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

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ABSTRACT

The synthesis and characterization of CdL$_n$X$_2$ m H$_2$O, where L = N$_2$H$_4$, n = 3, 2, 1.75 and 1; X = Cl$^-$, Br$^-$ and 1/2 SO$_4^{2-}$, and m = 0 or 0.5, have been done and their thermal studies have been carried out using a Shimadzu DT-30 thermal analyzer. Several complexes of the type CdL$_n$X$_2$, where n = 1.25, 1, 0.66, 0.33, have been synthesized pyrolytically in the solid state from parent complexes synthesized from solution. Several varieties of [CdL$_{0.66}$Cl$_2$] synthesized pyrolytically are indistinguishable by IR spectra but distinguishable by thermal profile. A similar phenomenon has been observed in cases of [CdL$_{0.33}$Cl$_2$], [CdL$_{0.66}$Br$_2$], [CdL$_{0.33}$Br$_2$], [CdL$_{0.66}$SO$_4$] and [CdL$_{0.33}$SO$_4$]. The unique feature of freshly prepared complexes synthesized from solution is that they undergo either internal rearrangement or lose one molecule of ligand at ambient temperature while keeping them in a desiccator for about 1 month. All these complexes are white in color and show bridging character of hydrazine evident from the IR spectral band. The decomposition reactions appear endothermic as well as exothermic.

INTRODUCTION

Cadmium complexes of hydrazine are well known in the literature [1–3], but not many thermal studies of these complexes have been reported [4]. Recently, we have reported thermal studies of Ni(II), Co(II) and Mn(II) complexes of hydrazine [5–7]. From these studies we have been able to synthesize several complexes by pyrolytic technique in the solid state. Cadmium has a unique role in coordination chemistry since it generates nonstoichiometric compounds. Also, cadmium has a vital role in the nuclear reactor. With these ideas we feel that some new findings may emerge from the thermal studies of cadmium complexes of hydrazine. The present paper reports the thermal studies of CdL$_n$X$_2$ · m H$_2$O, where L = N$_2$H$_4$; n = 3, 2, 1.75, 1.25, 1, 0.66, and 0.33; X = Cl$^-$, Br$^-$, 1/2 SO$_4^{2-}$; and m = 0 or 0.5.

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EXPERIMENTAL

Preparation of Cd(II) hydrazine(L) complexes

$[CdL_{1.75}Cl_2]$ *(1)*

Hydrazine hydrate (80%) (2 mmole)[†] was added to finely powdered $CdCl_2$ (1 mmole) with thorough stirring. The mixture was kept in a closed container for 24 h. The desired white shining crystals were filtered, washed thoroughly with water–ethanol (1 : 9) and finally with dry ethanol.

$[CdL_{1.75}Cl_2]$ *(1*)*

This was obtained by keeping compound (1) for about 1 month in a desiccator containing fused calcium chloride.

$[CdL_2Cl_2]$ *(2)*

Hydrazine hydrate (2 mmole) was added dropwise with constant stirring to the ammoniacal solution of $CdCl_2$ (1 mmole). The whole mixture was kept in a closed container for 24 h. The desired fine crystalline compounds were separated by the addition of absolute ethanol to the mixture. The separated solid compounds were washed thoroughly with water–ethanol (1 : 9) and finally with dry ethanol.

$[CdL_2Br_2]$ *(3)*

This was prepared by the procedure corresponding to the preparation of complex (1).

$[CdL_2Br_2]$ *(3*)*

This was obtained from complex (3) by applying the technique adopted for the preparation of complex (1*).

$[CdL_3]Br_2$ *(4)*

This was synthesized by the procedure corresponding to the preparation of complex (2).

$[CdL_2Br_2]$ *(4*)*

This was obtained from complex (4) by applying the technique followed for complex (1*).

$[CdL(H_2O)_{0.5}SO_4]$ *(5)*

This was prepared by the procedure corresponding to the preparation of complex (1).

[†] Excess hydrazine does not alter the composition of the complex.

$[CdLSO_4]$ (5)*

This was derived from complex (5) by applying the technique followed for the synthesis of complex (1*).

$[CdL_3]SO_4$ (6)

This was synthesized by the procedure used for the preparation of complex (1).

$[CdL_2SO_4]$ (6)*

This was obtained from complex (6) by applying the procedure adopted for the preparation of complex (1*).

$[CdL_{0\ 66}X_2]$, where $X = Cl^-$, Br^-, and 1/2 SO_4^{2-}. These were obtained from their parent compounds synthesized from solution by applying temperature arrest technique (Table 1) in an atmosphere of nitrogen.

$[CdL_{0\ 33}Cl_2]$, $[CdL_{0\ 33}SO_4]$, $[CdLSO_4]$ and $[CdL_{1\ 25}SO_4]$. These were synthesized following the procedure adopted for the synthesis of

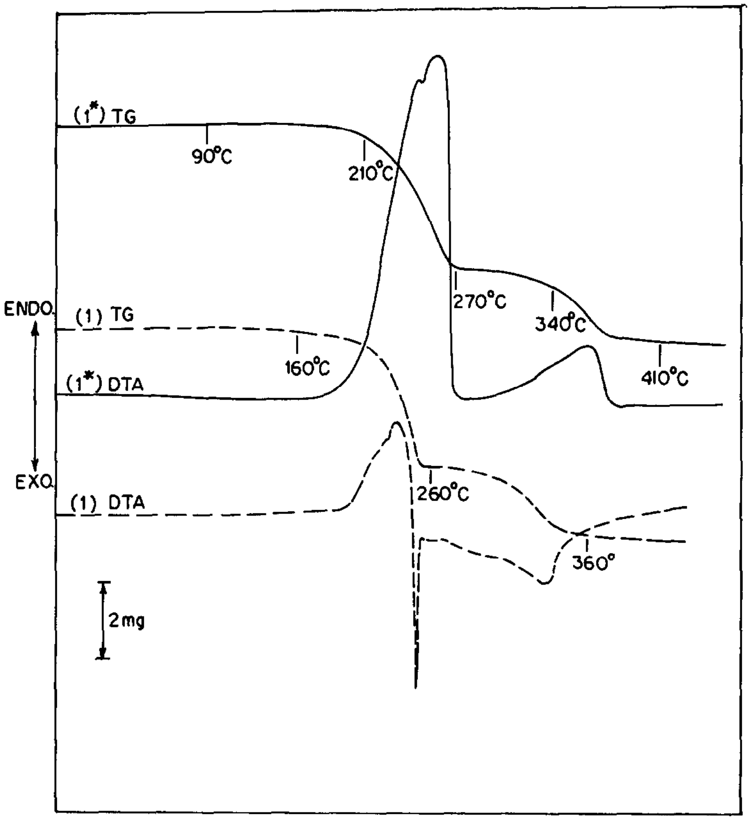

Fig. 1 Thermal curves of $[CdL_{1\ 75}Cl_2]$ (1) (— — —) and $[CdL_{1\ 75}Cl_2]$ (1*) (———) 24 07 and 25 50 mg of sample used, respectively

$[CdL_{0\ 66}X_2]$-type complexes in an atmosphere of nitrogen.

The apparatus employed in the investigations were the same as those reported earlier [7]. Thermal analysis was carried out using a thermal analyzer (Shimadzu, Model DT-30, Japan), and a constant flow of nitrogen (30 ml min^{-1}) was maintained. Platinum crucibles were used, and a heating rate of 5°C min^{-1} was maintained. The particle size of the sample was within 150–200 mesh, and aluminum oxide was used as reference.

RESULTS

The thermal curves of freshly prepared $[CdL_{1\ 75}Cl_2]$ (1) are shown in Fig. 1. Decomposition starts at 160°C and transformation to $[CdL_{0\ 66}Cl_2]$ occurs at 255°C in a single step, as evident from the TG curve. But the corresponding DTA curve shows three overlapping endotherms followed by an exotherm. On further heating, the derived $[CdL_{0\ 66}Cl_2]$ decomposes to $CdCl_2$ in single step, observed from its TG curve. But the corresponding DTA curve shows two overlapping exotherms. On keeping complex (1) in a desiccator for 1 month, its composition does not change but its thermal profile, shown in Fig. 1, does. The intermediate $[CdL_{0\ 66}Cl_2]$ as observed in its parent complex is also observed here. The interesting feature is that it shows no exotherms during the elimination of hydrazine.

$[CdL_2Cl_2]$ (2) starts decomposition at 195°C (Fig. 2) and transforms to $[CdL_{0\ 66}Cl_2]$ at 257°C in a single step evident from its TG curve. But its

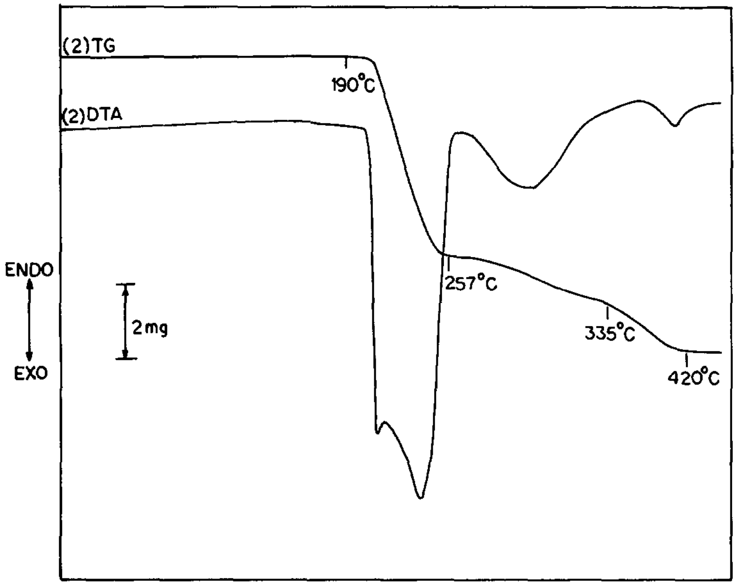

Fig 2 Thermal curves of $[CdL_2Cl_2]$ (2) 30 77 mg of sample used

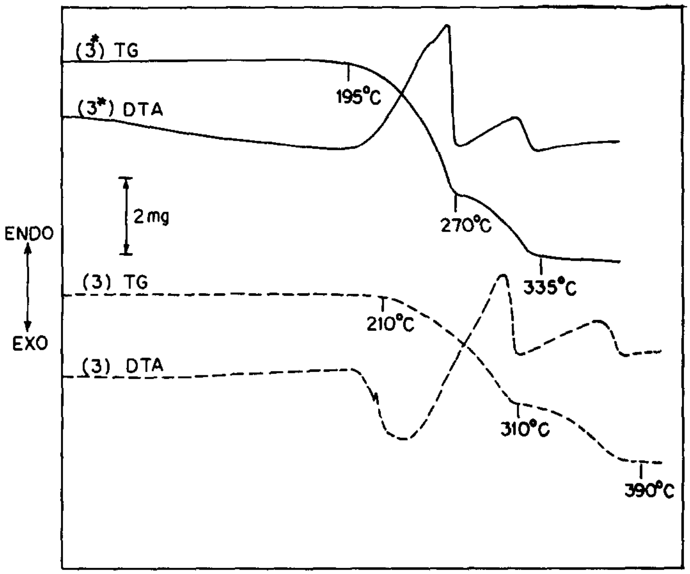

Fig 3 Thermal curves of $[CdL_2Br_2]$ (3) (— — —) and $[CdL_2Br_2]$ (3*) (———) 15 21 and 28 17 mg of sample used, respectively

DTA curve shows two overlapping exotherms. The derived $[CdL_{0\,66}Cl_2]$ starts decomposition at 287°C and transforms to $CdCl_2$ at 400°C through the formation of the intermediate $[CdL_{0\,33}Cl_2]$ observed from its TG curve. The corresponding DTA curve shows two distinct exotherms. The thermal

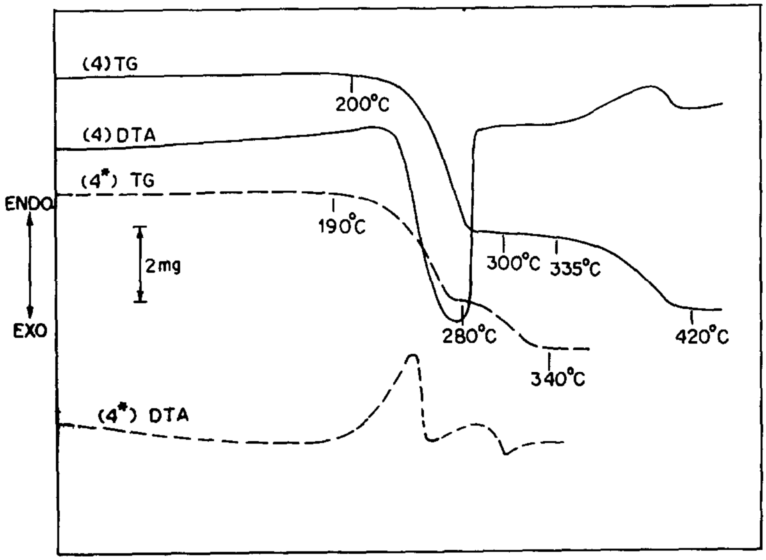

Fig 4 Thermal curves of $[CdL_3]Br_2$ (4) (———) and $[CdL_2Br_2]$ (4*) (— — —) 24 25 and 22 28 mg of sample used, respectively

profile of complex (2) does not change on keeping the fresh compound in a desiccator more than 1 month.

Figure 3 shows the thermal curves of freshly prepared $[CdL_2Br_2]$ (3). It starts to lose hydrazine at 210°C and transforms to $[CdL_{0\ 66}Br_2]$ at 305°C in single step evident from its TG curve. But the corresponding DTA curve shows two overlapping exothermic peaks at 210°C and 225°C followed by an endotherm. The derived $[CdL_{0\ 66}Br_2]$ on further heating starts decomposition at 315°C and transforms to $CdBr_2$ at 375°C in a single step. But on keeping the above complex (3) in a desiccator for 1 month the composition does not vary but a radical change in its thermal profile is observed. Here also the intermediate $[CdL_{0\ 66}Br_2]$ is observed like the parent species. The interesting phenomenon is that the exothermic peak vanishes here but the number of DTA peaks does not alter although a variation in peak temperature is noticed

The thermal curves of freshly prepared $[CdL_3]Br_2$ (4) are shown in Fig. 4. It decomposes at 200°C and transforms to $[CdLBr_2]$ at 287°C in a single step, showing an exothermic peak at 287°C. The derived $[CdLBr_2]$ on further heating starts decomposition at 335°C and transforms to $CdBr_2$ at

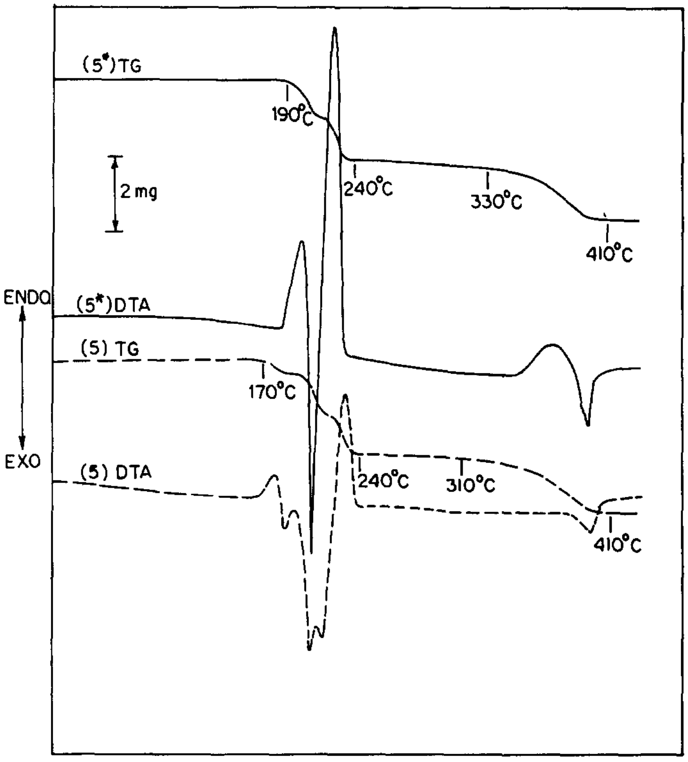

Fig 5. Thermal curves of $[CdL(H_2O)_{0\ 5}SO_4]$ (5) (— — —) and $[CdLSO_4]$ (5*) (———) 25.62 and 26 44 mg of sample used, respectively

410°C in a single step, showing an exothermic peak at 393°C. But on keeping this complex in a desiccator for 1 month, it transforms to a bis species which decomposes at 190°C and transforms to $[CdL_{0.66}Br_2]$ at 270°C in single step, showing an endotherm. The derived $[CdL_{0.66}Br_2]$ on further heating starts to lose hydrazine at 280°C and becomes $CdBr_2$ at 330°C, showing an endothermic peak at 310°C followed by an exothermic peak at 326°C.

Figure 5 shows the thermal curves of $[CdL(H_2O)_{0.5}SO_4]$ (5). It starts to lose its water molecule at 170°C and becomes anhydrous at 185°C in single step evident from its TG curves but its DTA curve shows an endothermic peak at 175°C followed by an exothermic peak at 180°C. The anhydrous species decomposes at 205°C and transforms to $[CdL_{0.66}SO_4]$ at 217°C in single step evident from its TG curve. The corresponding DTA curve shows an exotherm followed by an endotherm. This $[CdL_{0.66}SO_4]$ on further heating transforms to $[CdL_{0.33}SO_4]$ in a single step, showing an endothermic peak at 225°C. The derived $[CdL_{0.33}SO_4]$ starts decomposition at 320°C and transforms to $CdSO_4$ at 400°C, showing an exothermic peak at 395°C. On

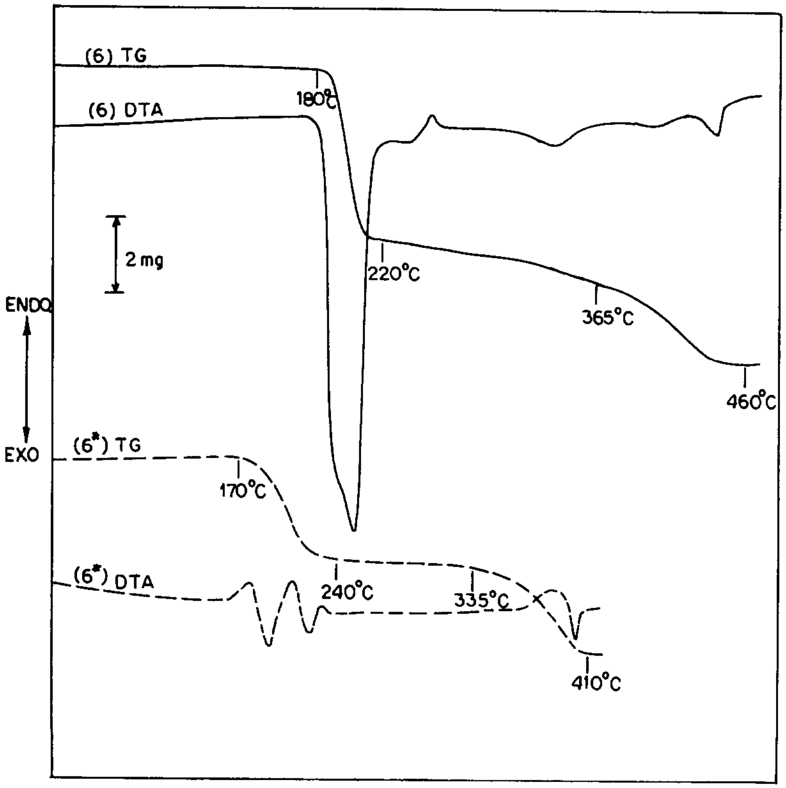

Fig 6 Thermal curves of $[CdL_3SO_4]$ (6) (———) and $[CdL_2SO_4]$ (6*) (— — —) 25.42 and 22.08 mg of sample used, respectively

keeping the complex (5) in a desiccator for 1 month it becomes anhydrous. The thermal profile of this anhydrous species differs from the parent species. The DTA curve for the elimination of 0.33 mole hydrazine in the first step shows an endotherm followed by an exotherm, and it shows another endotherm like the parent for the transformation of $[CdL_{0.66}SO_4] \rightarrow [CdL_{0.33}SO_4]$. An endothermic peak at 377°C is shown first, followed by two overlapping exotherms for the elimination of residual hydrazine.

$[CdL_3]SO_4$ (6) decomposes at 180°C and transforms to $[CdL_{1.25}SO_4]$ at 215°C in a single step, observed from its TG curve (Fig. 6) showing two overlapping exotherms. The derived $CdL_{1.25}SO_4$ starts decomposition at

TABLE 1

Thermal parameters of decomposition of cadmium hydrazine (L) complexes

Decomposition reactions	Temp range (°C)	DTA peak temp. (°C)	
		Exo	Endo
$[CdL_{1.75}Cl_2]$ (1) $\rightarrow [CdL_{0.66}Cl_2]$	160–255	250	213, 225, 235
$[CdL_{0.66}Cl_2] \rightarrow CdCl_2$	270–345	290, 335	
$[CdL_{1.75}Cl_2]$ (1*) $\rightarrow [CdL_{0.66}Cl_2]$	160–270		250, 260
$[CdL_{0.66}Cl_2] \rightarrow CdCl_2$	300–380		335, 370
$[CdL_2Cl_2]$ (2) $\rightarrow [CdL_{0.66}Cl_2]$	195–257	215, 247	
$[CdL_{0.66}Cl_2] \rightarrow [CdL_{0.33}Cl_2]$	287–365	310	
$[CdL_{0.33}Cl_2] \rightarrow CdCl_2$	365–400	400	
$[CdL_2Br_2]$ (3) $\rightarrow [CdL_{0.66}Br_2]$	210–305	210, 225	300
$[CdL_{0.66}Br_2] \rightarrow CdBr_2$	315–375		360
$[CdL_2Br_2]$ (3*) $\rightarrow [CdL_{0.66}Br_2]$	195–270		255, 265
$[CdL_{0.66}Br_2] \rightarrow CdBr_2$	275–330		320
$[CdL_3]Br_2$ (4) $\rightarrow [CdLBr_2]$	200–287	287	
$[CdLBr_2] \rightarrow CdBr_2$	335–410		393
$[CdL_2Br_2]$ (4*) $\rightarrow [CdL_{0.66}Br_2]$	190–270		260
$[CdL_{0.66}Br_2] \rightarrow CdBr_2$	280–330	310	326
$[CdL(H_2O)_{0.5}SO_4]$ (5) $\rightarrow [CdLSO_4]$	170–185	180	175
$[CdLSO_4] \rightarrow [CdL_{0.66}SO_4]$	205–217	207	215
$[CdL_{0.66}SO_4] \rightarrow [CdL_{0.33}SO_4]$	219–233		225
$[CdL_{0.33}SO_4] \rightarrow CdSO_4$	320–400	395	
$[CdLSO_4]$ (5*) $\rightarrow [CdL_{0.66}SO_4]$	190–213	210	205
$[CdL_{0.66}SO_4] \rightarrow [CdL_{0.33}SO_4]$	220–230		225
$[CdL_{0.33}SO_4] \rightarrow CdSO_4$	325–393	390, 393	377
$[CdL_3]SO_4$ (6) $\rightarrow [CdL_{1.25}SO_4]$	180–215	200, 207	
$[CdL_{1.25}SO_4] \rightarrow CdSO_4$	230–455	340, 400, 442	255
$[CdL_2SO_4]$ (6*) $\rightarrow [CdLSO_4]$	170–240	200,220	180, 210, 230
$[CdLSO_4] \rightarrow CdSO_4$	335–410	403	390

TABLE 2

Analytical data (calculated values in parentheses) of cadmium hydrazine (L) complexes

Compounds	Analyses %		
	Metal	Nitrogen	Halogen/sulfur
$[CdL_{1.75}Cl_2]$ (1)	46.92(46.95)	20.40(20.46)	29.63(29.65)
$[CdL_{1.75}Cl_2]$ (1*)	46.90(46.95)	20.38(20.46)	29.60(29.65)
$[CdL_2Cl_2]$ (2)	45.39(45.43)	22.61(22.63)	28.63(28.69)
$[CdL_2Br_2]$ (3)	33.38(33.43)	16.59(16.65)	47.46(47.53)
$[CdL_2Br_2]$ (3*)	33.37(33.43)	16.58(16.65)	47.50(47.53)
$[CdL_3]Br_2$ (4)	30.47(30.52)	22.76(22.81)	43.37(43.40)
$[CdL_2Br_2]$ (4*)	33.40(33.43)	16.58(16.65)	47.51(47.53)
$[CdL(H_2O)_{0.5}SO_4]$ (5)	44.95(45.06)	11.18(11.22)	12.82(12.83)
$[CdLSO_4]$ (5*)	46.70(46.75)	11.60(11.64)	13.24(13.31)
$[CdL_3]SO_4$ (6)	36.88(36.92)	27.51(27.57)	10.47(10.51)
$[CdL_2SO_4]$ (6*)	41.20(41.26)	20.47(20.55)	11.71(11.74)
$[CdL_{0.66}Cl_2]$ [a]	54.88(54.95)	8.80(9.03)	34.66(34.71)
$[CdLBr_2]$ [b]	36.89(36.94)	8.93(9.20)	52.45(52.53)
$[CdL_{0.66}Br_2]$ [c]	38.25(38.30)	6.25(6.29)	54.44(54.49)
$[CdL_{1.25}SO_4]$	45.22(45.24)	13.90(14.09)	12.81(12.88)
$[CdLSO_4]$ [d]	46.69(46.75)	11.59(11.64)	13.27(13.31)
$[CdL_{0.66}SO_4]$ [e]	48.94(48.97)	7.81(8.05)	13.85(13.94)
$[CdL_{0.33}SO_4]$ [f]	51.09(51.13)	4.18(4.21)	14.55(14.61)

[a] Derived from complex (1) [b] Derived from complex (4) [c] Derived from complex (4*) [d] Derived from complex (5). [e] Derived from complex (5*) [f] Derived from complex (5*)

230°C and transforms to $CdSO_4$ at 455°C, showing an endotherm followed by three exotherms. On keeping in a desiccator for 1 month at ambient temperature this transforms to $[CdL_2SO_4]$. This bishydrazine complex starts decomposition at 170°C (Fig. 6) and transforms to an isolable monohydrazine species at 240°C, showing an endotherm followed by an exotherm, endotherm, exotherm and endotherm overlapping. The derived monohydrazine complex decomposes at 335°C and transforms to $CdSO_4$ at 410°C, showing an endotherm followed by an exotherm.

Thermoanalytical data are given in Table 1. Analytical data and X-ray data are given in Tables 2 and 3, respectively.

DISCUSSION

Complexes derived from $CdCl_2$ and hydrazine

The synthesis and characterization of $[CdL_2Cl_2]$ have been done by several workers [1–3,8]. Other varieties of $CdCl_2$ complexes of hydrazine

TABLE 3

X-Ray diffraction data of $CdL_{1.75}Cl_2$ (1) and $CdL_{1.75}Cl_2$ (1*)

d_{hkl} (Å)	
$CdL_{1.75}Cl_2$ (1)	$CdL_{1.75}Cl_2$ (1*)
2.869 (s)	2.878 (s)
2.692 (s)	2.587 (s)
2.587 (s)	2.396 (s)
2.215 (m)	2.215 (m)
2.063 (m)	2.049 (m)
1.985 (w)	1.918 (m)
1.903 (s)	1.838 (w)
1.831 (w)	1.654 (w)
1.787 (w)	1.495 (m)
1.669 (w)	1.438 (w)
1.626 (w)	1.392 (w)
1.577 (w)	1.339 (w)
1.491 (m)	
1.445 (w)	
1.404 (w)	

s = Strong, m = Medium, w = Weak

were not known in the literature, but the preparative method described by us always affords [$CdL_{1.75}Cl_2$] (1) in one method and [CdL_2Cl_2] (2) in another method. IR spectral studies of both the complexes show the bridging character of hydrazine (ν_{N-N} bands at ~ 970 cm^{-1}) [9]. The reason for the occurrence of the compositional difference afforded by the two methods is difficult to explain. But this type of compositional difference due to the variation of the preparative procedure is observed while studying Co(II) and Mn(II) complexes of hydrazine [6,7]. The difference exhibited in the DTA profile on keeping the freshly prepared [$CdL_{1.75}Cl_2$] (1) for more than 1 month is probably due to some internal rearrangement, but it is a fact that this rearrangement is time dependent as, after a certain period, the complex attains permanent geometry. This type of rearrangement does not occur in [CdL_2Cl_2] (2). The interesting feature is that the TG curve of [$CdL_{1.75}Cl_2$] remains almost unaltered after rearrangement. Another interesting feature is that no differences in the IR spectral data of [$CdL_{1.75}Cl_2$] before and after rearrangement is observed, but the X-ray powder patterns of [$CdL_{1.75}Cl_2$] before and after rearrangement show some differences (Table 3). The intermediate complexes [$CdL_{0.66}Cl_2$] derived from complexes (1), (1*) and (2) show no difference in IR spectral data but their thermal profiles are distinctly different from each other (Table 1). In [$CdL_{0.66}Cl_2$] it is expected that the halide ions are involved in bridging in addition to the hydrazine bridging, as evidenced from the composition as well as the general tendency of becoming hexacoordinated [10]. The intermediate [$CdL_{0.33}Cl_2$] assumed from the TG curve of $[CdL_2Cl_2]$ (2) is very interesting though its characterization is not possible as it could not be isolated pyrolytically in a pure form.

Complexes derived from $CdBr_2$ and hydrazine

In the case of $CdBr_2$ hydrazine complexes only the compound having the composition $[CdL_2Br_2]$ has been reported in the literature [8,11–13], but we have been able to synthesize the trishydrazine complex (4) of $CdBr_2$ in addition to the bis complex (3). The literature shows only one trishydrazine complex of $Cd(NO_3)_2$ [10]. Bis- and trishydrazine complexes of $CdBr_2$ distinctly show the bridging character of hydrazine [11–13]. The attachments of hydrazine in these bis and tris complexes have been reported previously [10].

Here also we find some type of rearrangement taking place as in the case of $[CdL_{1.75}Cl_2]$ on keeping the complex for 1 month. The unique feature of the trishydrazine complex (4) is that it affords the bis complex (4*) simply on being kept in a desiccator for 1 month. Another interesting observation is that, upon heating, the tris species (4) generates monohydrazine, but the bis hydrazine species (3) and (3*), before and after rearrangement, respectively, and also the bis species (4*) derived from the tris species (4), afford $[CdL_{0.66}Br_2]$ instead of generating $[CdLBr_2]$. Intermediate complexes $[CdL_{0.66}Br_2]$ derived from $[CdL_2Br_2]$ before and after rearrangement and also from $[CdL_2Br_2]$ derived from $[CdL_3]Br_2$ (Table 1, Figs. 3 and 4) appear identical with respect to IR spectral data but their thermal profiles do not permit the suggestion that these three intermediates are identical in all respects. This is also applicable to the bis species derived in three ways. The monohydrazine variety derived pyrolytically from its tris variety appears very stable in comparison with its bis variety as well as $[CdL_{0.66}Cl_2]$.

Complexes derived from $CdSO_4$ and hydrazine

The chemistry of the hydrazine complexes of $CdSO_4$ is not well known [8]. We are able to synthesize two complexes from solution and a good number of complexes in the solid state from the two parent complexes either by keeping them in a desiccator for 1 month of pyrolytically to a desired temperature. Dehydration of $[CdL(H_2O)_{0.5}SO_4]$ (5) at an ambient temperature yields the anhydrous species (5*) which is not identical to the anhydrous species derived upon heating despite their identical IR data. The DTA profiles are reversed, (Fig. 5, Table 1) although their TG profiles are almost the same. This observation suggests that the water molecules present in the complex species plays an important role in the structure of the anhydrous species. The temperature at which the dehydration starts suggests the existence of water in the coordination sphere, although the IR spectral evidence of water coordination is not very clear. The intermediates $[CdL_{0.66}SO_4]$

derived from $[CdL(H_2O)_{0.5}SO_4]$ (5) and $[CdLSO_4]$ (5*) (Table 1) appear identical from spectral as well as thermal behavior, but intermediate complexes $[CdL_{0.33}SO_4]$ derived from their hydrated (5) and nonhydrated (5*) parent species show differences in thermal profiles although their spectral data are indistinguishable. In all these complexes the SO_4^{2-} group appears to be coordinated [7].

From the preparative method described here it appears that the presence of ammonia is probably the cause of the generation of cadmium trishydrazine complex (6), although in the case of $CdCl_2$ the presence of ammonia could not yield the tris species. In the trishydrazine complex, the SO_4^{2-} ion exists outside the coordination sphere [6]. The tris variety also transforms to the bis variety (6*) on keeping in a desiccator for 1 month, like that of hydrazine complexes of $CdBr_2$. It is interesting to note that hydrazine elimination takes place at ambient temperature from the tris species (6), while hydrazine elimination starts at elevated temperature ~ 180°C for the bis species. This also occurred in $[CdL_3]Br_2$. The pyrolytic synthesis of $[CdL_{1.25}SO_4]$ from $[CdL_3]SO_4$ is very interesting due to its composition. Intermediate complexes $[CdLSO_4]$ derived from $[CdL_2SO_4]$ (6*) obtained at ambient temperature and from $[CdL(H_2O)_{0.5}SO_4]$ (5) show radical differences in TG as well as DTA curves although their IR spectral data are the same. $[CdLSO_4]$ derived from complex (6*) has a high thermal stability similar to $[CdLBr_2]$ derived from complex (4).

CONCLUSION

In general, the Cd^{2+} ion has the unique property of generating complexes having nonstoichiometric composition, i.e. $3\ CdSO_4 \cdot 8\ H_2O$. Here also this prevails since synthesis of cadmium complexes of various composition in the solid state have been materialized. A unique property observed in cadmium complexes of hydrazine is that some exothermic reactions observed in the freshly prepared species disappear on being kept in .a desiccator for long hours and transform to endothermic character. In general, metal hydrazine complexes are known as solid fuels, as energy is involved during hydrazine elimination. In the case of nickel and cobalt complexes of hydrazine, exothermic reactions were observed in their hydrazine elimination processes [5,6]. In cadmium complexes some endothermic decomposition was observed. The cause of the exothermic reaction in the elimination of hydrazine from its complex is due to the instantaneous decomposition of hydrazine as soon as the evolution of hydrazine takes place. If this is the major cause of the exothermic reaction, then in an endothermic reaction hydrazine should not become dissociated while evolving from the complex species upon heating.

REFERENCES

1 H. Franzen and O. Mayer, Z. Anorg Chem., 60 (1908) 247.
2 P. Ray and P.B Sarkar, J. Chem. Soc., 117 (1920) 324.
3 P Ray and B.K. Goswami, Z. Anorg Chem , 168 (1928) 329
4 K C Patil, C Nesamani and V.R Pai Verneker, Synth. React. Inorg Met - Org Chem , 12 (1982) 383
5 B. Banerjee, P.K Biswas and N Ray Chaudhuri, Bull Chem. Soc Jpn , 56 (1983) in press.
6 B Banerjee, P K Biswas and N Ray Chaudhuri, communicated
7 B Banerjee, P.K Biswas and N Ray Chaudhuri, Thermochim. Acta, 68 (1983) 261.
8 R Ya Aliev, M N Guseinov and N.G. Klyuchnikov, Russ. J Inorg Chem., 17 (1972) 44
9 L. Sacconi and A Sabatini, J. Inorg. Nucl Chem., 25 (1963) 1389.
10 P Glavic, J Slivnik and A. Bole, J. Inorg Nucl Chem., 37 (1975) 345
11 A Ferrari, A Braibanti and A.M Lanfredi, Ann. Chim Roma, 48 (1958) 1238
12 A Braibanti and G Bigliardi, Z Kristallogr , 120 (1964) 261.
13 A. Braibanti, G Bigliardi, R.C. Padovani and F Dallavalle, Gazz Chim Ital , 95 (1965) 1212.