrow ZnS + ZnSO_4$
$CoSO_3 \cdot 1.5N_2H_4 \cdot H_2O$**	1	84-108	8.4	8.78	93 (Endo)	$CoSO_3 \cdot 1.5N_2H_4 \cdot H_2O \rightarrow$
	2	127-134	38	37.7	128 (Exo)	$CoSO_3 \cdot 1.5N_2H_4 \rightarrow CoSO_3$
	3	162-198	50		193 (Exo)	$CoSO_3 \rightarrow Co_3O_4 + CoSO_4$
$NiSO_3 \cdot 2N_2H_4 \cdot H_2O$**	1	130-176	7.8	8.15	148 (Endo)	$NiSO_3 \cdot 2N_2H_4 \cdot H_2O \rightarrow NiSO_3 \cdot 2N_2H_4$
	2	220-256	24.0	22.65	251 (Exo)	$NiSO_3 \cdot 2N_2H_4 \rightarrow NiSO_3$
	3	272	58.5		272 (Exo)	$NiSO_3 \rightarrow NiO + NiSO_4$

***Only solid residues on the product side are given

$CoSO_3 \cdot 1.5N_2H_4 \cdot H_2O$**

This is a yellow coloured complex which loses H_2O (8.4% loss) and N_2H_4 (38% loss) on heating, with weight loss in TG in the temperature ranges 84-108° and 127-134° respectively. The residue $CoSO_3$ so formed on further heating decomposes disproportionately to yield Co_3O_4 as a major component (together with traces of $CoSO_4$).

$NiSO_3 \cdot 3N_2H_4 \cdot H_2O$*

This complex which contains three N_2H_4 molecules is rose coloured. TG data indicates gradual loss of water starting below 100° (Fig 4). The weight loss is from 72-140°. Further decomposition occurs between 164-215° which is due to the loss of total hydrazine. Peaks at 98° (endo) and 182° (exo) are seen in the DTA. $NiSO_3$ is found to be stable upto 240°, subsequently decomposing into oxide (major) and sulfate similar [10] to hydrated $NiSO_3$.

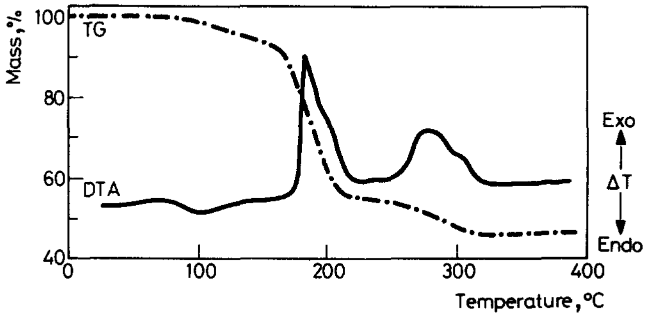

Fig. 4 TG and DTA $NiSO_3 \cdot 3N_2H_4 \cdot H_2O$

$NiSO_3 \cdot 2N_2H_4 \cdot H_2O$**

$NiSO_3 \cdot 2N_2H_4 \cdot H_2O$ is blue in colour and soluble in water. On addition of $N_2H_4 \cdot H_2O$ to its solution, it yields rose coloured complex which is identified as $NiSO_3 \cdot 3N_2H_4 \cdot H_2O$.

The relatively high decomposition temperature of this complex indicates its high stability in comparison to the other Ni-complex mentioned above. Thus it loses H_2O between 140-170° (7.8% loss in TG) followed by loss of N_2H_4 in the range 220-256° (24% loss in TG). DTA shows complementary peaks at 148° and 251°. Decomposition of $NiSO_3 \cdot N_2H_4$ follows immediately after the removal of N_2H_4 and exothermicity of decomposition of both N_2H_4 and $NiSO_3$ appears as one sharp exotherm (58.5% loss) with shoulder. The

X-ray diffraction pattern (Fig. 3) of the residue ~400° shows the presence of NiO [8].

$ZnSO_3 \cdot 2N_2H_4 \cdot 1.5H_2O$*

It is a colourless complex. It does not exhibit autocombustion and decomposition occurs above 100°. 23.5% weight loss in the range 115-155° indicates loss of total water. N_2H_4 decomposes between 200-236° with the weight loss of 40% observed in the TG. (Theor. 38.5%). Both these decomposition steps are seen in the DTA with endotherm at 145° and exotherm at 215°. $ZnSO_3$ so formed decomposes 368° exothermically to sulfide and sulfate.

Thus the total loss of water during decomposition occurs below 110° in the case of complexes of Fe, Co and Ni and exhibit autocatalytic decomposition. Whereas in contrast Zn and Mn complexes lose water around 145° and do not exhibit this property. Thus autocatalytic decomposition is due to loss of hydrated water at lower temperatures. Though disproportionation is observed in all the complexes, the combustion residues of all metal sulfite complexes are oxides. Which can be ascribed to very high heating rate together with exothermicity of hydrazine decomposition.

In metal sulfite hydrazine hydrate complexes, the temperatures at which the disproportionation occur are thus found to be relatively lower, which evidently suggests the presence of a strong metal - oxygen bond. Secondly, the detection of SO_2 gas as one of the products during the decomposition together with the fact that oxides are found to be the major residues, favours the presence of bonded sulfite group with a strong metal - oxygen bond.

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Zusammenfassung — Mittels chemischer Analyse, IR-Spektren, thermoanalytischen und Verbrennungsstudien wurden die Hydrazinhydrate der hergestellten Übergangsmetallsulfite $MSO_3 \cdot xN_2H_4 \cdot yH_2O$ mit M = Mn, Fe, Co, Ni und Zn beschrieben. Farbe sowie die Parameter x und y der Komplexe hängen von den Herstellungsbedingungen ab. Die thermische Zersetzung, bei der bei relativ niedrigen Temperaturen Metalloxide entstehen, ist von Metall zu Metall verschieden.