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THERMAL INVESTIGATION OF DIAMINE COMPLEXES OF Zn(II) IN THE SOLID STATE

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ABSTRACT

The complexes $[Zn(en)_3]X_2 \cdot n\ H_2O$, where en = ethylenediamine, X = Cl^-, Br^- or $\frac{1}{2}SO_4^{2-}$, $n = 1$ or 0.5, and $[Zn(tn)_2]X_2 \cdot n\ H_2O$, where tn = 1,3-diaminopropane, X = Cl^-, Br^- or $\frac{1}{2}SO_4^{2-}$, $n = 0$ or 0.25, have been synthesized and their thermal investigations carried out. The complexes were characterized by elemental analysis and IR spectral data. These complexes have been observed to decompose through several isolable as well as non-isolable complex species as intermediates during heating. $[Zn(tn)_2]SO_4$ undergoes solid-state phase transition in the temperature range 126–145°C. $ZnenSO_4$ and $ZntnX_2$ (X = Cl^-, Br^- or $\frac{1}{2}SO_4^{2-}$) have been synthesized pyrolytically in the solid state from their corresponding mother diamine complexes. $ZnenSO_4$ and $ZntnX_2$ (X = Cl^-, Br^- or $\frac{1}{2}SO_4^{2-}$) complexes decompose through non-isolable hemidiamine species. ZnX_2 (X = Cl^- or Br^-) complexes of tn undergo melting after formation of the monodiamine species. In contrast, the corresponding en complexes undergo melting at non-stoichiometric composition. Diamine (en or tn) is found to be bridging in all monodiamine (en or tn) complexes; whilst their mother complexes possess chelated en or tn. The thermal stability sequence of en and tn complexes of Zn(II) is $ZnCl_2 < ZnBr_2 < ZnSO_4$. ΔH values are reported for some steps of decomposition. Possible mechanistic paths have been reported for each step of decomposition.

INTRODUCTION

Studies on metal complexes of diamines are well-documented in the literature. Thermal investigations of transition metal diamine complexes have been carried out by several workers [1–4]. Thermal investigations of metal complexes of 1,2-diaminopropane are known [1]. But studies on the complexes of 1,3-diaminopropane (tn) are scarce [4,5]. Recently, we reported the thermal investigation of nickel(II) diamine complexes [5,6]. From this study we explored the possibility of synthesizing some new diamine complexes pyrolytically in the solid state, which cannot be synthesized from solution. Some conformational changes in nickel(II) diamine complexes have

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been observed in our laboratory [7]. Ethylenediamine (en) complexes of $ZnCl_2$ are well-documented in the literature [8–11]. The chemistry of the reactions between 1,3-diaminopropane (tn) and zinc salts have yet to be studied. The aim of the present study is to investigate the thermal decomposition of the en and tn complexes of Zn(II) and to isolate the possible intermediate products formed upon heating. This also deals with their characterization by elemental analyses, spectral and thermal data. The enthalpy changes and possible mechanisms for each step of decomposition are also reported.

EXPERIMENTAL

The metal salts used were all of analytical reagent grade purity. Ethylenediamine and 1,3-diaminopropane were purified by repeated distillation. Complexes $[Zn(en)_3]Cl_2 \cdot H_2O$ (1), $[Zn(en)_3]Br_2 \cdot H_2O$ (2), $[Zn(en)_3]SO_4 \cdot 0.5\ H_2O$ (3), $[Zn(tn)_2]Cl_2$ (4), $[Zn(tn)_2]Br_2$ (5) and $[Zn(tn)_2]SO_4 \cdot 0.25\ H_2O$ (6) were prepared following the method reported earlier [10]. In the case of tn complexes, we added tn (3 mmole) to the zinc salts (1 mmole) and the mixture was kept for 15 days in a closed container. Finally, the solid compounds were isolated and purified by washing with ethanol and dried in a vacuum desiccator. Complexes $ZnenSO_4$, $ZntnCl_2$, $ZntnBr_2$ and $ZntnSO_4$ were prepared pyrolytically from complexes (3), (4), (5) and (6) at 280, 195, 230 and 205°C in a nitrogen atmosphere, respectively (Table 2).

TABLE 1

Analytical data of zinc(II) diamine complexes

Compound	Compound no.	Colour	Analysis (%) [a]		
			Metal	Nitrogen	Halogen/ Sulphur
$[Zn(en)_3]Cl_2 \cdot H_2O$	(1)	White	19.42(19.55)	25.02(25.12)	21.01(21.23)
$[Zn(en)_3]Br_2 \cdot H_2O$	(2)	White	15.40(15.44)	19.71(19.84)	37.58(37.75)
$[Zn(en)_3]SO_4 \cdot 0.5\ H_2O$	(3)	White	18.61(18.66)	23.88(23.97)	9.01(9.13)
$ZnenSO_4$ [b]		Pale-yellowish	29.58(29.53)	12.50(12.64)	14.31(14.45)
$[Zn(tn)_2]Cl_2$	(4)	White	22.78(22.99)	19.75(19.69)	24.85(24.96)
$[Zn(tn)_2]Br_2$	(5)	White	17.53(17.51)	15.12(14.99)	42.51(42.80)
$[Zn(tn)_2]SO_4 \cdot 0.25\ H_2O$	(6)	White	20.89(20.82)	17.70(17.84)	10.23(10.19)
$ZntnCl_2$ [b]		White	31.27(31.07)	13.31(13.30)	33.59(33.74)
$ZntnBr_2$ [b]		White	21.84(21.85)	9.29(9.36)	53.12(53.41)
$ZntnSO_4$ [b]		White	27.78(27.77)	11.82(11.89)	13.39(13.59)

[a] Figures in parentheses are the required percentages.

[b] Compounds synthesized in the solid state.

TABLE 2

Thermal parameters of zinc(II) diamine complexes

Decomposition reactions	Temperature range (°C)	DTA [a] peak temperature (°C)	ΔH (kJ mole^{-1})
$[Zn(en)_3]Cl_2 \cdot H_2O$ (1) → $[Zn(en)_3]Cl_2$	66– 99	76	[d]
$[Zn(en)_3]Cl_2$ → $Zn(en)_{2.75}Cl_2$	99–122	117	[d]
$Zn(en)_{2.75}Cl_2$ → $Zn(en)_{2.25}Cl_2$	122–165	161	[d]
$Zn(en)_{2.25}Cl_2$ → $Zn(en)_{1.25}Cl_2$	165–200	184, 200 [b]	[d]
$Zn(en)_{1.25}Cl_2$ → $ZnenCl_2$	200–260	[c]	[d]
$ZnenCl_2$ → $ZnCl_2$	260–399	380	62
$[Zn(en)_3]Br_2 \cdot H_2O$ (2) → $[Zn(en)_3]Br_2$	46– 69	65	60
$[Zn(en)_3]Br_2$ → $Zn(en)_{1.75}Br_2$	145–205	190, 198, 205 [b]	[d]
$Zn(en)_{1.75}Br_2$ → $ZnenBr_2$	205–310	246, 300	[d]
$ZnenBr_2$ → $ZnBr_2$	310–405	380	82
$[Zn(en)_3]SO_4 \cdot 0.5\ H_2O$ (3) → $[Zn(en)_3]SO_4$	55–105	60, 91	[d]
$[Zn(en)_3]SO_4$ → $ZnenSO_4$	182–275	268	198
$ZnenSO_4$ → $Zn(en)_{0.5}SO_4$	327–395	385	35
$Zn(en)_{0.5}SO_4$ → $ZnSO_4$	400–427	405	48
$[Zn(tn)_2]Cl_2$ (4) → $ZntnCl_2$	91–186	150	95
$ZntnCl_2$ → $ZntnCl_2$	245–275	273 [b]	24
$ZntnCl_2$ → $Zn(tn)_{0.5}Cl_2$ [e]	275–360	335	47
$[Zn(tn)_2]Br_2$ (5) → $ZntnBr_2$	152–220	208	108
$ZntnBr_2$ → $ZntnBr_2$	255–285	282	26
$ZntnBr_2$ → $Zn(tn)_{0.5}Br_2$ [e]	285–351	305, 322, 328	[d]
$[Zn(tn)_2]SO_4 \cdot 0.25\ H_2O$ (6) → $[Zn(tn)_2]SO_4$	40– 65	60	30
$[Zn(tn)_2]SO_4$ → $Zn(tn)_2SO_4$	126–145	141	9
$[Zn(tn)_2]SO_4$ → $ZntnSO_4$	145–195	190	71
$ZntnSO_4$ → $Zn(tn)_{0.5}SO_4$	337–375	367	[d]
$Zn(tn)_{0.5}SO_4$ → $ZnSO_4$	375–428	[c]	[d]

[a] Endotherm.

[b] Peaks due to melting.

[c] Very weakly resolved.

[d] ΔH value could not be evaluated due to overlapping.

[e] $Zntn_{0.5}X_2$ (where $X = Cl^-$ or Br^-) species are volatile.

Elemental analyses

Zinc, chlorine, bromine and sulphur were analyzed gravimetrically. Nitrogen was analyzed in our laboratory by the Duma method. All the analytical data are shown in Table 1.

Thermal measurements

Thermal analyses were carried out using a Shimadzu DT-30 thermal analyzer (Japan). A constant flow of nitrogen (30 cm^3 min^{-1}) was maintained. Platinum crucibles were used. A heating rate of 10°C min^{-1} was

TABLE 3

IR spectral data of zinc(II) diamine complexes

Compound	Assignments (cm^{-1})								
	$\nu(NH_2)$	$\nu(CH_2)$	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_w(CH_2)$	$\tau(NH_2)+\rho_w(NH_2)+\tau(CH_2)$	Stretching vibrations of skeleton $\nu(C-N)+\nu(C-C)$	$\rho_r(CH_2)$	$\rho_r(CH_2)+\nu(M-N)$
$[Zn(tn)_2]Cl_2$	3345m, 3160vsbr, 3090vsbr	2940m, 2880w, 2855sh	1600w, 1575s, 1550sh, 1508m	1460w, 1450m, 1425w	1390vw, 1370wbr	1320m, 1310sh, 1300ms, 1285m, 1255w, 1230w, 1207w, 1178sh, 1150vs, 1128sh	1090sh, 1040m, 1030sh, 1020vw, 998m, 970m	949vw, 902ms, 850vw	670sbr, 615sh
$[Zn(tn)_2]Br_2$	3295m, 3200vsbr, 3120vsbr	2960m, 2905w, 2875vw	1600m, 1580s, 1550sh	1485w, 1472m, 1465sh, 1445vw	1410sh, 1392m, 1385w	1345w, 1330m, 1310m, 1281w, 1255m, 1225w, 1175vs, 1130sh	1070m, 1053w, 1040vw, 1020m, 995m	963sh, 925ms, 880vw	690sbr, 620sh
$[Zn(tn)_2]SO_4$ [a]	3280m, 3180vsbr, 3105vsbr	2942m, 2885w, 2860vw	1580m, 1565s, 1550sh	1470w, 1458m, 1450sh, 1430w	1390sh, 1379m, 1364w	1327w, 1315m, 1290m, 1265w, 1234m, 1210w, 1160vs, 1140sh	1049w, 1036w, 1020vw, 1002m, 978m	950sh, 908ms, 860vw	670sbr

$ZntnCl_2$ [b]	3250s, 3230s, 3145m	2940m, 2880w, 2860sh	1600s	1480mbr	1390m, 1380sh	1304m, 1295sh, 1215m, 1156vs, 1115m	1050m, 1030w, 968s		660m, 610w
$ZntnBr_2$ [b]	3290m, 3240s, 3140m	2960m, 2940sh, 2895m	1605s	1490m	1415m, 1395sh	1315m, 1280w, 1200m, 1160vs, 1108vw	1065w, 1045w, 1005s	950w	670sh, 640s
$ZntnSO_4$ [b]	3302s, 3260s, 3142m	2950m, 2890w, 2848w	1582s	1465m	1375m, 1350w	[c]	[c]	[c]	[c]
$ZnenSO_4$ [b]	3260s, 3210s, 3115m	2965vw, 2940m, 2908sh, 2880w	1560s	1451m	1365vw	1325m, [c]	[c]	[c]	[c]
$NitnCl_2$ [b,d]	3340m, 3315m, 3260m, 3040m	2970sh, 2900m, 2800w	1590sh, 1580s	1470s, 1460s, 1450sh	1405m	1315vw, 1265m, 1245vw, 1212m, 1185w, 1140s, 1120m	1100m, 1070sh, 1052w, 1010sh, 1000s	942s, 918m, 870vw	642br, 595vw, 550sh

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[a] Bands due to sulphate are omitted.

[b] Compounds synthesized in the solid state.

[c] Spectra complicated, not distinguishible due to overlapping of sulphate and ligand bands.

[d] Spectral data of $NitnCl_2$ is given for comparison.

vs = very strong, s = strong, sbr = strong broad, m = medium, mbr = medium broad, w = weak, wbr = weak broad, vw = very weak, sh = shoulder.

maintained. The particle size of the samples was within 150–200 mesh. Aluminium oxide was used as reference. Zn metal was used as calibrant for evaluation of enthalpy changes.

Spectral measurements

Infrared spectra in KBr (4000–400 cm^{-1}) and in polythene (400–250 cm^{-1}, in some cases) were recorded using a Beckman IR-20A and Perkin–Elmer 597 IR spectrophotometers, respectively.

RESULTS

$[Zn(en)_3]Cl_2 \cdot H_2O$ (1) starts to lose its water molecule at 66°C (Fig. 1, Table 2) and becomes anhydrous at 99°C. The anhydrous species immediately starts to decompose and decomposition proceeds through several non-isolable intermediates, $Zn(en)_xCl_2$ [$x = 2.75, 2.25, 1.25, 1$ and 0], accord-

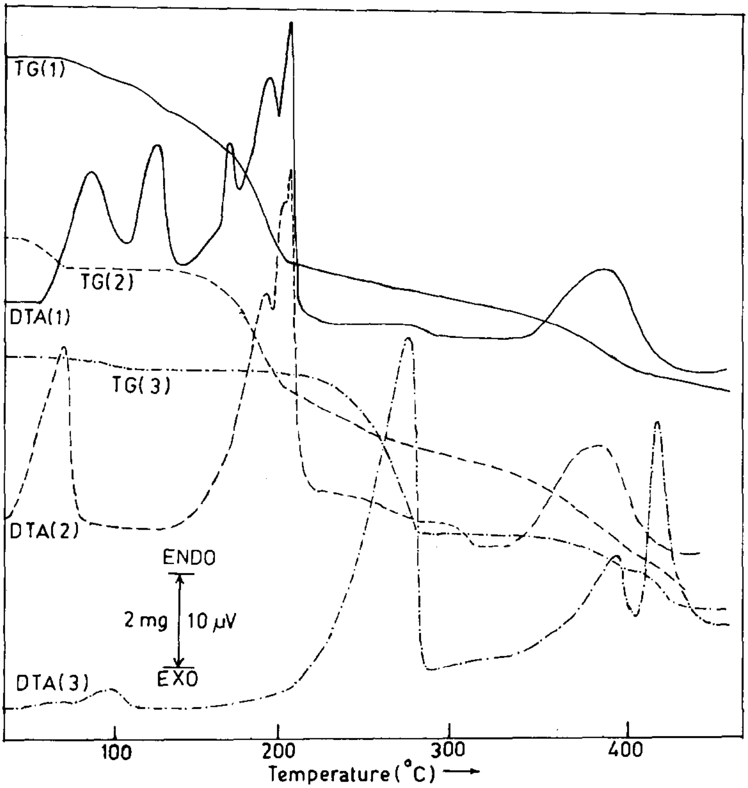

Fig. 1. Thermal curves of ———, $[Zn(en)_3]Cl_2 \cdot H_2O$ (1); - - - - - -, $[Zn(en)_3]Br_2 \cdot H_2O$ (2); and -·-·-, $[Zn(en)_3]SO_4 \cdot 0.5\ H_2O$ (3). Sample weights: 1, 11.69 mg; 2, 13.79 mg; 3, 10.44 mg.

ing to the TG curve. The corresponding DTA curve shows seven overlapping endotherms for the elimination of water together with two molecules of en evolved initially. It also shows another endotherm for the elimination of the remaining en molecule. The sharp endothermic peak at 200°C occurs due to melting at the composition $Zn(en)_{1.25}Cl_2$, as is evident from the TG curve.

$[Zn(en)_3]Br_2 \cdot H_2O$ (2) becomes anhydrous at 69°C (Fig. 1). The anhydrous species starts to decompose on further heating at 145°C and decomposes through several non-isolable intermediates, $Zn(en)_xBr_2$ ($x = 1.75$, 1 and 0) based on the TG curve. The corresponding DTA curve initially shows an endotherm for the elimination of the water molecule and then five overlapping endotherms for the elimination of the two en molecules. It also shows another endotherm for the elimination of the residual en molecule. The sharp DTA peak at 205°C occurs due to melting at the composition $Zn(en)_{1.75}Br_2$, as calculated from the TG curve.

$[Zn(en)_3]SO_4 \cdot 0.5\ H_2O$ (3) becomes anhydrous at 105°C (Fig. 1, Table 2) in a single step as is evident from its TG curve. But the corresponding DTA curve shows two overlapping endotherms indicating that the dehydration takes place in two steps. The anhydrous species decomposes at 182°C and

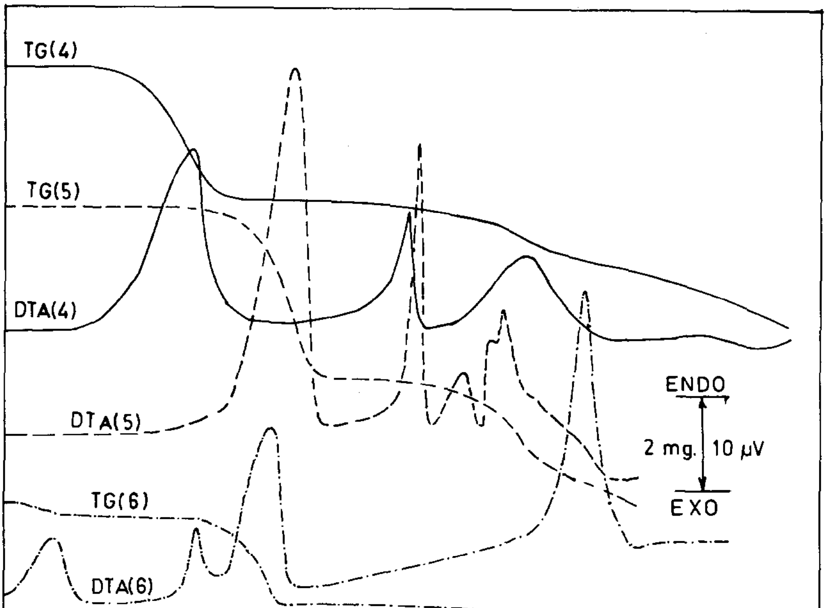

Fig. 2. Thermal curves of ———, $[Zn(tn)_2]Cl_2$ (4); — — —, $[Zn(tn)_2]Br_2$ (5); and ·—·—·, $[Zn(tn)_2]SO_4 \cdot 0.25\ H_2O$ (6). Sample weights: 4, 10.76 mg; 5, 17.84 mg; 6, 7.76 mg.

becomes $ZnenSO_4$ at 275°C in a single step, as is evident from its TG and DTA curves. The desired monodiamine species again starts to decompose at 327°C and decomposes to $ZnSO_4$ through the formation of the hemidiamine species as intermediate.

Figure 2 shows the thermal curves of $[Zn(tn)_2]Cl_2$ (4). It starts to lose one tn molecule at 91°C and transforms to $ZntnCl_2$ at 186°C in a single step showing an endothermic peak at 150°C. The monodiamine species starts melting at 246°C showing a sharp endothermic peak at 273°C. On further heating, it decomposes immediately after melting through a non-isolable intermediate, $Zn(tn)_{0.5}Cl_2$.

The thermal curves of $[Zn(tn)_2]Br_2$ (5) are shown in Fig. 2. It decomposes at 152°C and transforms to $ZntnBr_2$ at 220°C like the corresponding tn complex of $ZnCl_2$. The desired mono species starts to melt at 255°C giving a sharp endothermic peak at 282°C. On further heating, the melted species immediately decomposes through the formation of a non-isolable hemidiamine complex as an intermediate. Formation of the hemidiamine species from monodiamine occurs in one step, as is evident from the TG curve; but the corresponding DTA curve shows three overlapping endotherms.

Figure 2 shows the thermal curves of $[Zn(tn)_2]SO_4 \cdot 0.25\ H_2O$ (6). The TG curve shows that it becomes anhydrous at 65°C (Table 2) in a single step. The desired anhydrous species shows an endothermic peak at 141°C in the temperature region 126–145°C without showing any mass loss and then shows another endothermic peak at 190°C which corresponds to the elimination of one tn molecule. The monodiamine species derived at 195°C decomposes at 337°C and transforms to $ZnSO_4$ through the formation of a non-isolable hemidiamine species, as is evident from its TG curve.

DISCUSSION

Synthesis and characterization of tris, bis and mono ethylenediamine complexes of zinc salts are well-documented in the literature [8–11]. The reported tris complex of $ZnCl_2$ contains two molecules of water [10]. But the tris species (1) synthesized by us contains only one molecule of water. $ZnBr_2$ and $ZnSO_4$ yield tris species with en, having one and one half molecules of water, respectively (Table 1). The IR spectrum of $[Zn(en)_3]Cl_2 \cdot 2\ H_2O$ was reported earlier [10]. The IR spectrum of complex (1) is similar to the reported data. This shows that the en molecules are chelated. Complexes (2) and (3) are isostructural with complex (1), because complexes (2) and (3) possess IR bands like those of complex (1). It is interesting to note that isolation of anhydrous species from complex (1) is not at all feasible. On the contrary, complexes (2) and (3) yield thermally stable anhydrous compounds. It is also noticed that complex (1) starts dehydration at a higher temperature than those of complexes (2) and (3) (Tables 2). The foregoing anomalies are possibly due to the difference in the attachment of lattice water in the crystal. Since chlorine is more electronegative than bromine, it is reasonable to expect that the hydrogen bonding of the H_2O hydrogen with the Cl^- ion is more feasible, thereby causing the stability of lattice water in complex (1). Thermal profiles for the elimination of the first two molecules of en in complexes (1) and (2) appear very complicated as is evident from the number of overlapping endothermic peaks. In contrast, complex (3) exhibits a very simple thermal profile. The very pale-yellowish monodiamine complex, which was derived pyrolytically in a nitrogen atmosphere from complex (3), shows a very simple IR spectrum in comparison to those of the $[Zn(en)_3]^{2+}$ complexes. Newman and Powell [9] reported a series of $M(en)Cl_2$ [M = Zn, Cd or Hg] complexes where en acts as a bridging bidentate ligand and possesses *trans* configuration. Brodersen [12] corroborated the said structure of $M(en)Cl_2$, where M = Hg, by IR, Raman spectra and X-ray crystallographic studies. The possession of simpler and similar IR data by $ZnenSO_4$ (Table 3) compared with that reported for $Zn(en)Cl_2$, where en acts as a bridging bidentate ligand, suggests en is also bridging and possesses *trans* configuration in complex $ZnenSO_4$. It had been thought possible to synthesize bis as well as monodiamine complex species pyrolytically from the tris species upon heating. But the thermal profiles of complexes (1) and (2) show a slim possibility of synthesizing the mono species but we have failed to isolate this even after repeated attempts.

1,3-Diaminopropane complexes of ZnX_2 [$X = Cl^-$, Br^- or $\frac{1}{2}SO_4^{2-}$] were prepared following the procedure adopted for the corresponding en complexes. But it is interesting to note that, unlike en, tn cannot afford tris complexes with the zinc ion. This probably occurs due to the increase in chain length of the diamine. Here, the only $ZnSO_4$ complex contains a fractional molecule of water as lattice water. IR spectra (Table 3) of $[Zn(tn)_2]X_2$ [$X = Cl^-$, Br^- or $\frac{1}{2}SO_4^{2-}$] complexes show tn to be chelated. The IR spectrum of $[Zn(tn)_2]SO_4$ shows SO_4 is not coordinated to Zn [13]. Thermal as well as IR spectral data of $[Zn(tn)_2]Cl_2$ (4), $[Zn(tn)_2]Br_2$ (5) and $[Zn(tn)_2]SO_4$ (6) suggest that these probably possess a similar type of structure. Far-IR spectra (600–250 cm^{-1}) of complexes (4) and (5) are also similar to each other. The bands at 560w, 523m, 479m, 440sh, 425w and 395vw cm^{-1} of $[Zn(tn)_2]Cl_2$ (4) are possibly due to NH_2 rocking and M–N stretching vibrations [14,15]. Moreover, the bands at 345w and 298m cm^{-1} of (4) may be due to skeletal bending vibrations [14,15]. The corresponding bromo complex (5) gives bands at 560w, 521m, 435sh, 422w, 390sh, 343w and 300m cm^{-1} due to similar vibrations. The similar far-IR spectra of complexes (4) and (5) correspond to the non-coordination of the halide ion (Cl^- or Br^-) to the metal. Otherwise the distinguishing difference in the far-IR spectra would appear for the Zn–Cl and Zn–Br vibrations [10,16–18]. IR spectral studies of *cis*-$[Ni(tn)_2Cl_2]$ and *trans*-$[Ni(tn)_2(NCS)_2]$ have been reported [5,19]. IR spectra of complexes (4), (5) and (6) differ from the said complexes of nickel(II) indicating the structural difference between zinc and nickel tn complexes.

We have synthesized $ZntnCl_2$, $ZntnBr_2$ and $ZntnSO_4$ from their respective $[Zn(tn)_2]^{2+}$ complexes by heating up to the desired temperature (Fig. 2, Table 2). These monodiamine complexes give very simple IR spectra in comparison to their tn chelated parent complexes. We synthesized $[NitnCl_2]$ where tn is chelated and the chlorines are terminally coordinated [5]. Its IR spectrum (Table 3) is very complicated. From the foregoing discussion, it is very clear that tn may be bridging in $Zn(tn)X_2$ ($X = Cl^-$, Br^- or $\frac{1}{2}SO_4^{2-}$) complexes. Far-IR spectra of $ZntnCl_2$ and $ZntnBr_2$ are not identical. $ZntnBr_2$ gives two bands at 365m and 310s cm^{-1}, whereas, $ZntnCl_2$ gives bands at 360w, 320s and 310–275sbr (splitting nature) cm^{-1}. So it may be suggested that bands at 320 cm^{-1} and near 275 cm^{-1} are due to antisymmetric ν(Zn–Cl) and symmetric ν(Zn–Cl) stretching vibrations, respectively [10]. Other bands seem to be due to chain skeletal bending vibrations [10,16]. These two Zn–Cl stretching vibrations suggest that the anions are terminally attached to the metal. The bands in the 900–1200 cm^{-1} region of the IR spectrum of $ZntnSO_4$ are complicated: this may be due to overlapping of the SO_4 vibrations with the ligand vibrations. However, the similarity of the IR bands of $ZntnCl_2$ with those of $ZntnBr_2$ and $ZntnSO_4$ suggests that the coordination pattern of the ligands is similar in these three mono 1,3-diaminopropane complexes.

It is noticed that tn complexes of ZnX_2 [$X = Cl^-$ or Br^-] isolated in the solid state melt at the stoichiometric composition. But the corresponding complexes of en melt at different non-stoichiometric compositions. We could not isolate the hemidiamine species pyrolytically. It appears from Fig. 1 and Table 2 that complexes $[Zn(en)_3]X_2 \cdot H_2O$ ($X = Cl^-$ or Br^-) do not show any sign of hemidiamine formation as an intermediate in their respective thermal profiles. But it is true that the formation of this species is not unlikely, as we observed the formation of hemidiamine species with these ligands in the case of Ni(II) [5]. We tried to evaluate the values of ΔH for each step of the reaction from the DTA peak area. But, this proved impossible in some cases due to overlapping of the DTA peaks. However, some ΔH values tabulated in Table 2 show that values of the enthalpy change for transformation of $[Zn(tn)_2]X_2$ to $ZntnX_2$ [$X = Cl^-$, Br^- or $\frac{1}{2}SO_4^{2-}$] follow the order $Br^- > Cl^- > SO_4^{2-}$ in the respective complexes. Table 2 shows that thermal stability of tris en complexes with respect to the initial temperature of decomposition (T_i) follows the order $[Zn(en)_3]SO_4 > [Zn(en)_3]Br_2 > [Zn(en)_3]Cl_2$. This order prevails in the bis and mono tn complexes also.

The endotherm (Fig. 2) observed in the anhydrous species, $[Zn(tn)_2]SO_4$, derived from $[Zn(tn)_2]SO_4 \cdot 0.25\ H_2O$, is due to some phase transition phenomena. We arrested the species after phase transition at 145°C, cooled it down immediately at a rate equal to that of heating: no noticeable deviation in the cooling DTA curve was observed. But, on keeping the same sample for ~ 2 h in a desiccator, it showed the endotherm appearing again in the same temperature range. It is also observed that the extent of reversibility of the phase transition phenomenon is accelerated in the open air. This shows that the reversibility of this phase transition is time dependent. We could not characterize the species after phase transition due to its reversible character. As a result, it would not be prudent to suggest anything relating to this phase transition.

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