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Thermal studies of N^1-isopropyl-2-methyl-1,2-propanediamine complexes of zinc(II) and cadmium(II) in the solid phase

Chandi Pariya, Ashutosh Ghosh [1], Sarmishtha Ganguli,
Nirmalendu Ray Chaudhuri *

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

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Abstract

$CdL_3(ClO_4)_2$, ZnL_2X_2, $CdL_2X'_2 \cdot nH_2O$ (where L is N^1-isopropyl-2-methyl-1,2-propanediamine, X is Cl, Br, I, ClO_4, SCN, $0.5SO_4$ and $0.5SeO_4$; $n = 0$ when X′ is Cl, Br, I, SCN and $0.5SO_4$; $n = 3$ when X′ is ClO_4; $n = 4$ when X′ is $0.5SeO_4$) and MLX_2 (M is Zn(II) or Cd(II) and X is Cl, Br and I) were synthesized from solution. The species $CdL_2(ClO_4)_2$ and MLX_2 (M is Zn(II) or Cd(II) and X is Cl, Br and I) were synthesized from the corresponding parent complexes by the temperature-arrest technique. $CdL_2(SCN)_2$ exists in two isomeric forms and both have been synthesized. One of the isomers undergoes an irreversible phase transition (102–120°C, $\Delta H = 12.8\ \text{kJ mol}^{-1}$) and transforms to the other form in the solid phase. $ZnL_2(ClO_4)_2$ shows a reversible phase transition (178–208°C, $\Delta H = 9.2\ \text{kJ mol}^{-1}$) upon heating in the solid phase. $CdL_2(ClO_4)_2$ undergoes a reversible phase transition (73–98°C, $\Delta H = 4.4\ \text{kJ mol}^{-1}$) and then on further heating shows time-dependent reversible phase transitions (136–190°C, $\Delta H = 15.3\ \text{kJ mol}^{-1}$) in the solid phase. The phase transition in $CdL_2(SCN)_2$ is due to the change in coordination mode of the thiocyanate ion, whereas in $CdL_2(ClO_4)_2$, the time-dependent reversible phase transition is due to conformational changes in the diamine chelate rings.

Keywords: Coupled technique; Cadmium compound; Diamine; DTA; Isomer; Phase transition; TG; XRD; Zinc compound

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* Corresponding author.

[1] Present address: Department of Chemistry, Jhargram Raj College, Jhargram 721 507, West Bengal, India.

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1. Introduction

The syntheses, thermally induced phase transitions and decompositions of metal (Ni(II), Zn(II) and Cd(II)) diamine complexes have been reported previously [1-9]. The phase transitions were found to be due to either conformational changes in the diamine chelate rings [1, 2] or geometrical rearrangements of the ligands about the metal ion [3]. Decomposition of the complexes can provide a simple method for isolation of the intermediate species [2, 4-9] which could not otherwise be obtained from solution, or only with difficulty.

In general, the thermal stability of the complexes decreases as the number and bulkiness of the substituents at the diamine nitrogen increase and, in many cases, this steric hindrance is high enough to prevent the formation of tris complexes [2, 10-12]. Moreover, quite interestingly, it has been found that several complexes of N-substituted diamine on heating undergo conformational changes [2, 11, 12] of the chelate rings. In contrast, C-substituted diamine complexes show a square-planar $\rightleftharpoons$ octahedral transition (especially in Ni(II)) [13]. However, studies in which the diamine which is both C- and N-substituted are rare in the literature [13]. We chose the ligand N^1-isopropyl-2-methyl-1,2-propanediamine for this purpose. There are several reports [14-16] on the structural analysis of mono and bis complexes of this ligand with Cu(II), Ni(II) and Zn(II). But to our knowledge, neither a thermal analysis nor any tris complex of this ligand has been reported. Here we report the syntheses of $[CdL_3](ClO_4)_2$ and ML_2X_2 (M is Zn(II) or Cd(II), L is N^1-isopropyl-2-methyl-1,2-propanediamine, X is Cl, Br, I, ClO_4, SCN, $0.5SO_4$ and $0.5SeO_4$) and the thermal analyses of all the complexes.

2. Experimental

High purity N^1-isopropyl-2-methyl-1,2-propanediamine was purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were AR grade. The equipment employed to record the IR spectra, and the TG-DTA and elemental analyses were described earlier [3]. The enthalpy changes of the phase transitions were measured using a Perkin-Elmer differential scanning calorimeter model DSC-7. X-ray powder diffraction patterns were taken using Cu Kα radiation with a Phillips X-ray generator (PW 1130) and X-ray diffractometer (PW 1710). Elemental analyses, and thermal and X-ray powder diffraction data are shown in Tables 1, 2 and 3, respectively.

2.1. Preparation of the complexes

ZnL_2Cl_2 (**1**), ZnL_2Br_2 (**2**), ZnL_2I_2 (**3**), $ZnL_2(SCN)_2$ (**6**), $ZnL_2(ClO_4)_2$ (**7**), CdL_2Cl_2 (**8**), CdL_2Br_2 (**9**), CdL_2I_2 (**10**) and $CdL_3(ClO_4)_2$ (**14**) were prepared by adding 3-4 mmol of the diamine (L) dropwise with stirring to 1 mmol of the corresponding metal salt in ethanolic medium. The complexes which separated out were purified by washing with ethanol and stored in a desiccator.

Table 1
Elemental analyses (found (calc)/%) for N^1-isopropyl-2-methyl-1,2-propanediamine (L) complexes of Zn(II) and Cd(II)

Compound	No.	Nitrogen	Carbon	Hydrogen
ZnL_2Cl_2	**1**	14.0 (14.1)	42.6 (42.4)	9.4 (9.1)
$ZnLCl_2$	**1a**	10.9 (10.5)	31.8 (31.5)	6.9 (6.8)
ZnL_2Br_2	**2**	12.0 (11.5)	35.1 (34.6)	7.5 (7.4)
$ZnLBr_2$	**2a**	7.7 (7.9)	23.5 (23.6)	4.9 (5.1)
ZnL_2I_2	**3**	10.0 (9.7)	28.5 (29.0)	6.3 (6.2)
$ZnLI_2$	**3a**	6.0 (6.2)	18.4 (18.7)	4.2 (4.0)
ZnL_2SO_4	**4**	12.9 (13.3)	40.2 (39.9)	8.3 (8.5)
$ZnLSO_4$	**4a**	10.0 (9.6)	28.9 (28.8)	5.9 (6.2)
ZnL_2SeO_4	**5**	12.1 (11.9)	36.0 (35.8)	7.4 (7.7)
$ZnLSeO_4$	**5a**	8.5 (8.3)	25.1 (24.8)	5.4 (5.3)
$ZnL_2(SCN)_2$	**6**	18.5 (19.0)	42.7 (43.5)	7.9 (8.1)
$ZnL_2(ClO_4)_2$	**7**	11.0 (10.7)	31.8 (32.0)	7.0 (6.9)
CdL_2Cl_2	**8**	12.4 (12.6)	38.1 (37.9)	8.0 (8.1)
$CdLCl_2$	**8a**	9.3 (8.9)	26.9 (26.8)	5.8 (5.7)
CdL_2Br_2	**9**	10.1 (10.5)	31.9 (31.5)	6.6 (6.8)
$CdLBr_2$	**9a**	7.1 (7.0)	21.0 (20.9)	4.7 (4.5)
CdL_2I_2	**10**	8.7 (8.9)	27.1 (26.8)	5.6 (5.7)
$CdLI_2$	**10a**	5.8 (5.6)	17.1 (16.9)	3.5 (3.6)
CdL_2SO_4	**11**	12.1 (11.9)	36.2 (35.8)	7.8 (7.7)
$CdLSO_4$	**11a**	8.1 (8.3)	24.9 (24.8)	5.2 (5.3)
$CdL_2SeO_4 \cdot 4H_2O$	**12**	9.6 (9.5)	29.0 (28.6)	7.3 (7.5)
CdL_2SeO_4	**12a**	10.7 (10.9)	32.4 (32.6)	7.3 (7.0)
$CdLSeO_4$	**12b**	7.0 (7.3)	22.1 (21.8)	4.7 (4.7)
$CdL_2(SCN)_2$ [a]	**13**	17.3 (17.2)	39.0 (39.3)	7.2 (7.4)
$CdL_3(ClO_4)_2$	**14**	11.7 (12.0)	35.8 (35.9)	7.7 (7.7)
$CdL_2(ClO_4)_2$ [a]	**14a**	9.9 (9.8)	29.4 (29.4)	6.6 (6.3)
$CdL_2(ClO_4)_2 \cdot 3H_2O$	**14e**	9.0 (8.9)	26.6 (26.9)	6.8 (6.7)

[a] The analytical data for the post-phase species are similar to those for the pre-phase species.

$CdL_2(SCN)_2$ (**13**) was prepared by adding excess diamine to $Cd(SCN)_2$ dissolved in a minimum quantity of water at approx. 5°C. The desired compound separated out immediately as a white solid from the resulting solution.

$CdL_2(SCN)_2$ (**13a**) was prepared by slowly adding 2 mmol of diamine with stirring to 1 mmol of $Cd(SCN)_2$ dissolved in methanol (10 cm^3). The resulting solution was kept in a desiccator for several days, when white crystalline complex separated out. These were filtered, washed with methanol and stored in a desiccator. Complex **13a** was also prepared by thermolysis (102–120°C, Table 2) of complex **13** in the solid phase or on crystallization from methanol.

ZnL_2SO_4 (**4**), ZnL_2SeO_4 (**5**), CdL_2SO_4 (**11**) and $CdL_2SeO_4 \cdot 4H_2O$ (**12**) were prepared by adding 2–3 mmol of diamine to the corresponding metal salt (1 mmol) dissolved in water (5 cm^3). These were filtered, washed with aqueous ethanol (1:1) and dried in a desiccator.

$CdL_2(ClO_4)_2 \cdot 3H_2O$ (**14e**) was synthesized by refluxing 2 mmol of the parent tris complex (**14**) and 1 mmol of $Cd(ClO_4)_2$ in ethanol for 20 h. On keeping the

Table 2
Thermal parameters for the Zn(II) and Cd(II) complexes of N^1-isopropyl-2-methyl-1,2-propanediamine (L)

Thermal reactions	Temp. range/ °C	DTA peak temp./°C	
		Endothermic	Exothermic
ZnL_2Cl_2 (**1**) → $ZnLCl_2$ (**1a**)	130-182	172	-
$ZnLCl_2$ (**1a**) → $ZnCl_2$	260-400	270 [b], 330	-
ZnL_2Br_2 (**2**) → $ZnLBr_2$ (**2a**)	132-190	182	-
$ZnLBr_2$ (**2a**) → A [a]	250-450	240 [b], 330, 385	-
ZnL_2I_2 (**3**) → $ZnLI_2$ (**3a**)	130-175	168	-
$ZnLI_2$ (**3a**) → A [a]	260-450	200 [b], 330, 390	420
ZnL_2SO_4 (**4**) → $ZnLSO_4$ (**4a**)	120-180	160, 176 [b]	-
$ZnLSO_4$ (**4a**) → $ZnL_{0.66}SO_4$ (**4b**)	230-280	240	-
$ZnL_{0.66}SO_4$ (**4b**) → $ZnSO_4$	280-388	312, 350	370
ZnL_2SeO_4 (**5**) → $ZnLSeO_4$ (**5a**)	122-190	180	-
$ZnLSeO_4$ (**5a**) → $ZnSeO_4$	220-270	-	266
$ZnL_2(SCN)_2$ (**6**) → $ZnL_{1.5}(SCN)_2$ (**6a**)	125-162	160	-
$ZnL_{1.5}(SCN)_2$ (**6a**) → A [a]	162-400	176 [b], 290	270 [b], 312
$ZnL_2(ClO_4)_2$ (**7**) → $ZnL_2(ClO_4)_2$ (**7a**)	178-208	194	-
CdL_2Cl_2 (**8**) → $CdLCl_2$ (**8a**)	145-210	182, 192, 208 [b]	-
$CdLCl_2$ (**8a**) → $CdL_{0.33}Cl_2$ (**8b**)	235-268	255	-
$CdL_{0.33}Cl_2$ (**8b**) → $CdCl_2$	285-342	-	339
$CdLCl_2$ (**8a***) [c] → $CdL_{0.5}Cl_2$ (**8c**)	180-235	210	-
$CdL_{0.5}Cl_2$ (**8c**) → $CdL_{0.33}Cl_2$ (**8d**)	235-261	258	-
$CdL_{0.33}Cl_2$ (**8d**) → $CdCl_2$	286-355	351	-
CdL_2Br_2 (**9**) → $CdL_{1.25}Br_2$ (**9b**)	130-178	176	-
$CdL_{1.25}Br_2$ (**9b**) → $CdBr_2$	178-337	175	335
CdL_2I_2 (**10**) → $CdL_{1.15}I_2$ (**10b**)	120-178	148, 175	-
$CdL_{1.15}I_2$ (**10b**) → A [a]	178-370	-	-
CdL_2SO_4 (**11**) → $CdLSO_4$ (**11a**)	110-180	164	-
$CdLSO_4$ (**11a**) → $CdSO_4$	195-285	278	-
$CdL_2SeO_4 \cdot 4H_2O$ (**12**) → CdL_2SeO_4 (**12a**)	50-80	55, 71	-
CdL_2SeO_4 (**12a**) → $CdLSeO_4$ (**12b**)	148-193	189	-
$CdLSeO_4$ (**12b**) → $CdSeO_4$	210-330	270	290
$CdL_2(SCN)_2$ (**13**) → $CdL_2(SCN)_2$ (**13a**)	102-120	112	-
$CdL_2(SCN)_2$ (**13a**) → $CdL_{1.67}(SCN)_2$ (**13b**)	125-160	152	-
$CdL_{1.67}(SCN)_2$ (**13b**) → $Cd(SCN)_2$	160-340	184, 250	278
$CdL_3(ClO_4)_2$ (**14**) → $CdL_2(ClO_4)_2$ (**14a**)	132-180	168	-
$CdL_2(ClO_4)_2$ (**14b***) [d] → $CdL_2(ClO_4)_2$(**14c**)	73-98	90	-
$CdL_2(ClO_4)_2$ (**14c**) → $CdL_2(ClO_4)_2$ (**14d**)	136-190	169, 181	-
$CdL_2(ClO_4)_2 \cdot 3H_2O$ (**14e**) → $CdL_2(ClO_4)_2$ (**14c**)	75-120	108	-

[a] A, products not been characterized.
[b] Peak due to melting.
[c] **8a***, obtained from solution.
[d] **14b***, obtained from **14a** on storing overnight in a humid atmosphere.

resulting solution for a few hours, finely crystalline complex separated out. This was filtered, washed with dry ethanol and stored in a desiccator.

$ZnLCl_2$ (**1a**), $ZnLBr_2$ (**2a**), $ZnLI_2$ (**3a**), $CdLCl_2$ (**8a**), $CdLBr_2$ (**9a**) and $CdLI_2$ (**10a**) were synthesized by refluxing 1 mmol of the parent diamine complex with

Table 3
Prominent lines, *d* in Å, in the X-ray powder patterns of the complexes

Complex	Lines
$CdL_2(SCN)_2$ (**13**)	8.67s, 7.37vs, 7.03w, 6.66s, 6.33m, 5.01vw, 4.85vw, 4.56w, 4.31w, 4.13vw, 3.87vw, 3.66w, 3.39m
$CdL_2(SCN)_2$ (**13a**) [a]	8.28vs, 7.72m, 6.17s, 5.18m, 4.79w, 4.23vw, 3.98w, 3.83vw, 3.60m, 3.49w, 3.34w

Key: vs, very strong; s, strong; m, medium; vw, very weak; w, weak.

[a] Species obtained after the product of the phase transition of **13** was cooled in a desiccator; X-ray powder patterns were taken immediately.

1 mmol of the corresponding metal salt in ethanol, and following the procedure for synthesis of complex **14e**. The species $ZnLCl_2$ (**1a**), $ZnLBr_2$ (**2a**), $ZnLI_2$ (**3a**) and $CdLCl_2$ (**8a**) were also synthesized in the solid state from the corresponding parent complex by the temperature-arrest technique (Table 2).

$ZnLSO_4$ (**4a**), $ZnLSeO_4$ (**5a**), $CdLSO_4$ (**11a**), CdL_2SeO_4 (**12a**) and $CdLSeO_4$ (**12b**) were isolated pyrolytically from their corresponding parent complexes using the temperature-arrest technique (Table 2). $CdL_2(ClO_4)_2$ (**14a**) was prepared pyrolytically either from $CdL_3(ClO_4)_2$ (**14**) or $CdL_2(ClO_4)_2 \cdot 3H_2O$ (**14e**) in the solid state (Table 2).

3. Results and discussion

The ligand N^1-isopropyl-2-methyl-1,2-propanediamine is an asymmetrically C- and N-substituted ethylenediamine derivative. Because the isopropyl group is very bulky, formation of tris chelate complexes with the first-row transition metals is not reported [14–17]. In the present study, all the zinc and cadmium salts, except $Cd(ClO_4)_2$, also yield bis diamine complexes if the ligand : metal ratio is 2:1 or higher. $Cd(ClO_4)_2$ provides the only tris species (Table 1), probably due to the larger size of Cd(II) and the poor coordinating ability of the ClO_4 group.

3.1. Structure of the complexes

It is well known that the larger size of Cd(II) compared to that of Zn(II) makes it more likely to assume a coordination number of six [18]. As a result, all the bis diamine complexes of Cd(II) are considered to possess pseudo-octahedral geometry. The non-conducting behavior of CdL_2Cl_2 in ethanol and methanol also supports this supposition. The conductance of all the complexes could not be measured because of their low solubility in common organic solvents. The diamine is chelated in all the complexes, as demonstrated by their IR spectra which are similar to those of known structures [17].

It is probable that steric hindrance of the isopropyl group will prevent Zn(II) adopting a coordination number more than four. Therefore, all the Zn(II) complexes probably possess pseudo-tetrahedral geometry. Here also we could not

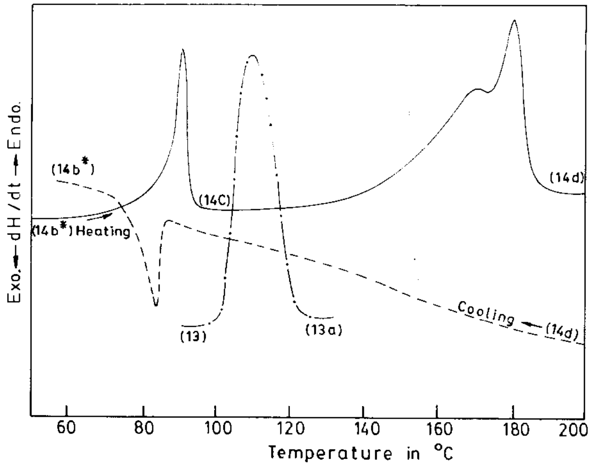


Fig. 1. DSC curves of $CdL_2(ClO_4)_2$ (**14b***) (sample mass, 8.86 mg): ——, heating; – – –, cooling; — · — · —, $CdL_2(SCN)_2$ (**13**) (sample mass, 5.6 mg).

measure the conductance data in support of the non-coordinating anions due to their insolubility in common organic solvents.

3.2. Phase transition in $CdL_2(SCN)_2$ (13)

On heating, the complex $CdL_2(SCN)_2$ (**13**) undergoes an irreversible endothermic phase transition (102–120°C, $\Delta H = 12.8\ \mathrm{kJ\ mol^{-1}}$, see Fig. 1), yielding an isomer without any mass loss as is evident from the TG–DTA curve. Compound **13a** is readily soluble in methanol but **13** dissolves with difficulty. Recrystallized products from both **13** and **13a** are identical. Compound **13** cannot be obtained by crystallization. Therefore it is obvious that **13** is metastable and on crystallization transforms to the thermodynamically stable form **13a**. For this reason, precautions have to be taken during its preparation. X-ray powder diffraction patterns of **13** and **13a** (Table 3) are appreciably different indicating a major change in the unit cell of these two isomers. IR-active vibrations of the diamine show that it is chelated in both complexes, although the conformations of the chelate rings are probably different as there are some changes in the spectra [1–3]. The most striking differences in the IR spectra, however, are at approx. 2050 and 750 $\mathrm{cm^{-1}}$, where the ν(CN) and ν(CS) bands of thiocyanate occur [19]. In the spectrum of **13**, ν(CN) splits into three bands, at approx. 2040, 2055, and 2192 $\mathrm{cm^{-1}}$ (Fig. 2), whereas for **13a**, only a single ν(CN) band at approx. 2045 $\mathrm{cm^{-1}}$ is observed. The ν(CS) band of **13** also splits at approx. 745 and 860 $\mathrm{cm^{-1}}$, whereas that of **13a** occurs as a single band at approx. 780 $\mathrm{cm^{-1}}$. These differences in the IR spectra lead us to assume that both bridging and N-bonded thiocyanate are present in **13**, whereas in **13a** the thiocyanate group is only present as N-bonded (Scheme 1). This bridging to N-bonded thiocyanate transformation corroborates the drastic change in the X-ray powder patterns and also the insolubility of **13** in water.

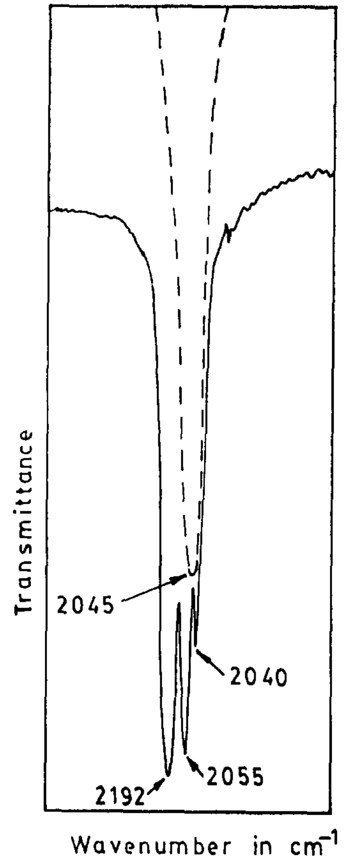
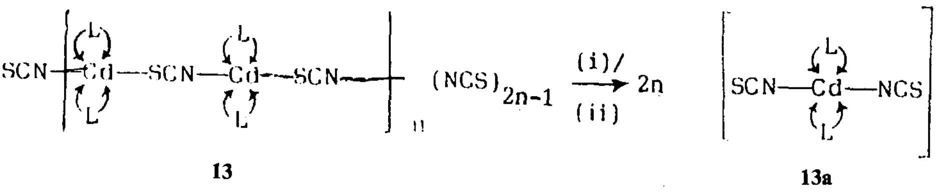


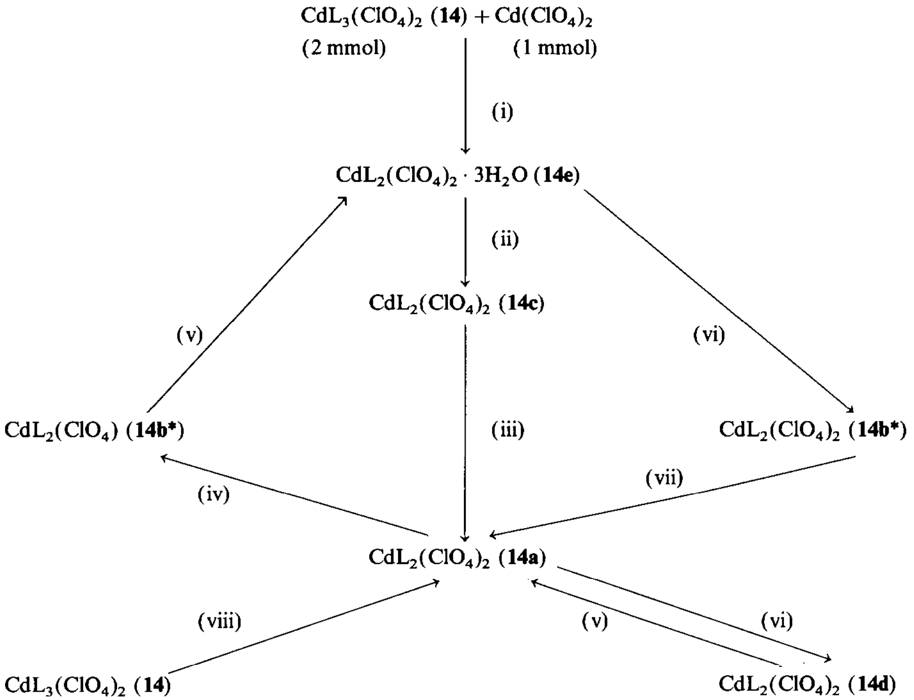
Fig. 2. IR spectra: ——, $CdL_2(SCN)_2$ (**13**); and – – – , $CdL_2(SCN)_2$ (**13a**).



Scheme 1. (i) Heating 102–120°C; (ii) recrystallization from methanol.

3.3. Phase transition in bis diamine perchlorate of Cd(II) and Zn(II)

Refluxing of $CdL_3(ClO_4)_2$ (**14**) with $Cd(ClO_4)_2$ in ethanolic medium produces crystals of $CdL_2(ClO_4)_2 \cdot 3H_2O$ which, on heating, first lose water (75–120°C, Table 2) and then undergo an endothermic phase transition (136–190°C, $\Delta H = 15.3$ kJ mol^{-1}, see Fig. 1 and Table 2). The species produced, on cooling to ambient temperature and reheating immediately, undergoes another reversible endothermic phase transition (73–98°C, $\Delta H = 4.4$ kJ mol^{-1}, see Table 2) which is



Scheme 2. (i) Refluxing in ethanolic medium for 20 h; (ii) heating 75–120°C; (iii) heating 136–190°C; (iv) keeping overnight; (v) heating 78–98°C; (vi) cooling to 25°C; (vii) heating at 190°C; (viii) heating 132–180°C.

not observed during the first heating as it is masked by the large endothermic deaquation peak. It is interesting to note that when the after-phase species is kept overnight and reheated, both endothermic phase transitions (73–98°C and 136–190°C, see Fig. 1 and Table 2) are observed. Therefore, the endothermic transition occurring at 136–190°C (Table 2) is time-dependently reversible. The compound $CdL_2(ClO_4)_2$ (**14a**) can also be obtained by thermal decomposition of $CdL_3(ClO_4)_2$ (**14**) (Table 2, Scheme 2) and behaves identically to the compound obtained by heating the deaquated product of **14e** at 75–120°C (Scheme 2, Table 2).

The X-ray diffraction powder patterns and IR spectra of **14b*** and **14d** have been recorded: they show hardly any differences. The spectral patterns in the region 1250–900 cm^{-1} indicate that the perchlorate anion is not involved in partial covalent bonding in either form, as in the case of thermochromic $ML_2(ClO_4)_2$ (M is Cu(II) and Ni(II), L is *N,N*-diethylethylenediamine) [20, 21]. The observed enthalpy change of the time-dependent reversible transition is also comparable with the above-mentioned thermochromic Cu(II) and Ni(II) salts [22], indicating that the reason for the transition is probably the same, i.e. conformational changes of the diamine chelate rings.

The nature of the reversible phase transition **14b*** → **14c** (73–98°C, Table 2) remains unexplored due to the lack of facilities for obtaining spectral and structural data at higher temperatures. The corresponding $ZnL_2(ClO_4)_2$ undergoes a similar endothermic reversible phase transition (178–208°C, $\Delta H = 9.2$ kJ mol^{-1}, Table 2). The nature of this transition has also not been explored for the same reason as stated above.

3.4. Decomposition

ZnL_2X_2 (X is Cl, Br, I, $0.5SO_4$ and $0.5SeO_4$) and CdL_2X_2 (X is Cl, $0.5SO_4$ and $0.5SeO_4$) (Figs. 3–5) undergo decomposition via the thermally stable mono di-

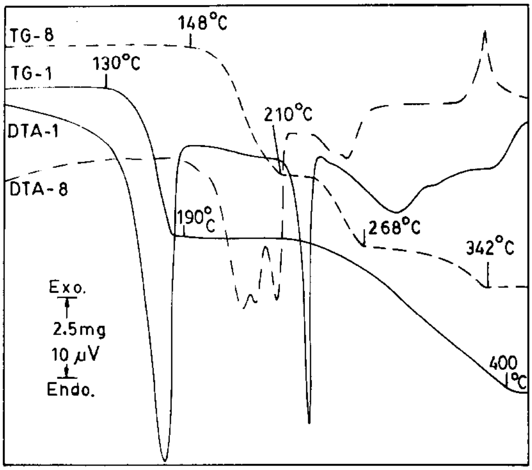


Fig. 3. TG–DTA curves: ——, ZnL_2Cl_2 (**1**) (sample mass, 14.12 mg); and – – –, CdL_2Cl_2 (**8**) (sample mass, 12.92 mg).

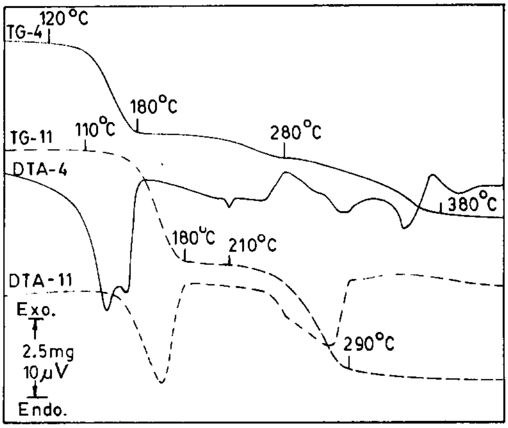


Fig. 4. TG–DTA curves: ——, ZnL_2SO_4 (**4**) (sample mass, 9.34 mg); and – – –, CdL_2SO_4 (**11**) (sample mass, 12.33 mg).

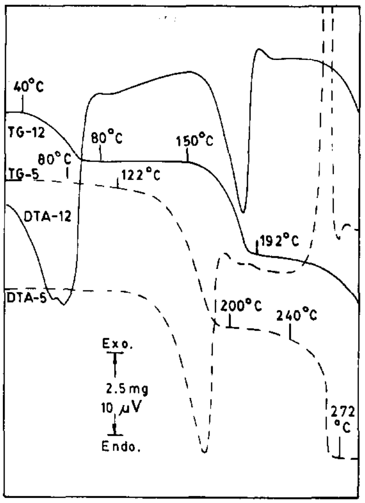


Fig. 5. TG–DTA curves: ——, ZnL_2SeO_4 (**5**) (sample mass, 14.65 mg); and – – –, $CdL_2SeO_4 \cdot 4H_2O$ (**12**) (sample mass, 12.90 mg).

amine species. However, the decomposition patterns of $ZnL_2(SCN)_2$ and CdL_2X_2 (X is Br, I and SCN) are complicated, showing several breaks in the TG curve corresponding to non-stoichiometric diamine species (based on mass loss) formed during pyrolysis (Table 2). Those species however cannot be isolated as the corresponding TG curves do not show any plateau, i.e. they start decomposition at the temperature of formation. The thermal behavior and IR spectra of mono diamine species that can be isolated in the solid state by the temperature-arrest technique are found to be identical to the corresponding mono diamine species synthesized from solution, except $CdLCl_2$ (**8a***) (Table 2) in which decomposition patterns differ appreciably probably due to differences in crystal packing.

$CdLSO_4$ loses diamine upon heating in a single step, whereas its zinc analogue decomposes to $ZnSO_4$ via $ZnL_{0.66}SO_4$ (Table 2, Fig. 4).

Dehydration of $CdL_2SeO_4 \cdot 4H_2O$ (Fig. 5) occurs in two overlapping steps. The dehydrated species rehydrates on standing in a humid atmosphere. However, $CdL_2(ClO_4)_2 \cdot 3H_2O$, once dehydrated on heating, does not absorb any water from the atmosphere.

The thermal stability (based on T_i, i.e. the initial temperature of decomposition) of ZnL_2X_2 does not change on variation of the anions (Table 2). However, in the corresponding cadmium analogues, some noticeable differences in thermal stability are observed (Table 2): $SeO_4 \geqslant Cl > Br > SCN \geqslant I > SO_4$.

An interesting observation is that the thermal stability of CdL_xSeO_4 ($x = 1$ or 2, see Fig. 5, and Table 2) is appreciably high with respect to its sulfate analog. In the case of ZnL_xAO_4 ($x = 1$ or 2, A is S or Se, see Figs. 4 and 5 and Table 2), there is no such observation.

4. Conclusions

The above results demonstrate that thermal decomposition is a very easy and effective technique for the preparation of $CdL_2(ClO_4)_2$ and MLX_2 (where M is Zn(II) or Cd(II), L is N^1-isopropyl-2-methyl-1,2-propanediamine, and X is Cl, Br, I, $0.5SO_4$ and $0.5SeO_4$) from their mother diamine complexes. The successful synthesis of $[CdL_3](ClO_4)_2$ proves that if the metal ion is large enough, three bulky N^1-isopropyl-2-methyl-1,2-propanediamine ligands can be accommodated around it. The smaller cation, Zn(II), however, fails to provide any tris complex, as in the case of Cu(II) and Ni(II).

The endothermic reversible phase transition in bis diamine perchlorate is compatible with the reported conformational changes in the N-substituted bis diamine complexes. However, the existence of both bridging and N-bonded thiocyanate in the case of Cd(II) but of only the N-bonded thiocyanate in Zn(II) complexes can be understood as being a soft-soft interaction between Cd(II) and S of SCN.

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