Thermochimica Acta, 77 (1984) 1-11
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL INVESTIGATIONS OF CADMIUM(II) DIAMINE COMPLEXES IN THE SOLID PHASE

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(Received 12 December 1983)

ABSTRACT

$[Cd(en)_3]X_2 \cdot n\,H_2O$, $[Cd(tn)_2X_2] \cdot m\,H_2O$ and $[Cd(tn)SO_4]$ (where en = 1,2-diaminoethane, tn = 1,3-diaminopropane; $X = Cl^-$, Br^- or $\frac{1}{2}SO_4^{2-}$; $n = 1$, 2 and 0; and $m = 0$ and 1) have been synthesized and their thermal investigations have been carried out using a Shimadzu thermal analyzer. $[Cd(en)X_2]$ (where $X = Cl^-$, Br^- and $\frac{1}{2}SO_4^{2-}$), $[Cd(en)_2Br_2]$ and $[Cd(tn)X_2]$ (where $X = Cl^-$ and $\frac{1}{2}SO_4^{2-}$) have been synthesized pyrolytically in the solid state by the temperature-arrest technique from their mother diamine complexes. Two $[Cd(tn)SO_4]$ complexes synthesized in two different ways, which are indistinguishable by IR spectra, give different thermal profiles. Diamine is found to be chelated in all the bis- and tris-diamine complexes. On the contrary, the ligand is bridged in mono(1,2-diaminoethane) complexes. 1,3-Diaminopropane is chelated in $[Cd(tn)Cl_2]$ but bridged in $[Cd(tn)SO_4]$ complexes. $[Cd(tn)X_2]$ ($X = Cl^-$ and Br^-) on heating undergoes some form of reversible phase transition with melting.

INTRODUCTION

Thermal investigations of transition metal diamine complexes have been previously performed [1–4]. In earlier communications [5–9], the thermal investigations of Ni^{2+} and Zn^{2+} diamine complexes in the solid phase were explored. During those investigations, several ligand deficient metal(II) diamine complexes were synthesized pyrolytically in the solid phase. Recently, thermally induced conformational changes of chelate rings in nickel(II) diamine complexes were observed [9]. The above studies have inspired us to undertake the thermochemical study of cadmium(II) diamine complexes.

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EXPERIMENTAL

The metal salts used were all of analytical reagent grade purity. 1,2-Diaminoethane (en) and 1,3-diaminopropane (tn) were purified by repeated distillation.

Preparation of the complexes

[Cd(en)$_3$]Cl$_2$ · H$_2$O (1), [Cd(en)$_3$]Br$_2$ · 2 H$_2$O (2). 1,2-Diaminoethane (4–5 mmol) was added to the respective cadmium salts and the mixture was kept for ~ 20 days in a sealed conical flask. Excess ligand was pumped off and finally the solid compound was extracted with ethanol, filtered, washed several times with ethanol, and dried over a fused $CaCl_2$ desiccator.
[Cd(en)$_3$]SO$_4$ (3). 1,2-Diaminoethane (3–4 mmol) was added dropwise with stirring to $CdSO_4$ (1 mmol) dissolved in a minimum quantity of water. On standing, colorless crystals separated out. These crystals were filtered, washed with ethanol, and dried over a fused $CaCl_2$ desiccator.
[Cd(tn)$_2$Cl$_2$] (4), [Cd(tn)$_2$Br$_2$] (5). 1,3-Diaminopropane (3 mmol) was added to the ethanolic solution of cadmium salts (1 mmol) with stirring, while white crystalline solids were separated out. The mixture was kept overnight, filtered, washed with ethanol, and dried over a fused $CaCl_2$ desiccator.
[Cd(tn)$_2$SO$_4$] · H$_2$O (6). 1,3-Diaminopropane (3 mmol) was added dropwise with stirring to $CdSO_4$ (1 mmol) dissolved in a minimum quantity of water. On mixing, instantaneous white precipitation occurred. The precipitate was removed by filtration and the filtrate was concentrated on a water bath. On adding an ether–methanol (1 : 1) mixture to the concentrated solution with vigorous stirring, shining flaky crystals were separated out. The crystals were washed throughly with ether, and dried over a fused $CaCl_2$ desiccator.
[Cd(tn)SO$_4$] (7). 1,3-Diaminopropane (3 mmol) was added dropwise with stirring to $CdSO_4$ (1 mmol) dissolved in water and filtered immediately. Ethanol was added to the derived filtrate. White crystalline solids, insoluble in water, were separated out. This was filtered off, washed with a water–ethanol (1 : 1) mixture and dried over a fused $CaCl_2$ desiccator.
[Cd(en)Cl$_2$] (8), [Cd(en)Br$_2$] (9), [Cd(en)SO$_4$] (10). These complexes were synthesized by keeping the complexes (**1**), (**2**) and (**3**) at 174, 200 and 264°C, respectively, in a dinitrogen gas atmosphere. The thermolysis was stopped when no more diamine was lost as evidenced by a constancy of weight.
[Cd(en)$_2$Br$_2$] (11). This was synthesized following the method adopted for the synthesis of complex (**8**) from complex (**2**) at ~ 145°C.
[Cd(tn)Cl$_2$] (12), [Cd(tn)SO$_4$] (13). These complexes were synthesized following the method adopted for the synthesis of complex (**8**) from complexes (**4**) and (**6**) at 167 and 197°C, respectively.

Analytical data for the above complexes are presented in Table 1.

The apparatus employed for carrying out the thermal analysis is the same as reported earlier [6]. Table 2 lists the thermal data.

TABLE 1

Analytical data of cadmium(II) diamine complexes

Compound		Colour	Analysis[a] (%)		
			Metal	Nitrogen	Halogen/sulphur
$[Cd(en)_3]Cl_2\cdot H_2O$	**(1)**	White	29.3 (29.5)	22.2 (22.0)	18.5 (18.6)
$[Cd(en)_3]Br_2\cdot 2\ H_2O$	**(2)**	White	22.8 (23.0)	17.1 (17.2)	32.1 (32.8)
$[Cd(en)_3]SO_4$	**(3)**	White	28.8 (28.9)	21.3 (21.6)	7.8 (8.2)
$[Cd(tn)_2Cl_2]$	**(4)**	White	34.2 (33.9)	16.6 (16.9)	21.5 (21.4)
$[Cd(tn)_2Br_2]$	**(5)**	White	26.8 (26.7)	13.1 (13.3)	38.8 (38.1)
$[Cd(tn)_2SO_4]\cdot H_2O$	**(6)**	White	30.1 (30.0)	15.2 (15.0)	8.8 (8.5)
$[Cd(tn)SO_4]$	**(7)**	White	39.9 (39.8)	10.2 (9.9)	11.8 (11.3)
$[Cd(en)Cl_2]$	**(8)**	White	46.2 (46.2)	11.6 (11.5)	29.3 (29.2)
$[Cd(en)Br_2]$	**(9)**	Pale yellowish	33.9 (33.8)	8.3 (8.4)	49.0 (48.3)
$[Cd(en)SO_4]$	**(10)**	White	41.2 (41.9)	10.0 (10.4)	11.7 (11.9)
$[Cd(en)_2Br_2]$	**(11)**	White	28.8 (28.6)	14.4 (14.3)	40.1 (40.8)
$[Cd(tn)Cl_2]$	**(12)**	White	43.5 (43.7)	11.2 (10.8)	27.1 (27.6)
$[Cd(tn)SO_4]$	**(13)**	White	39.5 (39.8)	10.1 (9.9)	11.8 (11.3)

[a] Figures in parentheses are the required percentages.

TABLE 2

Thermal parameters of cadmium(II) diamine complexes

Decomposition reactions	Temperature range (°C)	DTA peak temperature (°C)	
		Endo	Exo
$[Cd(en)_3]Cl_2\cdot H_2O$ **(1)** $\rightarrow [Cd(en)_3]Cl_2$	80–112	109	—
$[Cd(en)_3]Cl_2 \rightarrow [Cd(en)_2Cl_2]$	112–150	145	—
$[Cd(en)_2Cl_2] \rightarrow [Cd(en)Cl_2]$ **(8)**	150–174	168	—
$[Cd(en)Cl_2] \rightarrow [Cd(en)_{0.5}Cl_2]$	260–320	313	—
$[Cd(en)_{0.5}Cl_2] \rightarrow CdCl_2$	320–375	330[a]	342
$[Cd(en)_3]Br_2\cdot 2\ H_2O$ **(2)** $\rightarrow [Cd(en)_3]Br_2$	40– 72	68	—
$[Cd(en)_3]Br_2 \rightarrow [Cd(en)_2Br_2]$ **(11)**	105–155	152	—
$[Cd(en)_2Br_2] \rightarrow [Cd(en)Br_2]$ **(9)**	158–200	180, 195	—
$[Cd(en)Br_2] \rightarrow [Cd(en)_{0.5}Br_2]$	255–310	272[a]	—
$[Cd(en)_{0.5}Br_2] \rightarrow CdBr_2$	310–365	—	322 (sh), 328
$[Cd(en)_3]SO_4$ **(3)** $\rightarrow [Cd(en)SO_4]$ **(10)**	175–264	250	266
$[Cd(en)SO_4] \rightarrow CdSO_4$	285–380	370	—
$[Cd(tn)_2Cl_2]$ **(4)** $\rightarrow [Cd(tn)Cl_2]$ **(12)**	118–167	160	—
$[Cd(tn)Cl_2] \rightarrow CdCl_2$	215–370	241[b]	314, 347
$[Cd(tn)_2Br_2]$ **(5)** $\rightarrow [Cd(tn)Br_2]$	120–218	174 (sh), 177, 218[b]	—
$[Cd(tn)Br_2] \rightarrow CdBr_2$	218–410	—	350
$[Cd(tn)_2SO_4]\cdot H_2O$ **(6)** $\rightarrow [Cd(tn)_2SO_4]$	35– 60	45	—
$[Cd(tn)_2SO_4] \rightarrow [Cd(tn)SO_4]$ **(13)**	140–195	160, 190	—
$[Cd(tn)SO_4] \rightarrow CdSO_4$	300–385	375	—
$[Cd(tn)SO_4]$ **(7)** $\rightarrow CdSO_4$	290–400	330 (sh), 350, 380	390

[a] Peak due to melting with decomposition.

[b] Peak due to melting and some kind of reversible phase transition.

TABLE 3

IR spectral data (cm^{-1}) of cadmium(II) diamine[a] complexes[b]

Compound		$\nu(NH_2)$	$\nu(CH_2)$	$\delta(NH_2)$	$\delta(CH_2)$
$[Cd(tn)_2Cl_2]$	**(4)**	3310w, 3280m, 3235s, 3220sh, 3130m	2925m, 2909m, 2860m, 2840sh	1600m, 1588s	1465m, 1460sh, 1448w, 1430vw
$[Cd(tn)_2Br_2]$	**(5)**	3320w, 3282m, 3238s, 3220sh, 3135m	2938m, 2920m, 2862m, 2840w	1590m, 1580s	1460m, 1448sh, 1440vw, 1428vw
$[Cd(tn)_2SO_4]$	**(6)**	3320w, 3290m, 3240s, 3220sh, 3140m	2950m, 2940m, 2920sh, 2875m, 2860sh	1598s, 1582s, 1552sh	1468m, 1460sh, 1432w, 1402m
$[Cd(tn)SO_4]$	**(7,13)**	3330s, 3280s, 3162m	2970sh, 2955m, 2900m, 2861w	1582s	1475 m, 1460sh
$[Cd(en)Cl_2]$	**(8)**	3275s, 3240s, 3200sh, 3150w	2955w, 2940w, 2920sh, 2880vw	1610s, 1600sh	1475vw, 1460sh
$[Cd(en)Br_2]$	**(9)**	3270s, 3235s, 3200sh, 3145w	2960w, 2940w, 2920sh, 2880vw	1595s	1465vw, 1450sh
$[Cd(en)SO_4]$	**(10)**	3280s, 3238s, 3182sh, 3150m	2960w, 2940w, 2920sh, 2880w	1592s	1465w, 1460sh
$[Cd(en)_2Br_2]$	**(11)**	3328m, 3285s, 3252s, 3225s, 3198s, 3130s	2930m, 2910m, 2885m, 2820sh	1581s, 1568sh, 1550sh	1455sh, 1441m
$[Cd(tn)Cl_2]$	**(12)**	3280s, 3240s, 3138m	2940m, 2920m, 2900sh, 2868m, 2840sh	1575s, 1570sh, 1550sh	1455m, 1450m, 1426m

[a] IR spectra of $[Cd(en)_3]^{2+}$ are not shown owing to the similarity with the literature [10,11].

[b] w, weak; vw, very weak; m, medium; s, strong; vs, very strong; sh, shoulder; br, broad.

[c] Spectra are complicated and are not distinguishable due to the overlapping of sulphate (ν_3) and ligand bands.

$\rho_w(CH_2)$	Assignments $\tau(NH_2)+\rho_w(NH_2)+\tau(CH_2)$	Stretching vibrations of skeleton $\nu(C-N)+\nu(C-C)$	$\rho_r(CH_2)$	$\rho_r(CH_2)+\nu(MN)$
1398w, 1366m, 1360w	1297vw, 1270w, 1262m, 1242w, 1168m, 1139m	1122sh, 1113s, 1092s, 1081sh, 1052s, 1038sh, 1025vw, 1001s, 970s, 962s	931vw, 912vw, 830s, 755w	625m, 600s, 533sh, 485m, 440m
1395w, 1370m, 1358w	1295vw, 1260m, 1240w, 1162m, 1134m	1122sh, 1110s, 1090m, 1076m, 1048s, 1033sh, 1020vw, 995s, 965s, 958s	928vw, 910vw, 830s, 750w	609s, 520w, br 482m, 430m
1390w, 1375m, 1355w, 1320w,br	1302vw, 1275sh, 1268m, 1245w	[c]	932w, 900sh, 885s, 798w	[d]
1380m, 1354w	[c]	[c]	918m, 840vw	[d]
1378w, 1370sh	1325w	1090vs,br, 1006vs	—	532s, 440w
1375w, 1350sh	1322m	1080vw, br, 1000vs	—	530s, 432w
1350vw	1325m	(1230sh, 1165s, 1140s, 1105vs, 1065sh)[e] 1082s, 1010vs	978w[f]	(640sh, 620sh, 612s)[g] 530s, 430sh
1380w, 1361w	1320m, 1265w, 1261m	1115m, 1095sh, 1085m, 1055m, 1018s, 989vs, 980vs, 950vs	848w	615s, 595s, 555w, 470sh, 462s
1388m, 1372m, 1344 vw	1316w, 1305vw, 1270m, 1240w, 1140s, 1130sh	1090m, 1062m, 1044m, 1001s	932vw, 910s, 860w	595s, 553m, 450m

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[d] Spectra are complicated and are not distinguishable due to the overlapping of sulphate (ν_4) and ligand bands.

[e] Due to ν_3 of sulphate group.

[f] Due to ν_1 of sulphate group.

[g] Due to ν_4 of sulphate group.

Infrared spectra in KBr (4000–400 cm^{-1}) and in polythene (400–200 cm^{-1}, in some cases) were recorded using a Beckman IR-20A and a Perkin-Elmer 783 IR spectrophotometer, respectively and the corresponding data are given in Table 3.

RESULTS

$[Cd(en)_3]Cl_2 \cdot H_2O$ (**1**) starts to lose its water molecule at 80°C and becomes anhydrous at 112°C (Fig. 1, Table 2). The anhydrous species is not at all stable and starts to lose en immediately after dehydration and becomes $[Cd(en)Cl_2]$ at 174°C through a nonisolable intermediate $[Cd(en)_2Cl_2]$. $[Cd(en)Cl_2]$ is thermally stable up to 260°C. On further heating, it decomposes to $CdCl_2$ through a nonisolable hemi(diamine) species, $[Cd(en)_{0.5}Cl_2]$. The DTA curve shows a total of five endothermic peaks for the elimination of water (140°C): first molecule of en (145°C); second molecule of en (168°C); half of the third molecule of en (313°C); the last one at 330°C is due to the melting of the $[Cden_{0.5}Cl_2]$ species. An exothermic peak at 342°C is due to the elimination of residual diamine.

$[Cd(en)_3]Br_2 \cdot 2\ H_2O$ (**2**) becomes anhydrous at 72°C in a single step (Fig. 2, Table 2). The anhydrous species is stable up to 105°C. On further heating, $[Cd(en)_3]Br_2$ loses one molecule of en and becomes $[Cd(en)_2Br_2]$ at 155°C.

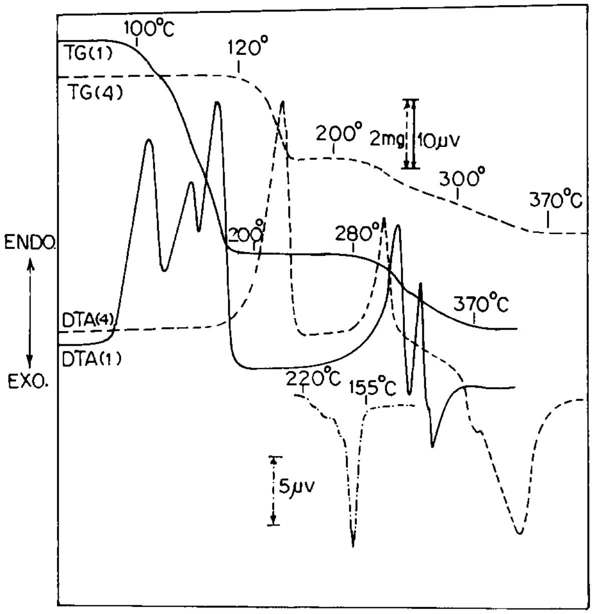

Fig. 1. Thermal curves of (————) $[Cd(en)_3]Cl_2 \cdot H_2O$, sample mass 16.68 mg; (- - - - - -), $[Cd(tn)_2Cl_2]$, sample mass 10.74 mg; and (– · – · –) cooling curve of $[Cd(tn)_2Cl_2]$ after heating the sample to 245°C. Sample mass 10.51 mg.

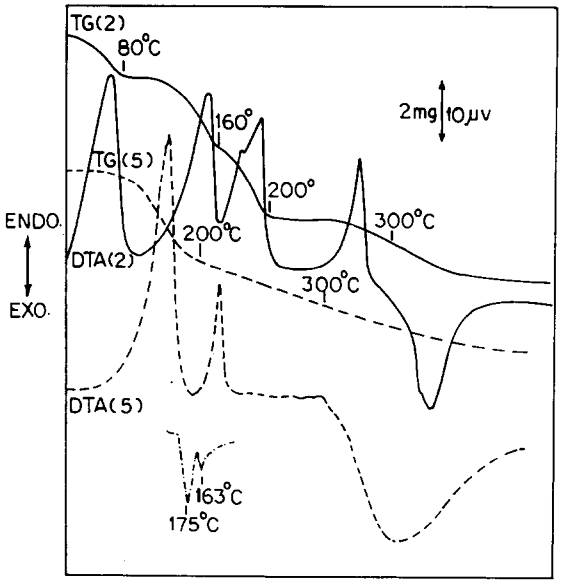

Fig. 2. Thermal curves of (————) $[Cd(en)_3]Br_2 \cdot 2\,H_2O$, sample mass 16.94 mg; (- - - - -) $[Cd(tn)_2Br_2]$, sample mass 15.28 mg; and (– · – · –) cooling curve of $[Cd(tn)_2Br_2]$ after heating the sample to 220°C, sample mass 15.35 mg.

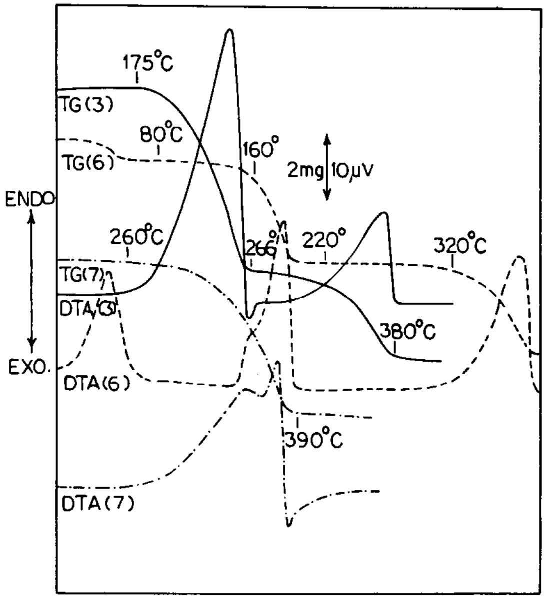

Fig. 3. Thermal curves of (————) $[Cd(en)_3]SO_4$, sample mass 16.90 mg; (- - - - -) $[Cd(tn)_2SO_4] \cdot H_2O$, sample mass 14.70 mg; and (– · – · –) $[Cd(tn)SO_4]$, sample mass 18.3 mg.

The bis(diamine) compound is not very stable at that temperature and decomposes to [Cd(en)Br_2] at 200°C in two steps as supported by its DTA profile. Here, the DTA shows two overlapping endothermic peaks at 180 and 195°C for the reaction [Cd$(en)_2Br_2$] → [Cd(en)Br_2] + en. [Cd(en)Br_2] is thermally stable up to 250°C. [Cd(en)Br_2] melts with decomposition at 250°C and becomes [Cd$(en)_{0.5}Br_2$] at 310°C, giving an endothermic peak at 272°C. [Cd$(en)_{0.5}Br_2$] starts to decompose as soon as it is formed and decomposes to $CdBr_2$ giving two overlapping exothermic peaks at 322 and 328°C.

[Cd$(en)_3$]SO_4 (**3**) starts to decompose at 175°C and generates thermally isolable [Cd(en)SO_4] at 266°C in a single step as observed from its TG curve. The corresponding DTA curve, however, shows a prominent endotherm followed by an exotherm (Fig. 3). The derived mono species decomposes at 284°C and transforms to $CdSO_4$ in a single step showing an endotherm in the DTA profile.

[Cd$(tn)_2Cl_2$] (**4**) starts to decompose at 118°C and generates [Cd(tn)Cl_2] at 167°C in a single step (Fig. 1, Table 2). The mono(diamine) complex melts at 215°C with decomposition and transforms to $CdCl_2$. The endothermic peak at 241°C is due to the melting and decomposition of the [Cd(tn)Cl_2] species. Two overlapping exothermic peaks at 314 and 347°C are due to further decomposition of the melted [Cd(tn)Cl_2] to $CdCl_2$. One interesting observation is that after completion of the endotherm at 241°C, five exothermic peaks are obtained, overlapping with each other (Fig. 1) in the temperature range 230–155°C, during cooling.

[Cd$(tn)_2Br_2$] (**5**) starts to decompose at 120°C and becomes [Cd(tn)Br_2] at 218°C (Fig. 2). One endothermic shoulder at 174°C and two endothermic peaks at 177 and 218°C in the DTA curve are observed in the temperature range 120–218°C. The endothermic peak at 218°C does not correspond with any noticeable mass-loss. [Cd(tn)Br_2] decomposes to $CdBr_2$ giving a broad exothermic peak in the DTA profile. Here, also, we get two exothermic peaks at 175°C and at 165°C during cooling after heating the sample to 220°C. If the sample heated to 190°C is cooled, an exotherm at 164°C is obtained. The same sample gives two distinctly separate endotherms if heated again, at 167 and 218°C without showing any mass-loss.

[Cd$(tn)_2SO_4$]$\cdot H_2O$ (**6**) starts deaquation at 35°C and becomes anhydrous at 60°C in a single step. On further heating, [Cd$(tn)_2SO_4$] starts to decompose at 140°C and transforms to thermally isolable [Cd(tn)SO_4]. The TG and DTA profiles indicate the elimination of the first mole of ligand taking place in two overlapping steps. The derived mono species starts to decompose at 300°C and transforms to $CdSO_4$ at 395°C in a single step as illustrated by its thermal profile.

[Cd(tn)SO_4] (**7**), synthesized from solution, decomposes at 290°C and affords $CdSO_4$ at 390°C. Its DTA curve shows, initially, an endothermic shoulder followed by two overlapping endotherms followed by an exotherm; although its TG curve does not show the deamination taking place in more than one step.

DISCUSSION

1,2-Diaminoethane complexes of Cd^{2+} are reported in the literature [10–12], but their thermal studies are not yet known. Recently, the thermal investigation of $[Zn(en)_3]X_2 \cdot H_2O$ [$X = Cl^-$ or Br^-] was reported [8], but $[Zn(en)_3]Cl_2$ was not isolated. Also the synthesis of anhydrous $[Cd(en)_3]Cl_2$ is not at all feasible. However, the synthesis of $[Cd(en)_3]Br_2$ is possible either by heating to a desirable temperature (Fig. 1, Table 2) or by vacuum treatment. As chlorine is more electronegative than bromine, the hydrogen bonding between an H_2O hydrogen and a Cl ion is more feasible, which causes higher stability of the lattice water in the $CdCl_2$ complex. This was also observed in the complexes $[Zn(en)_3]X_2 \cdot H_2O$ ($X = Cl^-$ or Br^-) [8].

Thermal profiles of $[Cd(en)_3]X_2$ ($X = Cl^-$, Br^- and $\frac{1}{2}SO_4^{2-}$) appear simple in comparison to those of the corresponding zinc complexes. Diamine is chelated and possesses a *gauche* configuration in $[Cd(en)_2Br_2]$ synthesized by the temperature-arrest technique. $[Cd(en)_2Br_2]$ is undoubtedly *cis* and possesses O_h configuration as evident from IR assignments [10–15]. Furthermore, IR spectra of $[Cd(en)_2Br_2]$ give close resemblance to those of *cis*$[Ni(en)_2Br_2]$ [5], indicating that these two bis species are probably isostructural. It is interesting to note that $[Cd(en)_2Br_2]$ decomposes to $[Cd(en)Br_2]$ in two steps, whereas its chloro-analogue decomposes in a single step, probably due to the size of the anion. $[Cd(en)_3]X_2$ ($X = Cl^-$ or Br^-) decomposes through bis species; on the contrary, $[Cd(en)_3]SO_4$ transforms to $[Cd(en)SO_4]$ in a single step which is probably due to the noncoordination of the SO_4 anion. The exothermic peak observed at 266°C may be due to some rearrangement taking place in $[Cd(en)SO_4]$ just after its formation, but it is difficult to define the type of rearrangement occurring here, since this exotherm is not reversible. Diamine is found to be bridged and possess a *trans* configuration in $[Cd(en)X_2]$ ($X = Cl^-$, Br^- and $\frac{1}{2}SO_4^{2-}$) derived pyrolytically, since these complexes give very simple and similar IR spectra like the $[Cd(en)Br_2]$ complex reported earlier [12].

It is well known that the effect of size makes Cd^{2+} more likely to assume a coordination number of six than Zn^{2+} [16]. The remarkable difference in IR spectra between $[Cd(tn)_2Cl_2]$ and $[Zn(tn)_2]Cl_2$ [8], the similarity with *cis*$[Ni(tn)_2X_2]$ ($X = Cl^-$, Br^- or $\frac{1}{2}SO_4^{2-}$) [5,7], and the presence of bands at 350 and 315 cm^{-1} in far-IR spectra, conclude that the bis(dihalodiamine)Cd^{2+} complexes possess O_h configuration. Far-IR spectra of $[Cd(tn)_2Cl_2]$ and $[Cd(tn)_2Br_2]$ (Fig. 4) show that bands at 350 and 315 cm^{-1} are absent in the bromo analogue. This observation indicates that these bands are due to ν_t(Cd–Cl) stretching vibrations [17,18]. However, similar spectral data of $[Cd(tn)_2Cl_2]$, $[Cd(tn)_2Br_2]$ and $[Cd(tn)_2SO_4]$ suggest that they are probably isostructural. The foregoing discussion helps to conclude that the latter three 1,3-diaminopropane complexes possess *cis* octahedral configuration. Diamine is found to be chelated in $[Cd(tn)Cl_2]$, whereas

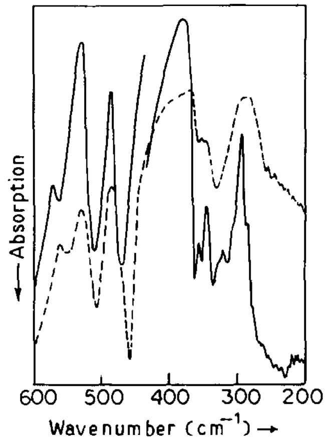

Fig. 4. IR spectra of (———) $[Cd(tn)_2Cl_2]$, and (- - - - -) $[Cd(tn)_2Br_2]$.

diamine is bridged in the $[Zn(tn)Cl_2]$ complex [8]. The IR spectra of $[Zn(tn)Cl_2]$ show twelve peaks and one shoulder, whereas those of $[Cd(tn)Cl_2]$ show 21 peaks and three shoulders, region 1600–400 cm^{-1} (Table 3), where most of the tn fundamental vibration modes occur. The complicated IR spectrum of $[Cd(tn)Cl_2]$ supports the chelation behaviour of tn [5,12]. Far IR spectra of $[Cd(tn)Cl_2]$ show the presence of a strong band at ~ 290 cm^{-1} which concludes that the compound probably possesses same structure as those reported for $[Cd(tn)Cl_2]$ [19] and $[Cd(chelate)X_2]$ [chelate = 2,2-dimethyl-1,3-diaminopropane, $X = Cl^-$ or Br^-] [20]. $[Cd(tn)SO_4]$ was prepared in two ways; one from solution and the other by the thermolysis of $[Cd(tn)_2SO_4]$. Both the $[Cd(tn)SO_4]$ complexes give exactly similar IR spectra and fewer bands in the region 1600–400 cm^{-1} compared to $[Cd(tn)Cl_2]$, which indicates a polymeric bridging character [12] of 1,3-diaminopropane in the complexes. Although the two $[Cd(tn)SO_4]$ complexes are indistinguishable by their IR spectra, they seem to be structurally different as their thermal decomposition patterns are not the same (Fig. 3). It is a very interesting fact that $[Cd(tn)Cl_2]$ shows five overlapping exotherms in the temperature range 230–155°C (Fig. 1) while cooling after heating to 245°C. As a result, the endotherm observed at 241°C in the heating curve is not only due to melting but also accounts for some kind of reversible phase transition.

$[Cd(tn)Br_2]$ melts at 218°C although it was not isolated. The two exothermic peaks observed at 173 and 165°C during the cooling of the melted sample are due to the solidification of the mass and some kind of reversible phase transition, respectively.

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