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THERMAL DECOMPOSITION OF COMPOUNDS CONTAINING THE HYDRAZINIUM CATION AS A LIGAND

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ABSTRACT

A thermal investigation of $M(N_2H_5)_2(SO_4)_2$, where M = Mn(II) or Co(II), has been carried out. On heating, the complexes become MSO_4 via an intermediate compound, $M(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$. The intermediate compound has been isolated and characterised by elemental analyses, IR spectra, diffuse reflectance spectra, magnetic and conductance data. The intermediate compound seems to possess pseudo-tetrahedral coordination where one SO_4 group is tetradentate and bonded with four different metal ions which are surrounded by HSO_4 groups and hydrazines bridging two metal ions The X-ray powder diffraction pattern of the intermediate derived from the cobalt(II) complex has been obtained and the *d*-values are reported. Activation energies (E^*) and enthalpy changes (ΔH) for each decomposition step have also been calculated. The probable mechanisms of decompositions are discussed

INTRODUCTION

Numerous metal hydrazine complexes are reported in the literature [1—4]. Hydrazinium metal complexes are also widely known [5—7]. Thermal investigations of these complexes are very scanty. Tsuchiya et al. [8] carried out some thermal investigations of Ni(II) halide hydrazine complexes and reported the intermediate bridge complexes formed on heating the unidentate hydrazine complex. Recently, some attention has been given to the mechanism of thermal decomposition of some hydrazinium salts [9—12], but the thermal investigation of complexes having the hydrazinium cation as ligand [13] has not yet been done. This paper describes the mechanism of thermal decomposition of $M(N_2H_5)_2(SO_4)_2$, where M = Mn(II) or Co(II). It reports the thermal stability, maximum decomposition temperature, activation energy and enthalpy change for each decomposition step, and also deals with the characterisation of the intermediate compound formed while heating.

EXPERIMENTAL

All the chemicals used were A.R. grade.

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Preparation of $M(N_2H_5)_2(SO_4)_2 \cdot n\,H_2O$*, where M = Mn(II) or Co(II),* n = *1 in Mn(II) and* n = *0 in Co(II)*

These were prepared in two ways. (1) An aqueous solution of hydrazine sulphate (2 mmole) was neutralised by drop-wise addition of dilute ammonia solution. This neutralised solution was mixed with MSO_4 (1 mmole) dissolved in water while stirring vigorously for a few minutes; a fine crystalline mass separated. The crystals were collected, washed several times with water and finally with ethanol, and then dried in a desiccator containing fused calcium chloride. (2) This procedure is almost identical with procedure (1). Here aqueous hydrazine sulphate solution instead of neutralized hydrazine sulphate solution was used. By this procedure, the complexes do not possess any water.

Thermal measurements

The thermal analysis was carried out using a MOM derivatograph. A constant flow of dry air was maintained. Platinum crucibles were used and the heating rate was 4°C min^{-1}. The particle size of the samples was within 150—200 mesh. The volume of the sample in each case was the same. Enthalpy changes (ΔH) were calculated from the DTA peak area using indium metal as calibrant. The activation energy was calculated from TG and DTA curves using the equations of Freeman and Carroll [14] and Borchardt and Daniel [15], respectively.

Elemental analyses

Elemental analyses were carried out in the microanalytical section of the Australian Mineral Development Laboratories as well as in the microanalytical laboratory of our institute.

Spectral measurements

Infrared spectra (KBr disk, 4000—400 cm^{-1}) and diffuse reflectance spectra (visible range) were recorded using a Beckman IR spectrophotometer, model IR-20A, and a Cary 17D spectrophotometer, respectively.

Magnetic measurement and conductivity data

Magnetic moments of the compounds were evaluated at room temperature from the magnetic susceptibilities of the samples, corrected by applying Pascal's constants of the elements involved, using the Guoy technique where $Hg[Co(SCN)_4]$ was taken as standard. Conductivity data were obtained using a Philips conductivity bridge.

X-Ray powder diffraction

X-Ray powder diffraction patterns of the compounds were obtained on a Philips powder diagram camera, using CoK_α radiation.

RESULTS

$Mn(N_2H_5)_2(SO_4)_2 \cdot H_2O$ prepared by procedure (1) loses its molecule of water in a single step (Fig. 1). The dehydrated compound decomposes to manganous sulphate via an intermediate compound (I_1; Table 1). The manganous complex prepared by procedure (2) does not contain any water. The pattern of decomposition of this compound differs little from the previous one, as shown in Fig. 1, and it appears from Table 1 that the starting temperature of decomposition of the anhydrous as well as the intermediate compound is lower than that of the decomposition of the complex derived by procedure (1). The DTA curve shows a sharp exotherm for the formation of an intermediate compound. On the other hand, the DTA curve exhibits no notable drift of the curves from the baseline for the decomposition of the intermediate compound to metal sulphate. In the case of the cobalt(II) complex, unlike the manganese(II) complex, both the preparation procedures produce complexes similar in composition. The nature of the thermal curves (Fig. 1) of cobalt(II) complexes is identical to that of manganese(II) com-

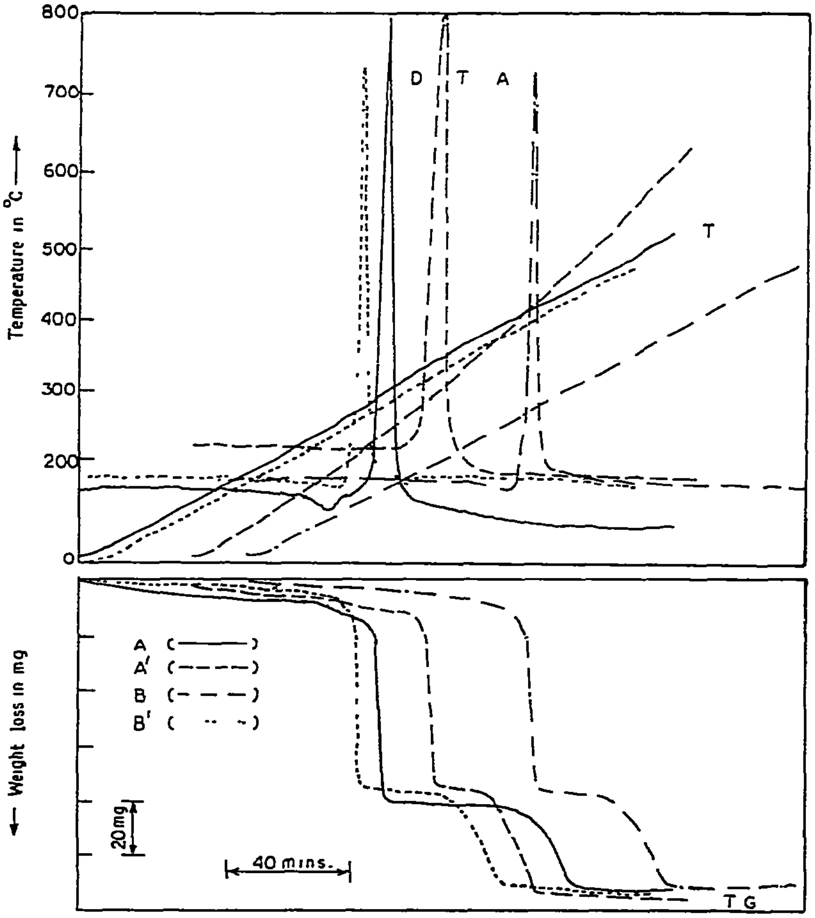


Fig. 1. Thermal curves of $Mn(N_2H_5)_2(SO_4)_2 \cdot H_2O$ (A) prepared by procedure (1); $(Mn(N_2H_5)_2(SO_4)_2$ (A') prepared by procedure (2); $Co(N_2H_5)_2(SO_4)_2$ (B) prepared by procedure (1); and $Co(N_2H_5)_2(SO_4)_2$ (B') prepared by procedure (2).

TABLE 1

Thermal parameters of decomposition of the complexes containing hydrazinium cation as ligand and their intermediate compounds

Decomposition reactions	Temp. range (°C)	DTA peak temp. (°C)	Activation energy (E^*) (kJ mole^{-1})		Enthalpy change (ΔH) (kJ mole^{-1})
			DTA	TG	
(Ia) $Mn(N_2H_5)_2(SO_4)_2 \cdot H_2O$ [a] $\rightarrow Mn(N_2H_5)_2(SO_4)_2$	235—260	256	c	c	d
(Ib) $Mn(N_2H_5)_2(SO_4)_2 \rightarrow Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	275—300	295	386.40	c	137.34
(Ic) $Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \rightarrow MnSO_4$	358—415	e	c	483.0	d
(IIa) $Mn(N_2H_5)_2(SO_4)_2$ [b] $\rightarrow Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	250—285	280	359.10	c	132.25
(IIb) $Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \rightarrow MnSO_4$	350—390	e	c	478.80	d
(IIIa) $Co(N_2H_5)_2(SO_4)_2$ [a] $\rightarrow Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	240—280	275	223.69	c	60.90
(IIIb) $Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \rightarrow CoSO_4$	320—380	e	c	313.95	d
(IVa) $Co(N_2H_5)_2(SO_4)_2$ [b] $\rightarrow Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	230—275	270	211.30	c	50.82
(IVb) $Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \rightarrow CoSO_4$	315—410	e	c	307.44	d

[a] Prepared by procedure (1).

[b] Prepared by procedure (2).

[c] E^* could not be evaluated.

[d] ΔH could not be evaluated.

[e] DTA peak temperature could not be evaluated

TABLE 2

Analytical (calculated values in parentheses) magnetic and conductance data obtained from the complexes containing hydrazinium cation as ligand and their intermediate compounds

Compound	Colour	Analysis %			$\mu_{eff.}$ (BM)	Λ (mho cm^2 mole^{-1})
		N	S	Metal		
$Mn(N_2H_5)_2(SO_4)_2 \cdot H_2O$ a	White	16.41 (16.92)	20.62 (19.33)	16.10 (16.60)	5.91	367
$Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	White	6.60 (6.48)	22.45 (22.22)	24.88 (25.44)	6.01	267
$Mn(N_2H_5)_2(SO_4)_2$ b	White	17.59 (17.89)	21.01 (20.45)	17.08 (17.50)	5.80	340
$Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	White	6.38 (6.48)	22.50 (22.22)	24.80 (25.44)	6.11	270
$Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \cdot 2\ H_2O$	White	5.35 (5.55)	18.43 (19.05)	21.10 (21.80)	5.95	
$Co(N_2H_5)_2(SO_4)_2$ ^{a}	Pink	17.16 (17.66)	20.07 (20.19)	18.10 (18.60)	4.70	255
$Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	Grey	6.37 (6.36)	22.37 (21.82)	26.85 (26.79)	5.25	219
$Co(N_2H_5)_2(SO_4)_2$ ^{b}	Pink	18.01 (17.66)	20.12 (20.19)	18.15 (18.60)	4.75	250
$Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	Grey	6.02 (6.36)	22.13 (21.82)	26.82 (26.79)	5.22	225
$Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \cdot 2\ H_2O$	Pink	5.29 (5.47)	19.12 (18.75)	22.30 (23.20)	4.81	

[a] Prepared by procedure (1).
[b] Prepared by procedure (2).

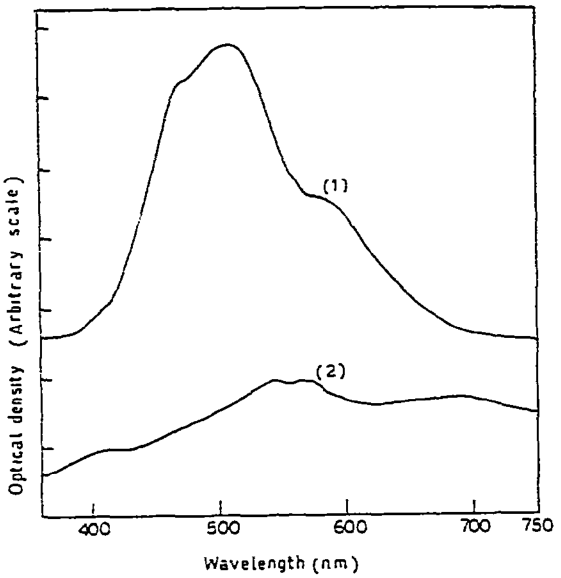


Fig. 2. Diffuse reflectance spectra of $Co(N_2H_5)_2(SO_4)_2$ (1) and $Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$ (2).

plexes. The temperature ranges, DTA peak temperatures, values of enthalpy changes and activation energies for each decomposition step are shown in Table 1. Both the intermediate compounds (I_1 and I_2) are highly soluble in water. Molar conductances of complexes and their intermediate compounds are shown in Table 2. Magnetic data of complexes as well as intermediate compounds are also tabulated in Table 2. Reflectance spectra (in the visible range) of the cobalt(II) complex and its intermediate compound (I_2) are shown in Fig. 2. Infrared data of both the complexes and the intermediate compounds (I_1 and I_2) are shown in Table 3. The derived intermediate compounds separate as shining, transparent crystals [colourless for Mn(II) and pink for Co(II)] from a water—ethanol mixture on long standing. The composition of I_1 and I_2 changes to $M(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \cdot 2\ H_2O$. The intermediate ($I_2$) derived from the cobalt complex is dark grey in colour but changes to pink in water. Magnetic data of both the hydrated intermediate compounds are given in Table 2. Infrared data of the hydrated intermediate compounds are also shown in Table 3. *d*-Values of $Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$ are shown in Table 4. *d*-Values of the corresponding manganese(II) compound could not be recorded because of the non-availability of proper radiation. Analytical data of the complexes and their intermediate compounds are given in Table 2.

DISCUSSION

It is noted in Fig. 1 that the thermal curves are dependent on the prepara-

TABLE 3

Infrared spectral data (cm^{-1}) of the complexes containing hydrazinium cation as ligand and their intermediate compounds

Compound	$\nu(NH_2)/\nu(NH_3^+)$	βNH_2	$\nu_3(SO_4^{2-})$ + (N—H) wagging	ν(N—H)	$\nu_4(SO_4^{2-})$ + (N—H) deformation
$Mn(N_2H_5)_2(SO_4)_2$	3290—2650 vs,br	1500 s, 1310 m	1180—1050 vbr	1005 m	640—570 vs,br
$Co(N_2H_5)_2(SO_4)_2$	3300—2600 vs,br	1505 s, 1330 m	1200—1020 vbr	995 m	580—630 vs,br
$Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	3300—3050 vs,br	1425 vs	1130 vs, 1080 s	1035 m	645 s, 625 s, 600 s
$Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$	3300—3050 vs,br	1420 vs	1145 s, 1095 s	1030 (sh)	640 s, 625 s, 600 s
$Mn(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$ $2 H_2O$	3400 (sh), 3200—3050 vs,br	1630 [a] m, 1400 vs	1170 vs, 1110 vs	1050 s	645 s, 620 s, 600 s
$Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \cdot 2 H_2O$	3400—3100 vs,br	1640 [a] m, 1400 s	1145 vs, 1100 vs	1040 (sh)	650 s, 630 s, 610 m

ν = stretching, β = bending, vs = very strong, br = broad, s = strong, m = medium, (sh) = shoulder.

[a] (HOH) bending

TABLE 4

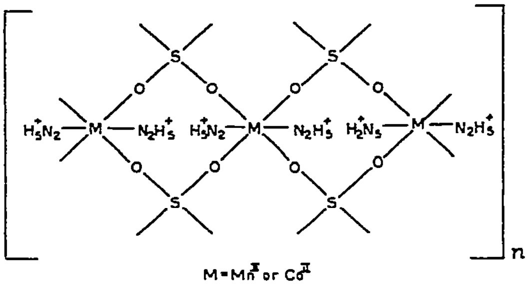
X-Ray diffraction data of $Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$ [I_2]

d_{hkl} (Å)	I/I_0 (~)	d_{hkl} (Å)	I/I_0 (~)
4 170	80.0	2.499	50.0
3 728	60 0	2.221	35.0
3.377	100.0	2.001	25.0
3.016	80.0	1.895	30.0
2 815	40.0	1.768	30.0

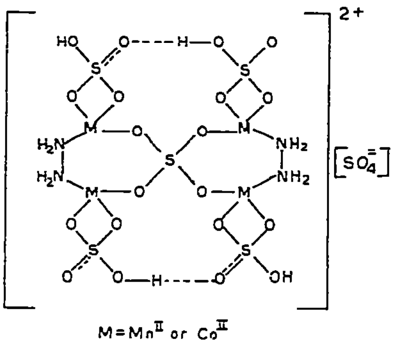
tion procedure of the complexes. On the other hand, no remarkable distinction is observed in the IR spectra, diffuse reflection spectra and magnetic moments of the complexes prepared in two different ways. The manganese(II) complex isolated by procedure (1) contains one molecule of water which was not observed by Nieuwpoort and Reedijk [13]. Initially, we thought that the $M(N_2H_5)_2(SO_4)_2$ complex would generate $H_2M(SO_4)_2$ as an intermediate compound [16] transforming to MSO_4 upon heating. In practice repeated elemental analysis of the intermediate compounds corroborates $M(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$ (Table 2). The weight loss also corroborates the derived composition.

Identification of intermediate compounds

The reported absorption bands in Table 3 are attributed to the vibrations of $N_2H_5^+$ and the SO_4^{2-} species in the complexes and their intermediate compounds on the basis of the work of Nieuwpoort and Reedijk [13] on hydrazinium complexes. The vibrations in the cobalt(II) and manganese(II) complexes are similar to the reported vibrations of the same salts by Nieuwpoort and Reedijk [13]. The loss of symmetry due to the coordination of SO_4 groups to the metal ion structure (1) as evident from the study of Prout et al. [5,6] should be clearly visualised in the IR spectra of the complexes, but the very broad band at 1100 cm^{-1} is possibly due to the overlap of wagging of (N—H), ν(N—N) and $\nu_3(SO_4^{2-})$ vibrations. The broad band at ~600 cm^{-1} may be due to the (N—H) deformation in NH_3^+ and $\nu_4(SO_4^{2-})$. Another broad band centred at 3000 cm^{-1} and the absence of extension of this broadness up to ~2600 cm^{-1}, which is exhibited in the complexes, indicate the absence of the $N_2H_5^+$ group in the intermediate compound. The splitting of the broad band at ~1100 cm^{-1} in the intermediate compound may be due to the presence of the coordinated SO_4 groups existing in different ways, which cause a greater loss of symmetry of the SO_4 groups in the compound. Similarly, a rather complex line pattern of at least three lines at ~600 cm^{-1} in the intermediate compounds may be due to $\nu_4(SO_4)$ and (N—H) deformation vibrations [13]. A medium intensity band at ~995 cm^{-1} which may be ascribed to (N—N) stretching [13] in the complex is found to shift to higher energy by about 35 cm^{-1} for I_1 and I_2. It is shown in the literature [2,17] that ν(N—N) shifts to a higher wavenumber if hydrazine behaves as a bidentate chelate bridging two metals. On the basis of this, it is presumed that hydra-



(1)



(2)

Fig. 3. Structures of $M(N_2H_5)_2(SO_4)_2$ (1) and $M(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}$ (2).

zine acts as a bidentate chelate bridging two metal ions in the intermediates. Also, the bands at ~1500 cm^{-1} and ~1320 cm^{-1} in the complex are evidently due to (N—H) bending [13]. These two bands collapse to a single band at ~1420 cm^{-1}, which is tentatively attributed to the bending mode of vibrations of two NH_2 groups which are coordinated and symmetrically the same. Thus IR spectra support the coordination of the bonding sites as shown in structure (2) for the intermediate compound in Fig. 3.

The observed diffused reflectance spectrum of $Co(N_2H_5)_2(SO_4)_2$ is in good agreement with a basically octahedral geometry around [13] the metal ion, while in the case of $Co(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5}(I_2)$ the spectrum closely resembles the pseudo-tetrahedral solid state reflectance spectrum of a complex [18] having the same chromophore.

The magnetic moments of the hydrazinium complexes signify octahedral geometry, but those of the intermediate compounds appear high and it is difficult to comment on the high mangetic moment of the pseudo-tetrahedral complex as evident from reflectance spectra. The high conductance value of the manganese(II) compound in water indicates that it exists as a double salt in water rather than as a complex, which is expected in the case of the cobalt(II) compound as evident from its 1 : 2 electrolytic behaviour in water. Intermediate compounds (I_1 and I_2) in water clearly indicate 1 : 2 electrolytes. To satisfy all the physical data available so far, the intermediate compound is presumed to exist as structure (2) in which one SO_4 group is coordinated to four different metal ions, and four bisulphate groups acting as bidentate chelates are coordinated to four different metal ions and the two hydrazine units are bridging two metal ions. Moreover, the aqueous solution of the intermediate compounds is neutral which indicates that the bisulphate groups are strongly hydrogen bonded (Fig. 3).

Reaction of the intermediate compound

Since the intermediate compound (I_2) exhibits octahedral geometry in water, as evident from its pink colour, its solution spectra and magnetic moment, it is clear that two water molecules are coordinated to the metal ion satisfying the octahedral geometry. The IR spectra of hydrated intermediate compounds show a close similarity with the IR spectra of thermally obtained intermediate compounds and the exhibited differences are due to the coordinated water molecule.

If the hydrated intermediate of cobalt(II) is heated, a grey intermediate product develops. This phenomenon supports the formation of the hydrated intermediate compound. The existence of this hydrated intermediate compound also supports structure (2) proposed for the dehydrated intermediate compounds.

MECHANISM

From the foregoing results and discussions, the probable mechanism of decomposition may be as follows

$$Mn(N_2H_5)_2(SO_4)_2 \cdot H_2O \rightarrow Mn(N_2H_5)_2(SO_4)_2$$

$$\left.\begin{array}{l} 4\ M(N_2H_5)_2(SO_4)_2 \rightarrow 2(N_2H_5)_2SO_4\uparrow + 2\ N_2H_4\uparrow \\ \quad + 4\ M(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \\ 4\ M(N_2H_4)_{0.5}(HSO_4)(SO_4)_{0.5} \rightarrow 4\ MSO_4 + 2\ N_2H_4\uparrow + 2\ H_2SO_4 \end{array}\right\} \begin{array}{l} M = Mn(II) \\ \text{or } Co(II) \end{array}$$

The first decomposition step may take place in two ways.

(1) A proton of the hydrazinium ion coordinated to the metal ion bonds with the oxygen of the SO_4 group and this accelerates breakage of the M—O bond. This phenomenon continues while two SO_4 groups become highly activated for the collisions between them, and this promotes the liberation of the SO_4 group; hydrazine is bridged between two metal ions in parallel. While liberating the SO_4 group as H_2SO_4 from the system, the hydrazinium ion acting as a unidentate ligand cannot exist in the activated state. Consequently, the hydrazinium ion is evolved as hydrazine along with H_2SO_4.

(2) At the time of decomposition, it may also be expected that the eight protons attached to the hydrazinium ion become bound to the oxygen of the SO_4 groups while the two hydrazines are evolved and four hydrazines form a compound with two H_2SO_4 molecules; these two moieties evolve simultaneously, as evident from the sharp DTA curve. At the same time, the remaining two hydrazine molecules are bridged between two metal ions. Because of the sharp DTA profile it is difficult to infer exactly which pathway is predominant. However, either of the two ways may facilitate the for-

mation of structure (2) from structure (1) given in Fig. 3.

The second decomposition step may also take place in two ways.

(1) The hydrazine moiety bridging two metal ions is liberated from the system. During liberation of the hydrazines the four M—O bonds formed from four oxygens of a SO_4 group bound to four metal ions break. Consequently, simultaneous liberation of two molecules of hydrazine and H_2SO_4 takes place from the intermediate compound.

(2) Alternatively, the M—O bond formed from the centred SO_4 group first becomes ruptured, followed by breakage of the M—N bond. As a result, liberation of hydrazines along with H_2SO_4 occurs.

Elimination of the hydrazine moiety from the complex is an exothermic process, while elimination of sulphuric acid is endothermic. The given mechanisms imply that exo- and endo-processes are going on in parallel in both decomposition steps. In the first step, elimination of the hydrazine moiety (in mole) is exceedingly high in comparison with the elimination of sulphuric acid (in mole), which accounts for the formation of the sharp DTA peak; whereas in the second decomposition step, elimination of both hydrazine and sulphuric acid is proportionate. As a result, the drift in the DTA baseline is negligible due to the counter-action of exo- and endo- run in parallel. Because of the similar nature of the decomposition of the complexes, manganese(II) and cobalt(II) complexes should have very similar values of activation energy as well as enthalpy change. However, in practice, wide differences in the values of thermal parameters (ΔH and E^*) of the two complexes are exhibited (Table 1).

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