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THERMAL STUDIES OF Mn(II) HYDRAZINE COMPLEXES IN THE SOLID STATE

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ABSTRACT

Several $MnL_nX_2 \cdot m\ H_2O$ complexes, where $L = N_2H_4$; $n = 2, 1.5, 1$; $X = Cl^-, Br^-, \frac{1}{2} SO_4^{2-}$; and $m = 0$ or 1, have been synthesised from solution and their thermal investigations carried out. The decomposition of these complexes has been found to occur through the formation of thermally stable as well as unstable complex species. Several MnL_nX_2 complexes, where $n = 1, 0.66, 0.5$; and $X = Cl^-, \frac{1}{2} SO_4^{2-}$, have been synthesised in the solid state by thermolysis of Mn(II) complexes of hydrazine obtained from solution. All the hydrazine complexes of Mn(II) have been characterised by elemental analyses, and magnetic and IR data.

INTRODUCTION

Hydrazine complexes of Mn(II) are known in the literature [1–3]. Thermal investigation of hydrazine complexes of Mn(II) is, however, scanty [3]. We have already reported a thermal investigation of a Mn(II) complex having the hydrazinium cation as ligand [4]. We have also carried out thermal investigations of Co(II) [5] and Ni(II) [6] complexes of hydrazine and found some unusual thermal behaviours. These studies led us to investigate the Mn(II) complexes of hydrazine. This paper reports the synthesis of Mn(II) chloride, bromide and sulfate complexes of hydrazine together with their thermal investigations.

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EXPERIMENTAL

Preparation of Mn(II) hydrazine (L) complexes

$[MnL_{1.5}Cl_2]$ (1). Hydrazine hydrate (80%) (2 mmole *) was added to the concentrated aqueous solution of $MnCl_2$ (1 mmole). While stirring, fine white crystals of complex (1) separated out slowly. The crystals were filtered, washed thoroughly with water–ethanol (1 : 9) and finally with dry ethanol.

$[MnL_2Cl_2]$ (2). Hydrazine hydrate (2 mmole) was added dropwise with constant stirring to the $MnCl_2$ (1 mmole) solution in ammoniacal medium. Fine white crystals of complex (2) separated out. The crystals were collected and washed in the same way as complex (1).

$[MnL_{0.5}Cl_2]$ (1A). This complex was prepared by pyrolysis of $[MnL_{1.5}Cl_2]$ (1) at ~ 300°C in a nitrogen atmosphere.

$[MnL_{0.66}Cl_2]$ (2A). This complex was synthesised by pyrolysis of $[MnL_2Cl_2]$ (2) at ~ 280°C in a nitrogen atmosphere.

$[MnL_2Br_2]$ (3). This complex was prepared by the procedure corresponding to the preparation of complex (1). Here, 2 mmole hydrazine hydrate were used.

$[MnL_2Br_2]$ (4). This complex was prepared by the procedure corresponding to the preparation of complex (2).

$[MnL_{1.5}SO_4] \cdot H_2O$ (5). This complex was synthesised by the procedure corresponding to the preparation of the complex (1). Here, 2 mmole of hydrazine hydrate were used.

$[MnLSO_4 \cdot H_2O]$ (6). This complex was prepared by the procedure corresponding to the preparation of complex (2).

$[MnLSO_4]$ (5A). This was obtained from $[MnL_{1.5}SO_4] \cdot H_2O$ (5) by the temperature arrest technique at ~ 190°C in a nitrogen atmosphere.

$[MnLSO_4]$ (6A). This complex was obtained from $[MnLSO_4 \cdot H_2O]$ (6) by a pyrolytic technique at ~ 180°C in a nitrogen atmosphere.

Thermal measurements

Thermal analysis was carried out using a thermal analyzer (Shimadzu, Model DT-30, Japan). A constant flow of dry nitrogen (30 ml min^{-1}) was maintained. Platinum crucibles were used. The heating rate was maintained at 5°C min^{-1}. The particle size of the sample was within 150–200 mesh. Aluminum oxide was used as a reference.

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* Excess hydrazine hydrate does not alter the composition.

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}) were recorded using a Beckman infrared spectrophotometer, model IR-20A.

Magnetic measurements

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 Gouy technique where $Hg[Co(SCN)_4]$ was taken as standard.

RESULTS

The thermal curves of $[MnL_{1.5}Cl_2]$ (1) and $[MnL_2Cl_2]$ (2) are shown in Fig. 1. The TG curve shows that $MnL_{1.5}Cl_2$ transforms to an isolable $[MnL_{0.5}Cl_2]$ (1A) at 300°C. The derived species (1A), on further heating, transforms to the metal chloride at 440°C. The corresponding DTA curve shows that formation of $[MnL_{0.5}Cl_2]$ as well as decomposition of complex (1A) to $MnCl_2$ appear to take place in two steps.

The TG curve of $[MnL_2Cl_2]$ (2) shows that it transforms to an isolable $[MnL_{0.66}Cl_2]$ (2A) at 280°C. The derived species (2A), on further heating, transforms to the metal chloride at 430°C. The corresponding DTA curve indicates that the formation of complex (2A) from complex (2) takes place in two steps but transformation of complex (2A) to the metal chloride occurs in one step.

The TG curve of $[MnL_2Br_2]$ (3) (Fig. 2) shows that it transforms to the metal bromide through a non-isolable intermediate, $MnL_{0.5}Br_2$. The DTA curve shows that $MnL_{0.5}Br_2$ formation takes place in a single step and its decomposition to the metal bromide takes place in two steps.

The TG curve of $[MnL_2Br_2]$ (4) (Fig. 2) shows that it transforms to $MnBr_2$ at 400°C through the formation of a non-isolable intermediate, $MnL_{1.5}Br_2$. But the corresponding DTA curve shows that formation of $MnL_{1.5}Br_2$ takes place in a single step and its decomposition to the metal bromide takes place in three steps.

The TG curve of $[MnL_{1.5}SO_4]\cdot H_2O$ (5) (Fig. 3) shows that it first becomes anhydrous and then transforms to an isolable $[MnLSO_4]$ (5A). The

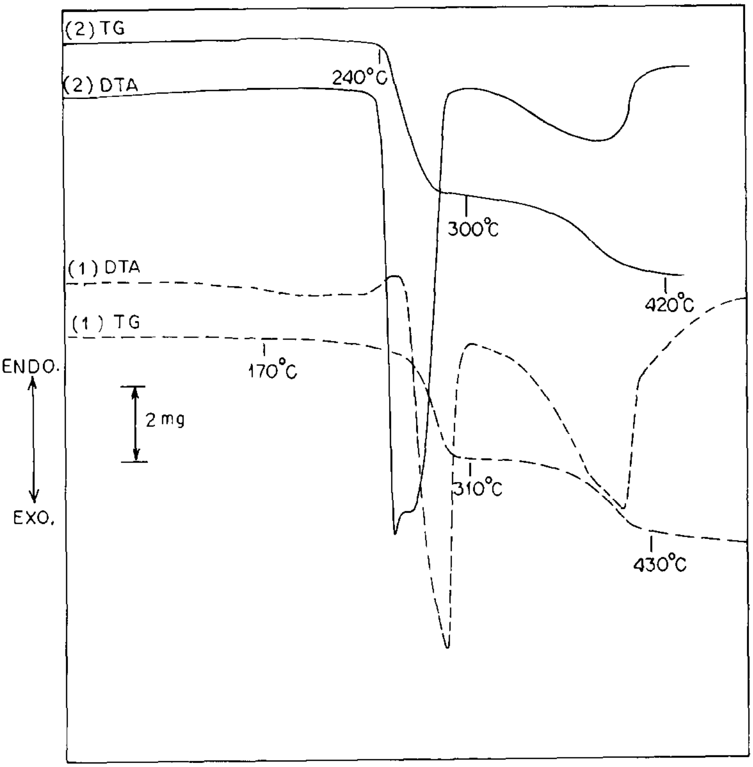

Fig. 1. Thermal curves of $[MnL_{1.5}Cl_2]$ (1) and $[MnL_2Cl_2]$ (2). Sample mass: complex (1), 17.68 mg; complex (2), 19.26 mg.

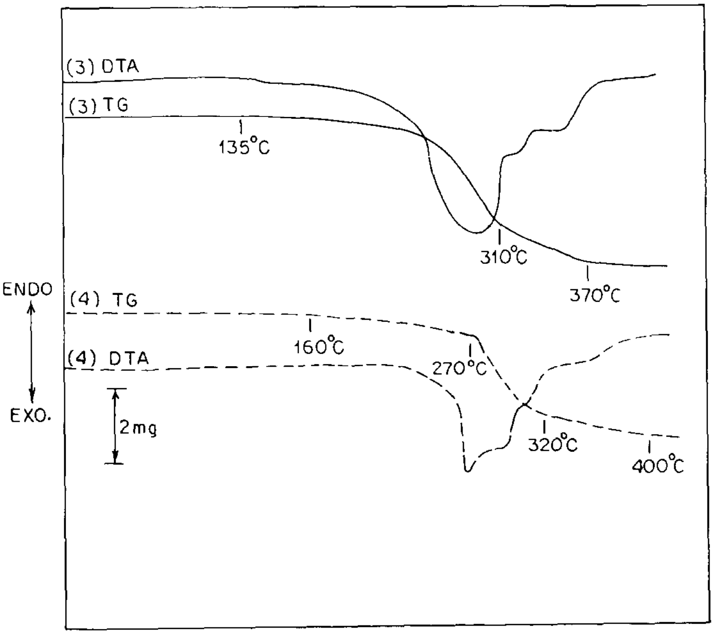

Fig. 2. Thermal curves of $[MnL_2Br_2]$ (3) and $[MnL_2Br_2]$ (4). Sample mass: complex (3), 19.73 mg; complex (4), 15.28 mg.

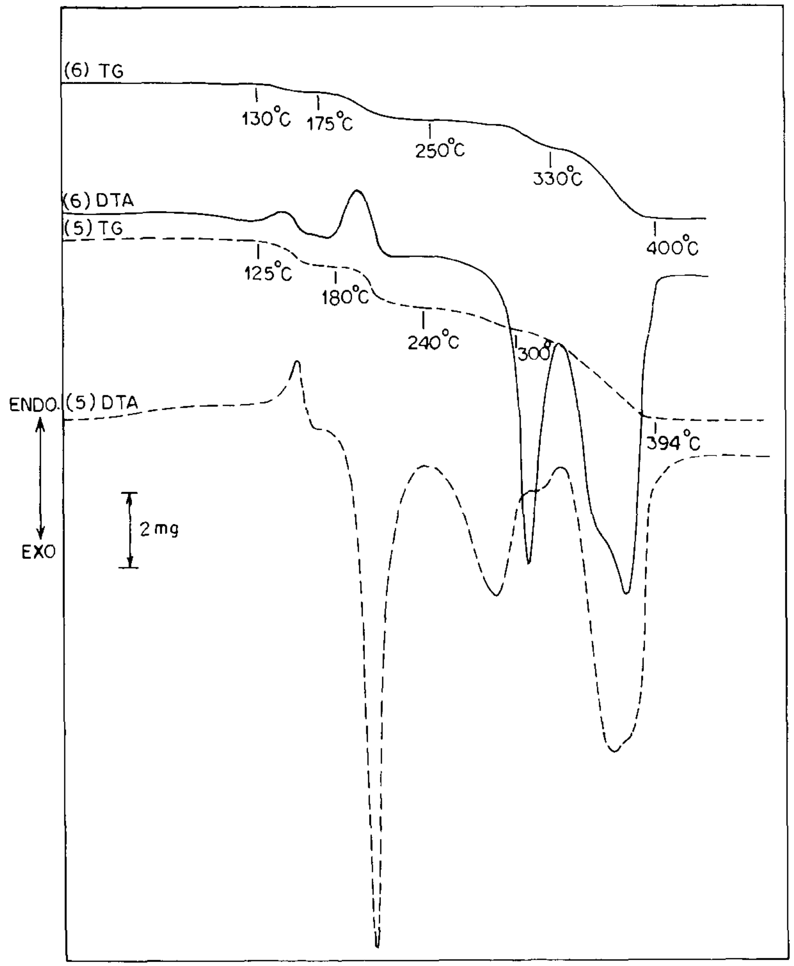

Fig. 3. Thermal curves of $[MnL_{1.5}SO_4]\cdot H_2O$ (5) and $[MnLSO_4\cdot H_2O]$ (6). Sample mass: complex (5), 18.81 mg; complex (6), 14.15 mg.

derived $[MnLSO_4]$ (5A), on further heating, transforms to the metal sulfate at ~ 394°C through the formation of a non-isolable intermediate, $MnL_{0.8}SO_4$. The corresponding DTA curve shows that the formation of $MnL_{0.8}SO_4$ from $[MnLSO_4]$ takes place in two steps and its decomposition to the metal sulfate also takes place in two steps.

The TG curve of $[MnLSO_4\cdot H_2O]$ (6) (Fig. 3) shows that it transforms to an isolable $[MnLSO_4]$ (6A) at 225°C through the formation of an isolable intermediate, $MnLSO_4\cdot 0.8\ H_2O$. On further heating, the derived species (6A) gives $MnL_{0.75}SO_4$ at 347°C and instantaneously transforms to the metal sulfate at 395°C. The DTA curve indicates that the decomposition of $MnL_{0.75}SO_4$ to the metal sulfate takes place in two steps.

Table 1 shows the thermal decomposition reaction scheme in detail along

TABLE 1

Thermal parameters of decomposition of Mn(II) hydrazine complexes

Decomposition reactions [a]	Temp. range (°C)	DTA peak temp. (°C)
$[MnL_{1.5}Cl_2]$ (1) → $[MnL_{0.5}Cl_2]$	170–300	260, 297
$[MnL_{0.5}Cl_2]$ → $MnCl_2$	340–440	396, 415
$[MnL_2Cl_2]$ (2) → $[MnL_{0.66}Cl_2]$	245–280	253, 265
$[MnL_{0.66}Cl_2]$ → $MnCl_2$	303–430	385
$[MnL_2Br_2]$ (3) → $MnL_{0.5}Br_2$	135–297	293
$MnL_{0.5}Br_2$ → $MnBr_2$	297–375	320,355
$[MnL_2Br_2]$ (4) → $MnL_{1.5}Br_2$	165–270	270
$MnL_{1.5}Br_2$ → $MnBr_2$	270–400	306, 317, 360
$[MnL_{1.5}SO_4]\cdot H_2O$ (5) → $MnL_{1.5}SO_4$	120–160	150
$MnL_{1.5}SO_4$ → $[MnLSO_4]$	190–235	208
$[MnLSO_4]$ → $MnL_{0.8}SO_4$	260–296	288, 296
$MnL_{0.8}SO_4$ → $MnSO_4$	296–394	363, 375
$[MnLSO_4\cdot H_2O]$(6) → $MnLSO_4\cdot 0.8\ H_2O$	130–158	145
$MnLSO_4\cdot 0.8\ H_2O$ → $MnLSO_4$	180–225	200
$[MnLSO_4]$ → $MnL_{0.75}SO_4$	283–347	320
$MnL_{0.75}SO_4$ → $MnSO_4$	347–395	360, 380

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[a] Hydrazine = L.

TABLE 2

Analytical and magnetic data of Mn(II) hydrazine complexes

Compounds [c]	Analyses (%) [a]			Magnetic moment, μ_{eff} (B.M.)
	Metal	Nitrogen	Halogen	
$[MnL_{1.5}Cl_2]$ (1)	30.64 (30.70)	23.44 (23.47)	39.62 (39.67)	6.17
$[MnL_2Cl_2]$ (2)	28.88 (28.92)	29.40 (29.48)	37.34 (37.38)	6.08
$[MnL_2Br_2]$ (3)	19.68 (19.71)	20.12 (20.09)	57.31 (57.36)	6.29
$[MnL_2Br_2]$ (4)	19.68 (19.71)	20.01 (20.09)	57.33 (57.36)	6.65
$[MnL_{1.5}SO_4]\cdot H_2O$ (5)	25.30 (25.32)	19.31 (19.36)	14.72 (14.75) [b]	6.68
$[MnLSO_4\cdot H_2O]$ (6)	27.30 (27.34)	13.89 (13.93)	15.90 (15.92) [b]	6.20
$[MnL_{0.5}Cl_2]$ (1A)	38.67 (38.70)	9.81 (9.86)	50.19 (50.02)	6.30
$[MnL_{0.66}Cl_2]$ (2A)	37.30 (37.35)	12.50 (12.56)	48.28 (48.27)	6.33
$[MnLSO_4]$ (5A)	30.10 (30.03)	15.25 (15.30)	17.48 (17.49) [b]	6.38
$[MnLSO_4]$ (6A)	30.11 (30.03)	15.24 (15.30)	17.44 (17.49) [b]	6.31

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[a] Calculated values in parentheses.

[b] Denotes sulfur.

[c] Hydrazine = L.

with the temperature range and DTA peak temperature for each step of the decomposition. Table 2 shows the analytical data of the hydrazine complexes and intermediate hydrazine complex species isolated by the temperature arrest technique along with their magnetic data. IR spectral data of all the hydrazine complexes are shown in Table 3.

DISCUSSION

The complexes derived from $MnCl_2$ and hydrazine hydrate

Treatment of a saturated aqueous $MnCl_2$ solution with hydrazine hydrate results in $[MnL_{1.5}Cl_2]$ (1) while treatment of $MnCl_2$ in ammoniacal medium with hydrazine hydrate generates $[MnL_2Cl_2]$ (2). Both complexes are perfectly white in color and show practically no difference in their magnetic values. The presence of a ν(N–N) band (Table 3) at ~ 960 cm^{-1} shows the bridging character [7,8] of hydrazine in both the complexes. These two complexes show a broad band at 1150 cm^{-1}, which is probably due to an NH_2 twisting mode of vibration. In complex (2), $\nu(NH_2)$ bands appear broad in comparison with that of complex (1). These observations indicate that hydrogen bonding occurs to a greater extent in complex (2) than in complex (1). According to the composition and preferential stereochemistry of the complexes, it is reasonable to expect that the chloride ligand probably acts as a bridging bidentate ligand in complex (1) and is unidentate in complex (2).

The complexes $[MnL_{0.5}Cl_2]$ (1A) and $[MnL_{0.66}Cl_2]$ (2A), which were derived pyrolytically from (1) and (2), respectively, are hygroscopic. Both the species show bridging character of hydrazine. The broad band at ~ 1150 cm^{-1} observed in complexes (1) and (2) is split in both (1A) and (2A). This is probably due to the lack of hydrogen bonding of the NH_2 hydrogens of the intermediates. It is observed that on transformation of complex (1) → (1A) as well as (2) → (2A), the magnetic moment increases slightly (Table 2): this is probably due to a lowering of symmetry. Considering the composition and the preferential stereochemistry of the Mn(II) ion, it is possible that the chloride ligands in (1A) and (2A) are bridging.

The complexes derived from $MnBr_2$ and hydrazine hydrate

Treatment of hydrazine hydrate with the concentrated aqueous solution of $MnBr_2$ affords $[MnL_2Br_2]$ (3), whilst treatment of hydrazine hydrate with $MnBr_2$ in ammoniacal medium results in $[MnL_2Br_2]$ (4). Both the species are identical in color. IR spectra show the bridging character of hydrazine in both complexes. But the thermal profile of complex (3) differs from complex (4) as shown in Fig. 2. Such differences are probably due to the loss of

TABLE 3

Infrared spectral data (cm^{-1}) of hydrazine complexes of Mn(II)

Compounds	ν NH$_2$	β NH$_2$	ρ_w NH$_2$	NH$_2$-twisting	ν(N–N)	ρ_r NH$_2$
[MnL$_{1.5}$Cl$_2$] (1)	3280vs	1595vs	1336m	1145vs, br	948s	590(sh)
	3220s	1562s	1290m			568m
	3138w					490s, br
[MnL$_2$Cl$_2$] (2)	3285vs, br	1675s	1350m	1162vs, br	962s	595(sh), 580m
	3220m	1608vs	1305m			560(sh), 500s, br
	3140w	1560s				
[MnL$_2$Br$_2$] (3)	3260vs	1592vs	1335m	1145s, br	948s	570m
	3210s	1562s	1295m			500m, br
	3138w	1550(sh)				
[MnL$_2$Br$_2$] (4)	3270s	1610s	1301w	1172w	955m	585m, 560(sh)
	3220m	1580m	1340w	1158vs		505m, br
[MnL$_{1.5}$SO$_4$]·H$_2$O [d] (5)	3480(sh) [a]	1630s [b]	1370w, br	1110s, [c]	990w	595w
	3370s	1580s, br	1295vw			580m
	3320vs					520w, br
	3180w					482m, br

$[MnLSO_4 \cdot H_2O]$[g] (6)	3400(sh)[a]	1625m[b]	1295w	1110s, vbr[c]	995(sh)	600w
	3330s	1585s, br				595m
	3310(sh)					520w, br
	3280s					490m, br
	3200m					
$[MnL_{0.5}Cl_2]$ (1A)	3270m	1605s	1340w	1170(sh)	960(sh)	560w, br
	3220(sh)	1572m	1302w	1152s	952m	505w, br
$[MnL_{0.66}Cl_2]$ (2A)	3260m	1605s	1342w	1175(sh)	960(sh)	570w, br
	3215(sh)	1570m	1300w	1160s	952m	510w, br
$[MnLSO_4]$[e] (5A)	3302vs, 3250s,	1625m[b]	1300(sh)	1115s, vbr[c]	990w	600w, 585m,
	3170w	1575m, br				520w, 490m
$[MnLSO_4]$[f] (6A)	3320vs, 3265s,	1632m[b]	1300(sh)	1115s, vbr[c]	1000w	600w, 590m,
	3180w	1585m, br				522w, 490m

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[a] νOH_2.

[b] $\delta(HOH)$.

[c] $\nu_3(SO_4^{2-})$+NH_2-twisting.

[d] $\nu_4(SO_4^{2-})$ appears at 630 cm^{-1} and 615 cm^{-1}.

[e] $\nu_4(SO_4^{2-})$ appears at 628 cm^{-1} and 610 cm^{-1}.

[f] $\nu_4(SO_4^{2-})$ appears at 630 cm^{-1} and 620 cm^{-1}.

[g] $\nu_4(SO_4^{2-})$ appears at 635 cm^{-1} and 620 cm^{-1}.

ν = stretching, β = bending, ρ_w = wagging, ρ_r = rocking, vs = very strong, s = strong, m = medium, w = weak, (sh) = shoulder, br = broad, vbr = very broad.

symmetry of complex (4) as is evident from its higher magnetic moment (Table 2) compared with that of complex (3). Considering the ν (NH_2), β (NH_2) and NH_2 twisting of complexes (3) and (4), it may be stated that the hydrogen bonding of the NH_2 hydrogens in complex (3) is greater than that in complex (4). These observations suggest that these two complexes are isomers, though it is reasonable to state that they are not geometrical isomers as the IR data support a *trans* configuration in both cases. The intermediate species, $MnL_{0.5}Br_2$ from complex (3) and $MnL_{1.5}Br_2$ from complex (4), whose formation is assumed from the respective TG curves (Fig. 2), could not be isolated pyrolytically in pure form even by maintaining a very slow rate of heating.

The complexes derived from $MnSO_4$ and hydrazine hydrate

A concentrated aqueous solution of $MnSO_4$ reacting with hydrazine hydrate results in $[MnL_{1.5}SO_4]\cdot H_2O$ (5) while treatment of hydrazine hydrate with $MnSO_4$ in ammoniacal medium affords $[MnLSO_4\cdot H_2O]$ (6). Both complexes are identical in color and show bridging character of the hydrazine as is evident from the IR spectra (Table 3). It is interesting to note that both the species become anhydrous first and that the anhydrous species are isolable. The dehydration takes place at a much higher temperature in complex (6) than in complex (5) (Table 1). This observation indicates that the water probably exists as coordinated water in complex (6) and as lattice water in complex (5) as is evident from the downward shift of $\nu(NH_2)$ of (6) in comparison to that of (5). The presence of δ(HOH) at $\sim 1630\ cm^{-1}$ also supports the presence of water in both cases. Dehydration of complex (6) appears to be very interesting. Isolation of the intermediate $MnLSO_4\cdot 0.8\ H_2O$ is feasible but it immediately forms species (6) on exposure to the air. Another interesting observation from the thermal decomposition of complexes (5) and (6) is that the complexes generate intermediate complexes of the same elemental composition but differing in structure as is shown by the different thermal profiles of complex (5A) and complex (6A). But, in contrast, the IR (Table 3) and magnetic data (Table 2) of both complexes (5A) and (6A) could not differentiate them. We could not characterise the intermediates $MnL_{0.8}SO_4$ derived from complex (5) and $MnL_{0.75}So_4$ derived from complex (6) from their TG curves.

CONCLUSION

The possibility of adduct formation by N_2H_4 is not unlikely. However, the thermal profiles do not indicate such adduct phenomena. In general, the bromide ligand shows greater bridging charactristics than the chloride ligand. As a result, we expected that the bromo complexes, like the chloro complexes, would produce isolable intermediate complexes upon heating. But, it is interesting to note that the bromo complexes yield $MnBr_2$ without the formation of any stable intermediate (Table 1). This phenomenon is possibly due to the close potentiality between the bromide ligand and hydrazine. The formation of intermediate complexes during heating of chloro complexes undoubtedly signify the polymeric nature of the parent species.

As to the sulfato complexes, it is reasonable to expect from visual observations that Mn(II) exists in O_h geometry, though they are ligand-deficient compounds. This geometry would only be possible if all the oxygens of one SO_4 group are coordinated [4,9].

It is interesting to note that variation in the methods of preparation could yield complexes of different compositions such as MnL_nCl_2, where $n = 1$, 1.5, etc. But no complexes other than $[MnL_2Cl_2]$ are reported in the literature [10]. However, it is clear that thermal techniques are very useful for differentiating very slight differences in the structures of complexes which are apparently identical.

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