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Thermal Studies of 1,2-Propanediamine Complexes of Zinc(II) and Cadmium(II) in the Solid Phase

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$[ML_3]X_2 \cdot nH_2O$, where $M = Zn^{II}$ and Cd^{II}; L = 1,2-propanediamine; $X = Cl^-$, Br^-, $0.5SO_4^{2-}$, and $0.5SeO_4^{2-}$ and $n = 1$, 1.5, and 2, have been synthesized and their thermal investigations carried out. $ZnL_{1.5}Cl_2$, $CdL_{1.5}X_2$ ($X = Cl^-$ and Br^-), and $CdLX_2$ ($X = Cl^-$, $0.5SO_4^{2-}$, and $0.5SeO_4^{2-}$) have been synthesized pyrolytically in solid state from their parent diamine complexes. These $ML_{1.5}X_2$ complexes are expected to exist as $[ML_3][MX_4]$. Only $[CdL_3][CdBr_4]$ species has been synthesized from solution. Syntheses of $ZnLCl_2$, $CdLCl_2$, and $CdLBr_2$ from solution have also been reported. IR spectra suggest that symmetry of the chelate ring in mono(diamine) complexes is lowered in comparison to the other complexes. $ML_{1.5}Cl_2$ show isomorphism with each other. Thermal stability sequence of $[ML_3]X_2$ ($X = Br^-$, $0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$) is $SO_4^{2-} < SeO_4^{2-} \leqslant Br^-$. $[ZnL_3]X_2$ and $ZnLX_2$ appear thermally more stable than those of cadmium complexes. All these complexes are thermally less stable than those of 1,2-ethanediamine complexes reported by us earlier.

We carried out thermal investigations of a good number of diamine complexes, synthesized several novel diamine complexes pyrolytically in solid state from the parent diamine complexes[1–7] and noticed, several interesting observations relating to the structures of diamine complexes derived in solid state with respect to the parent diamine complexes. Recently, we reported the thermal behavior of 1,2-propanediamine complexes of nickel(II)[8] and observed some noticeable difference in the thermal behavior from those of 1,2-ethanediamine and 1,3-propanediamine complexes of nickel(II) due to the methyl substitution in the methylene group of the diamine.

The coordination chemistry of d^{10} metal(II) is interesting. They show a variety of coordination numbers and geometries. The chemistry of diamine complexes of d^{10} metal(II) halides are now well established. Although the chemistries of zinc and cadmium are very similar, it is found that the effect of size is to make Cd^{II} more likely than Zn^{II} to assume a coordination number six.[9] In this context thermal studies on 1,2-propanediamine complexes of MX_2 ($M = Zn^{II}$ and Cd^{II}; $X = Cl^-$, Br^-, $0.5SO_4^{2-}$, and $0.5SeO_4^{2-}$) are relevent.

Experimental

Preparation of the Complexes. $[ZnL_3]Cl_2 \cdot 2H_2O$ (**1**), $[ZnL_3]Br_2 \cdot 1.5H_2O$ (**2**), $[CdL_3]Cl_2 \cdot 2H_2O$ (**5**), and $[CdL_3]Br_2 \cdot 2H_2O$ (**6**): 1,2-propanediamine (4 mmol) was added dropwise with vigorous stirring to MX_2 ($M = Zn^{II}$ or Cd^{II}; $X = Cl^-$ or Br^-) (1 mmol) dissolved in ethanol. The desired complexes were separated out and purified by washing with ethanol.

$CdLCl_2$ (5b) and $CdLBr_2$ (6b). These complexes were prepared by stoichiometric addition of the ligand to the metal salts adopting similar procedure as described above.

$[ZnL_3]SO_4 \cdot H_2O$ (3), $[ZnL_3]SeO_4 \cdot 1.5H_2O$ (4), $[CdL_3]SO_4$ (7), and $[CdL_3]SeO_4 \cdot 1.5H_2O$ (8). 1,2-Propanediamine (4 mmol) was added dropwise with vigorous stirring to MX_2 [$M = Zn^{II}$ or Cd^{II}; $X = 0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$] (1 mmol) dissolved in minimum quantity of water. The derived com-

TABLE 1. ANALYTICAL DATA OF 1,2-PROPANEDIAMINE(L) COMPLEXES OF ZINC(II) AND CADMIUM(II)

Compound		Elemental analyses/%[a]		
		Metal	Nitrogen	Halogen/sulfur/selenium
$[ZnL_3]Cl_2 \cdot 2H_2O$	(**1**)	16.3(16.6)	20.9(21.3)	17.6(18.0)
$ZnL_{1.5}Cl_2$[b]	(**1a**)	26.1(26.4)	16.8(16.9)	28.6(28.7)
$[ZnL_3]Br_2 \cdot 1.5H_2O$	(**2**)	13.5(13.8)	17.7(17.7)	33.8(33.7)
$[ZnL_3]SO_4 \cdot H_2O$	(**3**)	16.3(16.3)	20.5(20.9)	7.6(7.9)
$[ZnL_3]SeO_4 \cdot 1.5H_2O$	(**4**)	14.4(14.3)	18.1(18.3)	16.8(17.2)
$[CdL_3]Cl_2 \cdot 2H_2O$	(**5**)	25.4(25.5)	19.1(19.0)	15.9(16.1)
$CdL_{1.5}Cl_2$[b]	(**5a**)	37.9(38.2)	14.1(14.3)	23.8(24.1)
$CdLCl_2$[b]	(**5b**)	43.8(43.7)	10.7(10.9)	27.6(27.6)
$[CdL_3]Br_2 \cdot 2H_2O$	(**6**)	21.2(21.2)	15.8(15.8)	29.8(30.1)
$CdL_{1.5}Br_2$[b]	(**6a**)	29.2(29.3)	10.7(10.9)	41.1(41.7)
$CdLBr_2$	(**6b**)	32.3(32.4)	8.0(8.1)	46.0(46.2)
$[CdL_3]SO_4$[c]	(**7**)	25.8(26.1)	19.2(19.5)	7.5(7.4)
$CdLSO_4$[b]	(**7b**)	39.5(39.8)	9.5(9.9)	11.1(11.3)
$[CdL_3]SeO_4 \cdot 1.5H_2O$	(**8**)	21.9(22.3)	16.5(16.6)	15.0(15.6)
$CdLSeO_4$[b]	(**8b**)	33.7(34.1)	8.2(8.5)	23.4(23.9)

a) Figures in parentheses are the required percentages. b) Synthesized in the solid state. c) Analyzed in anhydrous form.

plexes were separated out on evaporating the mixture on a constant temperature bath (50±2 °C). The zinc and cadmium complexes were purified by washing with ethanol and isopropanol, respectively.

*$[CdL_3][CdBr_4]$ (**6a**).* To the aqueous solution (2 ml) of 1 mmol, $[CdL_3]Br_2\cdot 1.5H_2O$, 1 mmol $[Et_4N]_2[CdBr_4]$ (dissolved in 10 ml acetonitrile) was added with stirring. To the resulting solution ether was added till the desired product was separated out. It was purified by washing with ether. All the complexes were dried in $CaCl_2$ desiccator.

*$ZnL_{1.5}Cl_2$ (**1a**), $CdL_{1.5}Cl_2$ (**5a**), and $CdL_{1.5}Br_2$ (**6a**).* These complexes were synthesized by keeping the complexes **1**, **5**, and **6** at 170, 145, and 165 °C, respectively, following the method reported earlier.[4,5,7] Similarly $CdLCl_2$ (**5b**), $CdLSO_4$ (**7b**), and $CdLSeO_4$ (**8b**) were prepared from complexes **5**, **7**, and **8** at 210, 235, and 235 °C, respectively. Thermal curves do not tally the temperatures at which thermolytic syntheses were carried out. The respective temperatures are very much optimum for isolation of the complexes in pure form.

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

The apparatus employed for carrying out thermal analysis is same as reported earlier.[1–8] Tables 2a and 2b list the thermal data.

Results and Discussion

Diamine Complexes of Zinc Chloride. IR spectra (Table 3a) of $[ZnL_3]Cl_2\cdot 2H_2O$ (**1**) show that the diamines are chelated in it.[10] This tris species starts deaquation at 65 °C and transforms to $ZnL_{1.5}Cl_2$ (**1a**) at 175 °C showing three endothermic peaks in the DTA curve overlapping to each other (Fig. 1). Isolation of deaquated species is not feasible here like the

TABLE 2a. THERMAL PARAMETERS OF 1,2-PROPANEDIAMINE(L) COMPLEXES OF ZINC(II)

Decomposition reaction	Temperature range/°C	DTA peak temperature/°C
$[ZnL_3]Cl_2\cdot 2H_2O$ (**1**) → $ZnL_{1.5}Cl_2$ (**1a**)	65—175	105, 135, 165
$ZnL_{1.5}Cl_2$ → $ZnLCl_2$	185—270	205, 229, 247
$ZnLCl_2$ → $ZnCl_2$	270—410	365
$[ZnL_3]Br_2\cdot 1.5H_2O$ (**2**) → $[ZnL_3]Br_2\cdot H_2O$	55— 82	75
$[ZnL_3]Br_2\cdot H_2O$ → $[ZnL_3]Br_2$	82—125	115
$[ZnL_3]Br_2$ → ZnL_2Br_2	140—217	185, 205
ZnL_2Br_2 → $ZnLBr_2$	217—310	220
$ZnLBr_2$ → $ZnBr_2$	310—405	368, 375
$[ZnL_3]SO_4\cdot H_2O$ (**3**) → $[ZnL_3]SO_4$	45— 85	82
$[ZnL_3]SO_4$ → ZnL_2SO_4 (**3a**)	85—130	120
ZnL_2SO_4 → $ZnLSO_4$	185—270	260
$ZnLSO_4$ → $ZnSO_4$	270—390	305, 388, 358[a], 372
$[ZnL_3]SeO_4\cdot 1.5H_2O$ (**4**) → $[ZnL_3]SeO_4\cdot H_2O$	40— 75	70
$[ZnL_3]SeO_4\cdot H_2O$ → $[ZnL_3]SeO_4$	75—105	90
$[ZnL_3]SeO_4$ → ZnL_2SeO_4 (**4a**)	120—165	155
ZnL_2SeO_4 → $ZnSeO_4$	217—392	260, 280[a]

a) Denotes exothermic peaks, rest are endothermic.

TABLE 2b. THERMAL PARAMETERS OF 1,2-PROPANEDIAMINE(L) COMPLEXES OF CADMIUM(II)

Decomposition reaction	Temperature range/°C	DTA peak temperature/°C
$[CdL_3]Cl_2\cdot 2H_2O$ (**5**) → $CdL_{1.5}Cl_2$ (**5a**)	75—150	115, 145
$CdL_{1.5}Cl_2$ → $CdLCl_2$ (**5b**)	165—210	205
$CdLCl_2$ → $CdCl_2$	245—355	265, 330[a], 332, 337
$[CdL_3]Br_2\cdot 2H_2O$ (**6**) → $[CdL_3]Br_2\cdot H_2O$	50— 80	70
$[CdL_3]Br_2\cdot H_2O$ → $[CdL_3]Br_2$	80—100	95
$[CdL_3]Br_2$ → $CdL_{1.5}Br_2$ (**6a**)	100—170	165
$CdL_{1.5}Br_2$ → $CdBr_2$	180—355	200, 230, 328, 330, 340
$[CdL_3]SO_4$ (**7**) → CdL_2SO_4 (**7a**)	82—123	118
CdL_2SO_4 → $CdLSO_4$ (**7b**)	180—239	232
$CdLSO_4$ → $CdL_{0.66}SO_4$	245—272	265
$CdL_{0.66}SO_4$ → $CdSO_4$	282—322	288, 318
$[CdL_3]SeO_4\cdot 1.5H_2O$ (**8**) → $[CdL_3]SeO_4\cdot H_2O$	50— 66	63
$[CdL_3]SeO_4\cdot H_2O$ → $[CdL_3]SeO_4$	66—100	88
$[CdL_3]SeO_4$ → CdL_2SeO_4 (**8a**)	100—135	125
CdL_2SeO_4 → $CdLSeO_4$ (**8b**)	190—240	231
$CdLSeO_4$ → $CdSeO_4$	255—305	288, 294[a]

a) Denotes exothermic, rest are endothermic.

Table 3a. IR spectral data (4000—600 cm^{-1}) of 1,2-propanediamine(L) complexes of zinc(II) and cadmium(II) in KBr

Compound	Assignments							
	$\nu(NH_2)$	$\nu(CH_2)$	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_w(CH_2)$	$\tau(NH_2)+\rho_w(NH_2)$ $+\tau(CH_2)$	Stretching vibration of skeleton ν(C-N)+ν(C-C)	$\rho_r(CH_2)$
$[ZnL_3]Cl_2\cdot 2H_2O$[a]	3315 s , 3280 s , 3235 s , 3160 m	2960 m, 2935 m, 2870 m	1590 ms, 1557 sh	1462 sh, 1455 m,	1388m, 1378 sh, 1370 m	1336 w, 1303 m, 1227 vw, 1192 m, 1149 m	1100 w, 1070 ms, 1027 sh, 1015 vs, 985 sh	932 m, 900 vw, 835 w, 630 mb
$ZnL_{1.5}Cl_2$	3315 s , 3260 ms, 3170 m	2960 m, 2930 m, 2875 w	1580 ms, 1560 sh	1455 w	1390 w 1370 w	1330 vw, 1305 w, 1265 vw, 1190 w, 1140 w	1100 w, 1065 m, 1028 sh, 1010 vs, 984 sh	930 m, 900 vw, 835 w, 625 mb
$[CdL_3]Cl_2\cdot 2H_2O$[a]	3315 s , 3275 s , 3235 s , 3160 m	2960 ms, 2930 m, 2975 m	1585 s , 1555 sh	1458 m	1390 m, 1370 m,	1347 vw, 1335 vw, 1302 w, 1265 vw, 1182 m, 1135 ms	1095 w, 1055 s , 1000 sbr	922 ms, 898 w, 821 w, 650 sh,
$CdL_{1.5}Cl_2$	3315 vs, 3255 s , 3160 w	2950 ms, 2920 m, 2870 m	1575 ms, 1555 sh	1455 w	1380 w, 1370 w	1325 vw, 1300 w, 1260 vw, 1180 w, 1120 w	1095 w, 1050 m, 990 vs	920 ms, 890 w, 820 w, 650 w
$CdLCl_2$	3322 s , 3300 vs, 3272 ms, 3245 s , 3150 w	2998 sh, 2960 m, 2940 m, 2919 sh, 2879 w	1582 s , 1560 w	1468 w, 1460 w, 1450 w	1392 m, 1378 w	1327 vw, 1305 w, 1260 vw, 1192 m, 1130 m	1100 w, 1055 m, 1038 ms, 1027 m, 1001 s	930 m, 899 vw, 828 w, 615 ms
$CdL_{1.5}Br_2$	3320 vs, 3255 s , 3155 w	2955 ms, 2920 m, 2870 m	1575 s , 1555 sh	1455 w	1390 w, 1375 w	1330 vw, 1305 w, 1260 vw, 1180 m, 1120 w	1090 w, 1050 m, 978 vs	922 ms, 890 w, 821 w, 655 vw
$CdLSO_4$	3322 s , 3300 vs, 3265 ms, 3240 s , 3140 w	2960 m, 2935 m, 2918 sh, 2875 m	1578 s , 1555 sh	1465 w, 1450 w, 1447 w, 1442 sh	1388 m, 1370 w	1320 vw, 1300 w, 1258 vw, 1185 sh b)	1041 ms, 1027 s , 1015 ms, 991 s , 978 m[c]	920 m, 890 w, 820 w, 610 vs, 605 sh
$CdLSeO_4$	3322 s , 3300 vs, 3265 ms, 3240 vs, 3140 w	2960 m, 2935 m, 2918 sh, 2875 m	1578 s , 1555 sh	1460 w, 1450 w, 1445 w, 1440 sh	1388 w, 1370 w	1320 vw, 1300 w, 1258 vw, 1183 m, 1132 m	(1118 m, 1041 ms, 1108 m)[d], 1026 s , 1099 m, 1015 ms, 1090 sh[d], 991 s	920 m, 602 ms, (898 vs, 875 vs, 833 m)[d], 820 vw

a) Bands due to H_2O vibration are omitted; spectra of the other tris complexes are similar. b) Spectra complicated, not distinguishable due to overlapping of sulfate and ligand bands. c) Bands due to SO_4^{2-} vibration. d) Bands due to SeO_4^{2-} vibration: vs=very strong, s=strong, ms=medium strong, m=medium, w=weak, vw=very weak, sh=shoulder.

Table 3b. Far-infrared spectral data[a)] (600—100 cm^{-1}) of 1,2-propanediamine(L) complexes of zinc(II) and cadmium(II) in polythene disc

Compound	Assignments		
	$\rho_r(NH_2)+\nu(M\text{-}N)$ + chelate ring bend	$\nu_t(M\text{-}X)$	$\nu_b(M\text{-}X)$
$ZnL_{1.5}Cl_2$	528 s, 520 sh, 442 vs, 430 sh, 340 sh	279 vs br, 126 w	—
$CdL_{1.5}Cl_2$	580 s, 515 m, 435 s, 425 sh, 340 m	280 w, 260 vs, 245 vs	—
$CdLCl_2$	570 sh, 530 m, 461 m, 447 ms, 358 m	268 s	184 vs, 178 vs
$CdL_{1.5}Br_2$	595 s, 525 w, 505 w, 435 m, 422 m, 340 w	188 vs, 170 vs	—
$CdLSO_4$	565 sh, 518 m, 450 m, 422 ms, 345 w	—	—
$CdLSeO_4$	565 sh, 518 m, 449 m, 419 ms, 408 s[b)], 345 w	—	—

a) Done in FT-IR spectrometer, Polytec FIR 30. vs=very strong, br=broad, s=strong, ms=medium strong, m=medium, w=weak, sh=shoulder. b) Band due to SeO_4^{2-} vibration.

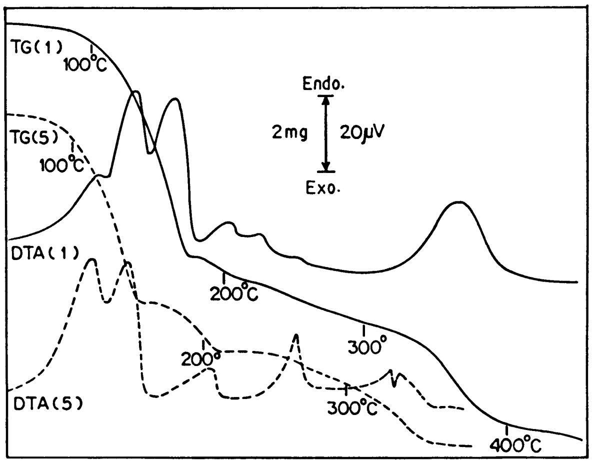

Fig. 1. Thermal curves of ——, $[ZnL_3]Cl_2\cdot 2H_2O$ (**1**) and - - -, $[CdL_3]Cl_2\cdot 2H_2O$ (**5**). Sample weights: **1**, 16.75 mg: **5**, 15.30 mg.

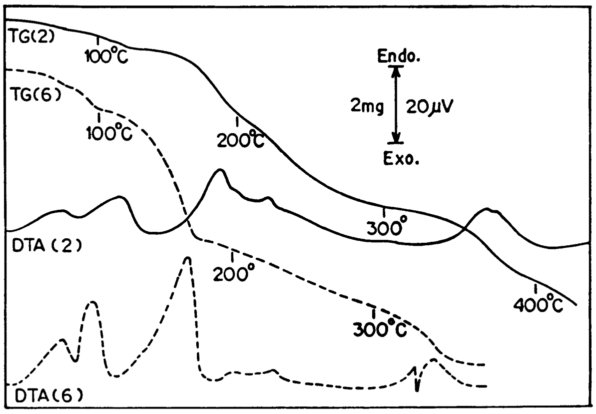

Fig. 2. Thermal curves of ——, $[ZnL_3]Br_2\cdot 1.5H_2O$ (**2**) and - - -, $[CdL_3]Br_2\cdot 2H_2O$ (**6**). Sample weights: **2**, 13.46 mg: **6**, 16.62 mg.

corresponding 1,2-ethanediamine complex.[4)] The synthesis of $ZnL_{1.5}Cl_2$ in solid state appears very interesting as such type of zinc diamine complex species is not known in literature although we reported[7)] the synthesis of $NiL_{1.5}Cl_2$ (L=1,4-butanediamine), where diamine behaves as chelating as well as bridging bidentate ligand. The complex **1a** may be presumed to exist in dimeric form. But dimerization of the complex **1a** becomes possible if one ligand (L) acts here as bridging bidentate. Interesting observation is that IR spectra of complex **1** and **1a** show practically no difference with respect to diamine bands (Table 3a). This observation does not support the bridging behavior of diamine in $ZnL_{1.5}Cl_2$.[†] So it may be thought that all the diamine present in complex **1a** are chelated which is possible if the species exists as $[ZnL_3][ZnCl_4]$. The far-infrared spectrum (Table 3b) of **1a** shows a very strong band at ≈279 cm^{-1} and a weak band at ≈126 cm^{-1} which supports the existence of $[ZnCl_4]^{2-}$ [13)] anion in complex. We tried to prepare this species from the equimolecular mixture of $[ZnL_3]Cl_2\cdot 2H_2O$ and $[Et_4N]_2[ZnCl_4]$, but we always obtained $ZnLCl_2$. On the other hand, synthesis of $[Fe(bpy)_3][FeBr_4]$[14)] from the pyrolysis of $[Fe(bpy)_3]Br_2$ in solid state does not rule out the above possibility. On further heating $ZnL_{1.5}Cl_2$ starts decomposition at 185 °C and transforms to $ZnCl_2$ through nonisolable intermediate $ZnLCl_2$ as supported from the TG curve (Fig. 1, Table 2a). Three broad overlapping endotherms in the DTA profile account the elimination of 0.5 molecule diamine per zinc atom from $ZnL_{1.5}Cl_2$. Endothermic peak appearing at 365 °C is due to the elimination of last molecule of diamine.

Diamine Complexes of Zinc Bromide. IR spectrum (Table 3a) of $[ZnL_3]Br_2\cdot 1.5H_2O$ (**2**) with respect to the diamine bands is similar to $[ZnL_3]Cl_2\cdot 2H_2O$ suggesting practically no difference in the nature of bonding between the two complex species. Complex **2** upon heating becomes anhydrous at 125 °C in two steps (Fig. 2, Table 2a). The anhydrous compound is isolable by temperature arrest technique. It decomposes at 140 °C and transforms to $ZnBr_2$ at 405 °C through the formation of unstable intermediates ZnL_2Br_2 and $ZnLBr_2$ as is evident from the TG curve. Three overlapping endotherms account for the elimination of two molecules of diamine per zinc atom. Last two overlapping endotherms account for the elimination of residual diamine (Fig. 2). None of the inter-

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[†] It is well established fact that different IR active vibrations will be allowed for chelated and bridged diamine in the respective metal complexes.[10–12)] If there is any real evidence for bridging as well as chelating behavior of diamine in complex (**1a**), then it should show some distinguishable difference in IR spectrum from that of (1).

mediate species is isolable in solid state by arresting temperature.

Diamine Complexes of Zinc Sulfate. $[ZnL_3]SO_4 \cdot H_2O$ (**3**) shows almost similar IR spectra with that of complex **1**. It becomes anhydrous at 85 °C showing an endothermic peak at 82 °C in DTA curve. On further heating the dehydrated complex starts to lose diamine and transforms to ZnL_2SO_4 (**3a**) at 130 °C (Fig. 3) showing an endothermic peak at 120 °C in DTA curve. We could not characterize the derived bis species owing to its extreme hygroscopic nature. So the prediction about the role of the SO_4^{2-} in the complex ZnL_2SO_4 is not possible here. But from our previous study[4] and the preference of tetracoordination of zinc(II) enables us to conclude that probably SO_4^{2-} is not coordinated here. On further heating the complex ZnL_2SO_4 decomposes in a complicated way. However, the TG curve indicates the decomposition taking place through the formation of an unstable intermediate $ZnLSO_4$.

Diamine Complexes of Zinc Selenate. IR spectra of $[ZnL_3]SeO_4 \cdot 1.5H_2O$ (**4**) show very close similarity with those of the complexes **1**, **2**, and **3**. It becomes anhydrous at 105 °C through the formation of monohydrate at 75 °C (Fig. 4). The anhydrous species starts decomposition at 120 °C and transforms to ZnL_2SeO_4 (**4a**) at 165 °C. Characterization of this bis species in solid state in anhydrous form is also not possible owing to the similar reason stated in the corresponding sulfate. The TG curve shows that it decomposes to $ZnSeO_4$ in single step. But the corresponding DTA curve shows an endotherm followed by an exotherm. The exothermic peak appearing at 280 °C might be due to the decomposition of ligand. This is very much likely as the residue obtained at 292 °C is $ZnSeO_4$+carbon.

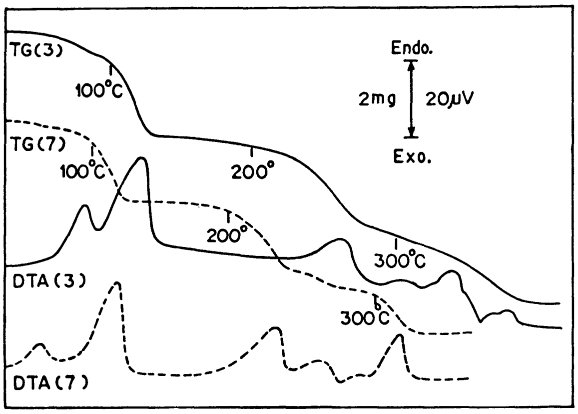

Fig. 3. Thermal curves of ——, $[ZnL_3]SO_4 \cdot H_2O$ (**3**) and - - -, $[CdL_3]SO_4$ (**7**). Sample weights: **3**, 12.21 mg: **7**, 10.96 mg.

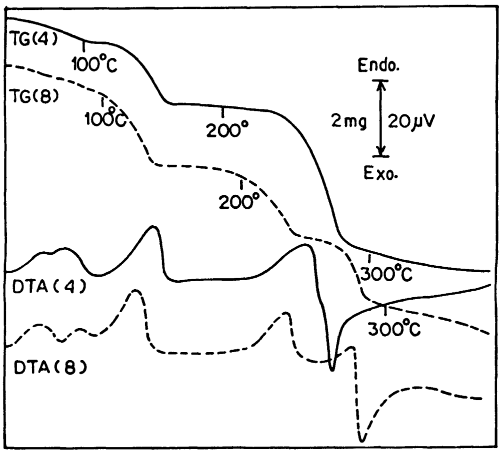

Fig. 4. Thermal curves of ——, $[ZnL_3]SeO_4 \cdot 1.5H_2O$ (**4**) and - - -, $[CdL_3]SeO_4 \cdot 1.5H_2O$ (**8**). Sample weights: **4**, 13.00 mg: **8**, 12.39 mg.

Diamine Complexes of Cadmium Chloride. IR spectrum of $[CdL_3]Cl_2 \cdot 2H_2O$ (**5**) (Table 3a) is similar to its zinc analogue. It starts deaquation at 75 °C and transforms to an isolable intermediate, $CdL_{1.5}Cl_2$ (**5a**) at 150 °C like that of complex (**1**) (Fig. 1). Here also, the later compound gives identical IR spectrum with that of its parent tris complex. Far-infrared spectrum (Table 3b) of $CdL_{1.5}Cl_2$ shows bands at 280(w), 260(s), and 245 cm^{-1} (s). These bands suggest here also the presence of $[CdCl_4]^{2-}$ anion in it[13,14] like that of zinc complex. It is noticed that the derived $[CdL_3][CdCl_4]$ appears to be isomorphous with $[ZnL_3][ZnCl_4]$ as is evident from their similar X-ray diffraction patterns (Table 4). Here also for comparative study we tried to prepare $[CdL_3][CdCl_4]$ by mixing $[CdL_3]Cl_2$ and $[Et_4N]_2[CdCl_4]$ in 1 : 1 proportion but failed to prepare it in pure form owing to the presence of $CdLCl_2$ in appreciable amount which could not be separated by

Table 4. The prominent lines in the X-ray powder photographs of the diamine complexes[a)]

$ZnL_{1.5}Cl_2$	$CdL_{1.5}Cl_2$	$CdL_{1.5}Br_2$[b)]
d, Å	d, Å	d, Å
8.80 vs[a)]	8.76 vs	7.44 w
5.70 s	6.78 s	6.42 s
5.29 s	5.44 w	5.81 w
4.84 m	4.90 m	5.16 vw
4.56 m	4.47 s	4.80 w
4.26 w	4.02 m	4.45 s
3.86 s	3.78 w	3.98 vw
3.53 w	3.62 vw	3.66 s
3.42 w	3.38 m	3.47 w
3.29 vw	3.23 vw	3.24 vw
2.93 vw	2.78 m	3.04 s
2.67 m	2.68 m	2.83 m
2.48 w	2.48 vw	2.68 vw
2.39 m	2.39 w	2.51 vw
2.18 w	2.26 w	2.38 w
2.06 w	2.13 vw	2.27 vw
2.00 vw	2.04 w	2.18 vw
1.93 vw	1.93 vw	2.10 s
1.88 m	1.80 w	1.99 w
1.77 vw	1.75 vw	1.90 w

vs=very strong, s=strong, m=medium, w=weak, vw=very weak. a) Intensities estimated visually. b) The X-ray powder photograph of $[CdL_3][CdBr_4]$ synthesized from solution is identical to it.

any means. The complex **5a** on further heating transforms to an isolable intermediate having composition CdLCl$_2$ (**5b**) unlike the corresponding zinc complex. IR spectra of this mono(diamine) species shows chelating bidentate character of the diamine whereas, CdenCl$_2$ synthesized by us earlier[5] possesses bridged en. CdLCl$_2$ synthesized from solution also shows similar physicochemical property with that of **5b**. Far-infrared spectral data of CdLCl$_2$ (**5b**) and CdLBr$_2$[††] (**6b**) are presented in Table 3b. Compariosn of the spectrum shows the presence of ν_t(Cd–Cl) at 268 cm^{-1} and ν_b (Cd–Cl) at 178 and 184 cm^{-1} in CdLCl$_2$ and ν_t(Cd–Br) at 207 cm^{-1} and ν_b(Cd–Br) at 154 and 163 cm^{-1} in CdLBr$_2$. These data clearly indicate the presence of bridging and terminal coordination of the halogen in the mono(diamine) complex. Reported crystal structure of analogous compound [Cd(dmpd)X$_2$][17] (dmpd =2,2-dimethyl-1,3-propanediamine) also corroborates our proposed bonding character of halogens and diamines to the metal ion. Again the splitting of the IR bands of the complex **5b** (Table 3a and b) in the region ≈3300, ≈1000, and 500 cm^{-1} which are due to ν_{NH_2}, ν_{CN}, and ν_{MN} indicate that the symmetry of the chelate ring is lowered in the complex. The decomposition of CdLCl$_2$ appears very complicated (Fig. 1). It initially melts showing an endothermic peak at 265 °C, then it decomposes and transforms to CdCl$_2$ at 355 °C. DTA curve shows overlapping endotherms as well as exotherm for the elimination of residual diamine from CdLCl$_2$.

Diamine Complexes of Cadmium Bromide. [CdL$_3$]-Br$_2$·2H$_2$O (**6**) starts decomposition at 50 °C and becomes anhydrous at 100 °C through the formation of monohydrate at 80 °C (Fig. 2, Table 2b). The derived anhydrous compound immediately starts decomposition and transforms to an isolable intermediate CdL$_{1.5}$Br$_2$ (**6a**) at 170 °C. This on further heating transforms to CdBr$_2$ at 355 °C. The DTA curve shows initially two overlapping endotherms for the elimination of water, then a prominent endotherm for the elimination of 1.5 molecule of diamine. The elimination of residual diamine occurs showing two overlapping broad endotherms and then an endotherm followed by one exotherm and endotherm (Fig. 2). IR spectra of CdL$_{1.5}$-Br$_2$, [CdL$_3$]Br$_2$, and CdL$_{1.5}$Cl$_2$ are very similar. The far-infrared spectral data of **6a** show bands at 170 and 188 cm^{-1} which are also found in [Et$_4$N]$_2$[CdBr$_4$][15] supporting the presence of [CdBr$_4$]$^{2-}$ anion in **6a**. Again we prepared [CdL$_3$][CdBr$_4$] from solution and observed similar thermal behavior, IR spectral data like CdL$_{1.5}$Br$_2$ (**6a**) isolated pyrolytically in solid state. X-ray powder patterns (Table 4) of two CdL$_{1.5}$Br$_2$ also appear same. The above observations suggest that the complex CdL$_{1.5}$Br$_2$ exists actually in [CdL$_3$][CdBr$_4$] form.

Diamine Complexes of Cadmium Sulfate. [CdL$_3$]-SO$_4$ (**7**) is hygroscopic in character. This complex starts decomposition at 82 °C and becomes CdL$_2$SO$_4$ (**7a**) at 123 °C (Fig. 3, Table 2b). Initial loss in TG curve and its corresponding endotherm in DTA curve (Fig. 3) is due to the elimination of water adsorbed while exposing the complex **7** in air. The derived bis species on further heating generates CdSO$_4$ at 322 °C through two intermediates, CdLSO$_4$ (**7b**) and CdL$_{0.66}$-SO$_4$ at 239 and 272 °C, respectively. The mono(diamine) species is isolable in solid state. The corresponding DTA curve shows altogether six endothermic peaks. The first three endotherms are due to water elimination and the first and second molecules of diamine, respectively. Fourth endotherm is due to elimination of 0.33 mole of diamine. The last two overlapping endotherms (Fig. 3) are due to elimination of 0.66 mole of diamine. Although we could not separate CdL$_{0.66}$SO$_4$ in pure form, but formation of this type of complex is not unlikely as literature show examples of this type of complex.[18,19] CdL$_2$SO$_4$ is also hygroscopic in nature like the corresponding zinc salts. As Cd^{II} prefers O$_h$ coordination and complex like [Cd(tn)$_2$SO$_4$] (tn=1,3-propanediamine)[5] is known, SO$_4$$^{2-}$ coordination is expected in this bis(diamine) species. IR spectrum of CdLSO$_4$ is almost identical to that of CdLCl$_2$ (Table 3a). The far-infrared spectra of these two complexes are also similar (Table 3b), though one could expect some M–O stretching vibration along with M–N stretching vibrations in the far-infrared region (500—200 cm^{-1}) owing to the coordination of SO$_4$$^{2-}$ to the metal atom. So it is clear that M–O stretching force constants are much smaller than the M–N stretching force constants here.[20]

Diamine Complexes of Cadmium Selenate. [CdL$_3$]-SeO$_4$·1.5H$_2$O (**8**) becomes anhydrous at 100 °C through the formation of monohydrate at 66 °C (Fig. 5). The derived anhydrous species immediately starts deamination and transforms to CdL$_2$SeO$_4$ (**8a**) at 135 °C. This on further heating decomposes at 190 °C and transforms to CdSeO$_4$ through the formation of an isolable intermediate, CdLSeO$_4$ (**8b**) at 240 °C. The corresponding DTA curve shows first an endotherm for the elimination of 0.5 mole of water, then an endotherm overlapping with another prominent endotherm for the elimination of residual water and one diamine molecule. The fourth endotherm accounts for the second molecule of diamine. The residual diamine elimination is associated with first an endotherm immediately followed by an exotherm. Appearance of exotherm might be due to the same reason as stated in the corresponding zinc complex. Here also, bis(diamine) species shows hygroscopic character. CdLSeO$_4$ appears to be isomorphous with CdLSO$_4$. It is interesting to note that [ZnL$_3$]SeO$_4$ does not yield any ZnL-SeO$_4$ while pyrolysis. This type of anomaly occurs probably due to the size factor of the two metal ions.

It is noticed that the decomposition temperature of [ML$_3$]X$_2$ (M=zinc(II) and cadmium(II); X=Br$^-$, 0.5SO$_4$$^{2-}$, and 0.5SeO$_4$$^{2-}$) follows the sequence SO$_4$$^{2-}$< SeO$_4$$^{2-}$⩽Br$^-$. [ZnL$_3$]X$_2$ and ZnLX$_2$ appear thermally more stable than those of cadmium complexes (Tables 2a and b). Our earlier investigation shows that zinc and cadmium complexes of 1,2-ethanediamine are thermally more stable than the corresponding 1,2-propanediamine complexes. [ML$_3$]SO$_4$ [M=zinc(II) or cadmium(II)] complexes particularly show surprisingly less stability than the corresponding 1,2-ethanediamine

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[††] Synthesized from solution for characterizing ν_t and ν_b (M–X) band from far-infrared spectra.

complexes.

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