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Thermal studies *N*-(2-aminoethyl)-1,3-propanediamine and *N*-(3-aminopropyl)-1,3-propanediamine complexes of cadmium(II)

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Abstract

[Cd(aepn)₂]X₂·*n*H₂O (where aepn is *N*-(2-aminoethyl)-1,3-propanediamine, and *n* = 1 when X is Cl[−] and Br[−], *n* = 0 when X is 0.5SO₄^{2−}, 0.5SeO₄^{2−}, NO₃[−] and I[−]), Cd(aepn)X₂ (where X is Cl[−], Br[−], I[−], 0.5SeO₄^{2−}, 0.5SO₄^{2−} and SCN[−]), and Cd(dpt)X₂·*n*H₂O (where dpt is *N*-(3-aminopropyl)-1,3-propanediamine, and *n* = 1 when X is 0.5SO₄^{2−} and 0.5SeO₄^{2−}, *n* = 0 when X is Cl[−], Br[−], I[−] and SCN[−]) have been synthesised and investigated thermally in the solid state. The species Cd(aepn)Cl₂, Cd(aepn)SO₄ and Cd(aepn)SeO₄ have also been synthesised pyrolytically in the solid state from the corresponding parent bis-complexes. Cd(aepn)(SCN)₂ and Cd(dpt)(SCN)₂ melt on heating and exist as supercooled liquids at ambient temperature. On heating and after deaquation, Cd(dpt)SO₄·H₂O shows two endothermic phase transitions (172–190°C, Δ*H* = 8.0 kJ mol^{−1} and 210–245°C, Δ*H* = 3.5 kJ mol^{−1}) and the low-temperature transition is reversible (182–165°C, Δ*H* = −7.8 kJ mol^{−1}). Conversely, the selenate analogue undergoes an irreversible endothermic phase transition (240–257°C, Δ*H* = 13.2 kJ mol^{−1}). [Cd(aepn)₂](NO₃)₂ and Cd(aepn)I₂ show irreversible endothermic phase transitions (198–218°C, Δ*H* = 5.9 kJ mol^{−1} for nitrate, and 195–202°C, Δ*H* = 8.3 kJ mol^{−1} for iodide). The transitions are assumed to be due to the conformational changes in the triamine chelate rings. The thermal stabilities are rationalized with respect to the carbon chain lengths of the triamine ligands.

Keywords: Cadmium triamine complex; DSC; Phase transition; TG–DTA; Thermal decomposition

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1. Introduction

The syntheses and characterisation of triamine complexes of transition and non-transition metals are of interest as they can potentially exist in three isomeric forms, i.e. mer, s-fac and u-fac [1–4]. The measurements of stability constants and thermochemical studies in solution reveal that the stability of these complexes decrease as the carbon chain length of the ligand increases [5, 6]. We first reported the thermal behaviour of diethylenetriamine (dien) of nickel(II) [7–9], zinc(II) and cadmium(II) [9] complexes in the solid phase and observed that geometrical isomerism, e.g. s-fac $\rightarrow$ mer, as well as conformational changes of the triamine chelate rings may occur on heating. Moreover, to study the dependence of the thermal stability of the complexes on the carbon chain length we recently carried out thermal studies of *N*-(2-aminoethyl)-1,3-propanediamine (aepn) and *N*-(3-aminopropyl)-1,3-propanediamine (dpt) complexes of Ni(II) [10, 11] and came to the same conclusion as we did from measurements of the stability constant from solution [5]. Thermal studies of zinc(II) and cadmium(II) with the other two triamines (aepn and dpt) have not been published. Here we report the thermal studies of *N*-(2-aminoethyl)-1,3-propanediamine and *N*-(3-aminopropyl)-1,3-propanediamine complexes of cadmium(II).

2. Experimental

High-purity *N*-(2-aminoethyl)-1,3-propanediamine and *N*-(3-aminopropyl)-1,3-propanediamine were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were AR grade. The enthalpy change of the phase transition was derived using a Perkin-Elmer DSC-2 differential scanning calorimeter using indium metal as calibrant. Other equipment employed to record IR spectra, X-ray powder diffraction data, elemental analyses and thermal measurements (TG–DTA) has been described previously [12]. Elemental analyses, X-ray diffraction and initial temperature of decomposition (T_i) data of the complexes are shown in Tables 1, 2 and 3, respectively.

2.1. Preparation of complexes

$[\text{Cd}(\text{aepn})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (1), $[\text{Cd}(\text{aepn})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$ (2), $[\text{Cd}(\text{aepn})_2]\text{I}_2$ (3), and $[\text{Cd}(\text{aepn})_2](\text{NO}_3)_2$ (7) were prepared by adding ethanolic solutions (5 cm^3) of triamine (2 mmol) to cadmium salts (1 mmol) dissolved in ethanol (5 cm^3). The resulting mixture on stirring at ambient temperature yielded the desired complex species. The complexes were separated by filtration, washed with cold ethanol and dried in a desiccator over CaCl_2 .

$[\text{Cd}(\text{aepn})_2]\text{SO}_4$ (4) and $[\text{Cd}(\text{aepn})_2]\text{SeO}_4$ (5) were prepared by adding ethanolic solutions (5 cm^3) of aepn (2 mmol) to cadmium salts dissolved in the minimum quantity of water. The desired complexes separated from the resulting mixture on treatment with isopropanol (10 cm^3). These were filtered, washed with isopropanol and dried in a desiccator over CaCl_2 .

Table 1

Elemental analyses data of *N*-(2-aminoethyl)-1,3-propanediamine (aepn) and *N*-(3-aminopropyl)-1,3-propanediamine (dpt) complexes of cadmium(II).

Complex	No.	Elemental analyses, % ^a		
		C	H	N
[Cd(aepn) ₂]Cl ₂ ·H ₂ O	1	27.5(27.5)	8.0(7.3)	19.4(19.3)
Cd(aepn)Cl ₂	1b	20.2(20.0)	5.3(5.0)	13.8(14.0)
[Cd(aepn) ₂]Br ₂ ·H ₂ O	2	22.8(22.9)	6.0(6.1)	15.9(16.0)
Cd(aepn)Br ₂	2b	15.6(15.4)	4.1(3.8)	10.8(10.8)
[Cd(aepn) ₂]I ₂	3	19.8(20.0)	5.0(5.0)	13.8(14.0)
Cd(aepn)I ₂	3a	12.4(12.4)	3.2(3.1)	8.6(8.7)
[Cd(aepn) ₂]SO ₄	4	27.0(27.1)	7.1(6.8)	18.9(19.0)
Cd(aepn)SO ₄	4a	18.3(18.4)	4.5(4.6)	13.1(12.9)
[Cd(aepn) ₂]SeO ₄	5	24.7(24.5)	6.0(6.1)	16.9(17.1)
Cd(aepn)SeO ₄	5a	16.0(16.1)	4.8(4.0)	11.2(11.3)
Cd(aepn)(SCN) ₂	6	24.4(24.3)	4.5(4.3)	20.0(20.2)
[Cd(aepn) ₂](NO ₃) ₂	7	25.6(25.5)	6.6(6.4)	23.6(23.8)
Cd(dpt)Cl ₂	8	23.2(22.9)	5.5(5.4)	13.3(13.3)
Cd(dpt)Br ₂	9	17.8(17.8)	4.5(4.2)	10.4(10.4)
Cd(dpt)I ₂	10	14.4(14.5)	3.5(3.4)	8.3(8.4)
Cd(dpt)SO ₄ ·H ₂ O	11	20.0(20.1)	5.6(5.3)	11.4(11.7)
Cd(dpt)SeO ₄ ·H ₂ O	12	17.6(17.8)	4.5(4.7)	10.1(10.4)
Cd(dpt)(SCN) ₂	13	27.0(26.7)	5.0(4.7)	19.2(19.5)

^a Percentages in parentheses are theoretically calculated values.

Cd(aepn)Cl₂ (**1b**), Cd(aepn)Br₂ (**2b**), Cd(aepn)I₂ (**3a**), Cd(aepn)(SCN)₂ (**6**), Cd(dpt)Cl₂ (**8**), Cd(dpt)Br₂ (**9**), Cd(dpt)I₂ (**10**) and Cd(dpt)(SCN)₂ (**13**) were synthesised following the same method as described for the corresponding bis-complexes, but changing the metal: ligand ratio to 1:1.

Cd(aepn)SO₄ (**4a**), Cd(aepn)SeO₄ (**5a**), Cd(dpt)SO₄·H₂O (**11**) and Cd(dpt)SeO₄·H₂O (**12**) were prepared using the technique adopted for their corresponding bis-complexes and varying the metal: ligand ratio to 1:1.

Cd(aepn)Cl₂ (**1b**), Cd(aepn)SO₄ (**4a**) and Cd(aepn)SeO₄ (**5a**) were derived pyrolytically in the solid state from the respective parent bis-complexes.

3. Results and discussion

N-(2-aminoethyl)-1,3-propanediamine yields bis- as well as mono-complexes with cadmium(II) salts, whereas in the case of *N*-(3-aminopropyl)-1,3-propanediamine, we have been able to synthesise only mono-species. All the complexes are stable in the open atmosphere except Cd(aepn)₂AO₄ (where A is S or Se) and Cd(aepn)Br₂ which are hygroscopic. All the complexes can be stored indefinitely in a desiccator over CaCl₂. We could not synthesise [Cd(aepn)₂](SCN)₂.

Table 2

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

Complex	$d/\text{Å}$
Cd(dpt)SO ₄ (11a)	5.67(vs), 3.86(w), 3.63(vs), 2.92(s), 2.83(vs), 2.71(vw), 1.89(vs), 1.83(s), 1.78(s), 1.74(s), 1.70(s), 1.66(vw), 1.64(s), 1.61(vs), 1.44(vs), 1.40(s), 1.37(w), 1.31(vs), 1.25(w), 1.20(w),
Cd(dpt)SO ₄ (11c)	5.71(vs), 2.83(vs), 2.42(w), 2.25(w), 2.12(w), 1.93(w), 1.78(vs), 1.72(vw), 1.64(vw), 1.55(vw), 1.47(vw), 1.44(w), 1.35(vw), 1.26(vw), 1.24(vw), 1.21(vw), 1.17(vw), 1.09(vw), 1.07(vw), 0.93(vw), 0.92(vw)
Cd(dpt)SeO ₄ (12a)	5.53(vs), 3.55(s), 3.12(w), 2.83(s), 1.99(vw), 1.91(s), 1.83(w), 1.76(w), 1.69(vw), 1.64(w), 1.46(s), 1.38(w), 1.36(w), 1.31(w)
Cd(dpt)SeO ₄ (12b)	5.71(vs), 3.96(vw), 2.83(vs), 2.39(vw), 2.19(s), 1.87(vs), 1.78(vw), 1.69(vw), 1.58(vw), 1.50(w), 1.41(vw), 1.35(vw), 1.27(vw), 1.25(vw)
[Cd(aepn) ₂](NO ₃) ₂ (7)	3.63(vs), 3.36(vs), 3.12(w), 2.92(s), 2.83(w), 2.67(vw), 2.49(w), 2.30(w), 2.14(s), 2.05(vw), 1.91(s), 1.85(s), 1.83(s), 1.80(vw), 1.77(vw), 1.72(s), 1.66(s), 1.61(vw), 1.59(vw), 1.56(vw)
[Cd(aepn) ₂](NO ₃) ₂ (7a)	3.63(vs), 3.37(vs), 3.12(s), 2.93(s), 2.83(w), 2.59(w), 2.49(w), 2.30(w), 2.25(w), 2.16(s), 2.07(vw), 2.03(vw), 1.91(s), 1.83(s), 1.80(vw), 1.72(s), 1.68(s), 1.56(vw), 1.51(s), 1.48(s)

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

Table 3

Comparative chart of T_i (initial temperature of decomposition in °C) for some of the bis- and mono-triamine (dien, aepn and dpt) complexes of cadmium(II)

Complex	L		
	dien	aepn	dpt
[CdL ₂]Cl ₂	185	160	—
CdLCl ₂	255	208	183
[CdL ₂]Br ₂	190	163	—
CdLBr ₂	240	208	187
CdLI ₂	237	210	205
[CdL ₂]SO ₄	195	134	—
CdLSO ₄	290	214	280
[CdL ₂]SeO ₄	210	130	—
CdLSeO ₄	—	181	275
CdL(SCN) ₂	—	237	219
[CdL ₂](NO ₃) ₂	265	223	170

Bis-complexes with linear triamines, such as dien, aepn and dpt, can potentially exist in three geometrical isomeric forms, s-fac, u-fac and mer [1, 13]. The mer isomer is thermodynamically the most stable and this is the most common geometry of the bis-triamine complexes reported so far.

For the dien complexes, IR spectroscopy has been found to be a valuable method for the characterisation of the different isomeric forms [13]. Unfortunately comparisons of the IR spectra of aepn complexes is not possible due to the lack of single-crystal X-ray analyses of bis-complexes. However, a recent study on aepn complexes of zinc(II) with ^{13}C NMR shows that the most probable configuration for bis-complexes of aepn is mer [10]. Thus we may assume that the bis-aepn complexes possess mer-octahedral geometry.

Among the mono-complexes considered here, the single-crystal X-ray structural analyses of CdLCl_2 (L is aepn and dpt) have been described in the literature [4]. In both these cases, pseudo-octahedral and dimeric structures prevail via chloride bridges, with trans- and cis-configuration for aepn and dpt respectively. The IR spectra of the complexes CdLX_2 (L is aepn and dpt, and X is Br^- , I^- and SCN^-) are similar to those of Cd(aepn)Cl_2 and Cd(dpt)Cl_2 respectively. Thus, we can assume that they also possess dimeric pseudo-octahedral geometry via halide (Br^- or I^-) or SCN^- bridges. The other mono-aepn complex of cadmium(II) is $\text{CdLAO}_4 \cdot n\text{H}_2\text{O}$ (L is aepn, A is S or Se when $n = 0$; L is dpt, A is S or Se when $n = 1$) shows an IR spectrum which is similar to that of the corresponding chloro analogue. Considering the bidentate nature of AO_4^{2-} (A is S or Se), the hydrated species are octahedral but the structure of the dehydrated species is still doubtful as the actual mode of coordination of AO_4^{2-} is not predictable simply from the IR spectra due to overlapping of the triamine bands, together with the unavailability of single-crystal structural analyses of the analogous complexes.

$\text{Cd(dpt)SO}_4 \cdot \text{H}_2\text{O}$ (**11**) starts to lose its water molecule at $\sim 110^\circ\text{C}$ and becomes dehydrated (**11a**) at $\sim 155^\circ\text{C}$ in two steps, as is evident from the two overlapping endotherms in the DTA curve (Fig. 1). The dehydrated species becomes rehydrated in a humid atmosphere (60% or more). It exhibits two successive endothermic phase transitions ($172\text{--}190^\circ\text{C}$, $\Delta H = 8.0 \text{ kJ mol}^{-1}$; $210\text{--}245^\circ\text{C}$, $\Delta H = 3.5 \text{ kJ mol}^{-1}$, Fig. 2) without showing any mass loss, as is evident from the TG-DTA curves (Fig. 1), and transforms to its isomer (**11c**) at $\sim 250^\circ\text{C}$ through the formation of another isomer (**11b**) as an intermediate. The isomer (**11c**) is not stable in a humid atmosphere and gradually transforms to (**11**), but it can be stabilised in a desiccator. It is interesting to note that the transformation **11a** $\rightarrow$ **11b** is reversible ($182\text{--}165^\circ\text{C}$, $\Delta H = -7.8 \text{ kJ mol}^{-1}$). X-ray powder diffraction patterns of (**11a**) and (**11c**) differ from each other (Table 2). The IR spectra also differ in the regions $1550\text{--}1600$, $1400\text{--}1500$, $1000\text{--}1050$, $850\text{--}900$, $780\text{--}820$ and 550 cm^{-1} . It is noted that the characterisation of isomer (**11b**) was not possible. The temperature range corresponding to water loss in $\text{Cd(dpt)SO}_4 \cdot \text{H}_2\text{O}$ seems high, which indicates that the water molecule is coordinated to cadmium(II) to satisfy its octahedral geometry. After elimination of water, the species (**11a**) is presumed to be penta-coordinated. This, upon heating, probably transforms to tetrahedral geometry (**11b**) as cadmium(II) prefers 6- and 4-coordination, yielding N_3O chromophore around cadmium(II) (Scheme 1). The isomerisation **11b** $\rightarrow$ **11c** is assumed to be due to the conformational changes in the chelate rings of the triamine, as deduced from their IR spectra.

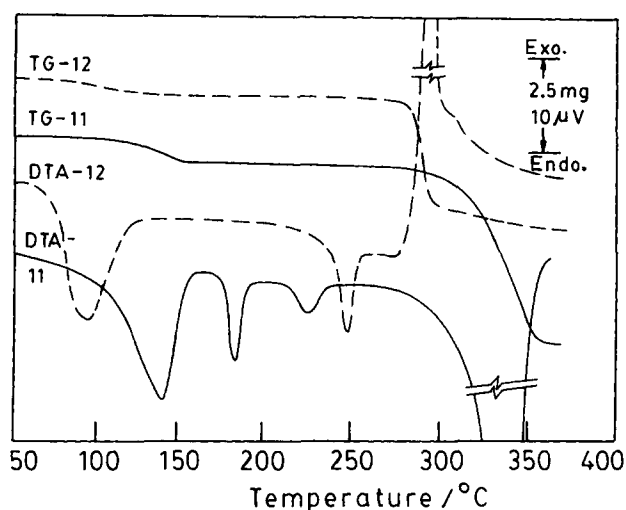


Fig. 1. TG-DTA curves:—, $\text{Cd(dpt)SO}_4 \cdot \text{H}_2\text{O}$ (11) (sample mass, 13.18 mg); and ---, $\text{Cd(dpt)SeO}_4 \cdot \text{H}_2\text{O}$ (12) (sample mass, 10.35 mg).

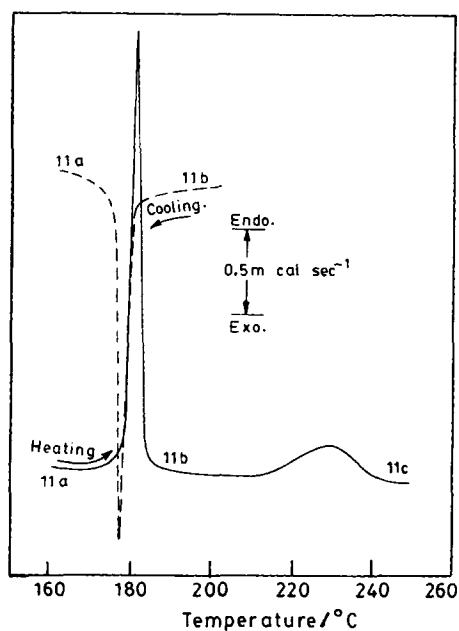
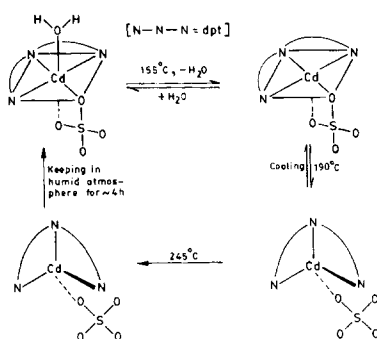


Fig. 2. DSC curves:—, heating; ---, cooling; Cd(dpt)SO_4 (11a) (sample mass, 8.00 mg).

$\text{Cd(dpt)SeO}_4 \cdot \text{H}_2\text{O}$ (12) starts dehydration at $\sim 85^\circ\text{C}$ and transforms to Cd(dpt)SeO_4 (12a) at $\sim 150^\circ\text{C}$, showing an endotherm in its DTA curve (Fig. 1). The dehydrated species on further heating undergoes an irreversible endothermic phase transition ($240\text{--}257^\circ\text{C}$, $\Delta H = 13.2 \text{ kJ mol}^{-1}$ Fig. 3) yielding an isomer Cd(dpt)SeO_4



Scheme 1.

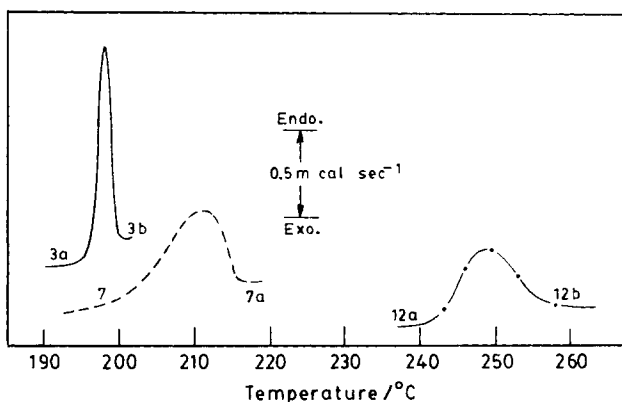


Fig. 3. DSC curves:—, $\text{Cd(aepn)}_2\text{I}_2$ (**3a**) (sample mass, 7.40 mg); ---, $[\text{Cd(aepn)}_2](\text{NO}_3)_2$ (**7**) (sample mass, 9.39 mg); - · - ·, Cd(dpt)SeO_4 (**12a**) (sample mass, 7.80 mg).

(**12b**) without showing any mass loss, as is evident from its TG–DTA curve (Fig. 1). The isomers (**12a**) and (**12b**) are not stable in a humid atmosphere, but they can be stabilised in a desiccator. The IR spectra of (**12a**) and (**12b**) differ appreciably in the regions $3200\text{--}3400$, $1500\text{--}1600$, $980\text{--}1200$, $800\text{--}935$ and $600\text{--}730\text{ cm}^{-1}$, which correspond to $\nu(\text{NH}_2)$, $\delta(\text{NH}_2)$, $\rho_w(\text{CH}_2) + \rho_w(\text{NH}_2) + \tau(\text{NH}_2) + \tau(\text{CH}_2)$ + stretching vibrations of the skeleton $\nu(\text{C}\text{--}\text{N}) + \nu(\text{C}\text{--}\text{C})$, $\rho_t(\text{CH}_2)$, $\rho_t(\text{CH}_2) + \nu(\text{MN})$. The X-ray powder patterns of (**12a**) and (**12b**) also differ appreciably (Table 2). The phase transition is assumed to be due to the conformational change of the triamine chelate ring as in the case of its sulphate analogue. In selenate, transformational (5-coordination $\rightarrow$ 4-coordination) as well as conformational (4-coordination $\rightarrow$ 4-coordination) changes are likely to take place simultaneously, as summation of ΔH values in the sulphate is nearly the same to that of the selenate.

On heating, $[\text{Cd(aepn)}_2](\text{NO}_3)_2$ (**7**) undergoes an irreversible endothermic phase transition ($198\text{--}218^\circ\text{C}$, $\Delta H = 5.9\text{ kJ mol}^{-1}$, Fig. 3). The high-temperature phase species (**7a**) is not stable in an open atmosphere. It slowly reverts to (**7**) but it can be stabilised in

a desiccator. The X-ray powder patterns (Table 2) and IR spectra of low-temperature and high-temperature phase species were recorded. The change in $\delta(\text{CH}_2)$ bands was not clearly seen owing to the overlapping of NO_3^- bands, but a broadening and shifting of other band positions were observed. We have noted in previous work that conformational isomers of the diamine [14–16] and triamine [7] systems show similar differences in their spectra. As a consequence, conformational changes of the triamine chelate rings are assumed to be responsible for the phase transition.

ΔH values for the phase transition due to conformational change of the chelate rings are reported to be of the order 3–15 kJ mol⁻¹ [10, 11, 13, 14, 16]. All the ΔH values obtained for the above phase transition are within this range, corroborating the conformational changes in the chelate ring.

$\text{Cd}(\text{aepn})\text{I}_2$ (**3a**) undergoes an irreversible endothermic phase transition (195–202°C, $\Delta H = 8.3$ kJ mol⁻¹, Fig. 3) transforming into its isomer (**3b**). The high-temperature phase species is not stable and it reverts completely to (**3a**) if it is stored for short periods in the open atmosphere. The characterisation of the isomer (**3b**) was not possible. Therefore, it is difficult to account for the occurrence of a phase transition.

$\text{Cd}(\text{dpt})(\text{SCN})_2$ (**13**) melts at $\sim 179^\circ\text{C}$ ($\Delta H = 49.0$ kJ mol⁻¹) but it does not solidify on cooling as is evident from its heating/cooling curve (Fig. 4). However, on reheating immediately after cooling to ambient temperature, two exotherms (62–80°C, $\Delta H = -14.8$ kJ mol⁻¹ and 110–140°C, $\Delta H = -8.7$ kJ mol⁻¹) are indicated and then on further heating, melting occurs at 179°C ($\Delta H = 49.0$ kJ mol⁻¹), see Fig. 4. The exothermic peaks occur due to the solidification of the supercooled liquid. It is interesting to note that if the melted complex is cooled to ambient temperature and reheated after some time (1–3 h), ΔH values of the exotherms (for solidification) decrease with time indicating that the supercooled liquid gradually solidifies and is complete in ~ 72 h. On scratching, however, the supercooled liquid solidifies instantaneously. $\text{Cd}(\text{aepn})(\text{SCN})_2$ (**6**) melts at $\sim 180^\circ\text{C}$ ($\Delta H = 58.1$ kJ mol⁻¹, Fig. 5) but does not solidify on cooling, as is evident from the corresponding heating-cooling curve. On reheating to $\sim 180^\circ\text{C}$ immediately after cooling, there is no base line drift in the

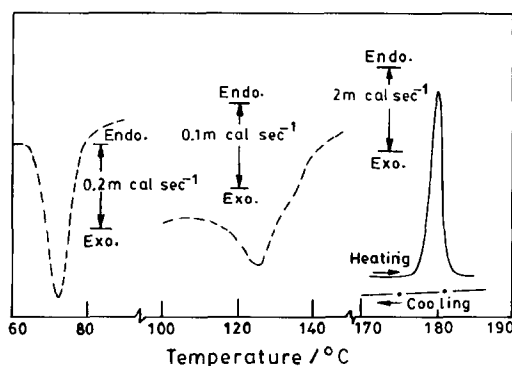


Fig. 4. DSC curves:—, first heating; ---, first cooling; -.-, second heating; $\text{Cd}(\text{dpt})(\text{SCN})_2$ (**13**) (sample mass, 2.15 mg).

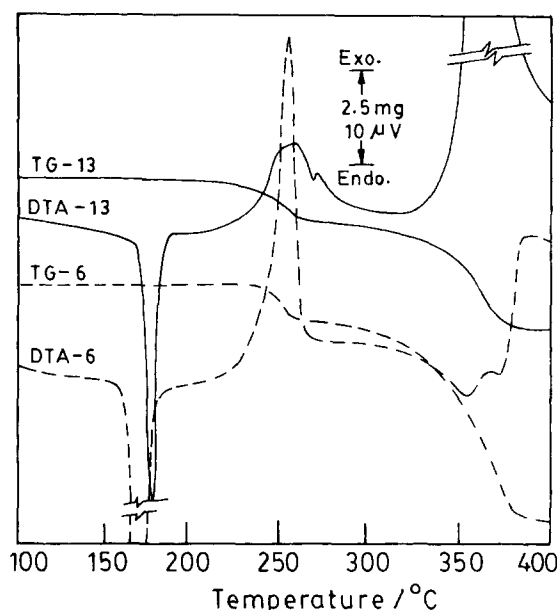


Fig. 5. TG-DTA curves:—, Cd(dpt)(SCN)_2 (**13**) (sample mass, 9.54 mg); and ----, Cd(aepn)(SCN)_2 (**6**) (sample mass, 13.32 mg).

corresponding DSC curve, indicating that the melted material remains as a supercooled liquid. This molten material remains supercooled at ambient temperature for 48 h and then its gradual solidification starts and completes in 72 h. It is interesting to note that this supercooled material never shows any exotherm upon heating even after partial solidification. This also solidifies instantaneously on scratching.

$[\text{Cd(aepn)}_2]\text{X}_2 \cdot \text{H}_2\text{O}$ (X is Cl^- , Br^-) lose their water molecule on heating and become dehydrated at $\sim 125^\circ\text{C}$ and $\sim 113^\circ\text{C}$, respectively. The dehydrated species becomes rehydrated on exposure to a humid atmosphere. These two dehydrated species and $[\text{Cd(aepn)}_2]\text{I}_2$ decompose upon heating to their respective metal salts through the formation of mono-species, as is evident from the plateau in their respective TG curves (only the decomposition of $[\text{Cd(aepn)}_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**1**) is shown in Fig. 6). Attempts to synthesise the mono-species pyrolytically in the solid state from the parent bis-complexes gave Cd(aepn)Cl_2 , which is identical to Cd(aepn)Cl_2 (**1b**) synthesised from solution.

$[\text{Cd(aepn)}_2]\text{AO}_4$ (A is S or Se) show a number of steps in their TG curves. Both curves show a mass loss at the beginning of the scan. The initial mass loss is due to the release of a water molecule associated with the complex. Then they start to lose a triamine molecule and ultimately transform to Cd(aepn)AO_4 (A is S or Se) which are identical to Cd(aepn)SO_4 (**4a**) and Cd(aepn)SeO_4 (**5a**) synthesized from solution (only decomposition of $[\text{Cd(aepn)}_2]\text{SO}_4$ (**4**) is shown in Fig. 6).

Decomposition of the mono-species is complicated as their TG-DTA curves are not well-resolved, although Cd(aepn)(SCN)_2 (**6**) and Cd(dpt)(SCN)_2 (**13**) do show

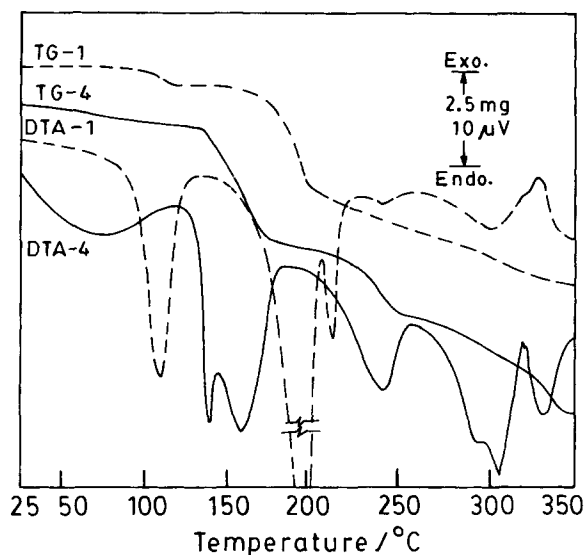


Fig. 6. TG-DTA curves: —, $[\text{Cd}(\text{aepn})_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (sample mass, 14.85 mg); and ----, $[\text{Cd}(\text{aepn})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (1) (sample mass, 11.80 mg).

a well-resolved two-step decomposition, as evident from their TG-DTA curves (Fig. 5). The plateau observed at the initial stage of decomposition corresponds to $\text{Cd}(\text{aepn})_{0.66}(\text{SCN})_2$ and $\text{Cd}(\text{dpt})_{0.66}(\text{SCN})_2$.

4. Conclusion

The aepn yielded several bis- and mono-compounds but dpt yielded only mono-species. No bis-species can be isolated for dpt even with excess of ligand. The increased steric hindrance caused by the larger chelate rings formed by dpt is probably responsible for this. The complexes $[\text{Cd}(\text{aepn})_2](\text{NO}_3)_2$, $\text{Cd}(\text{aepn})\text{I}_2$, $\text{Cd}(\text{dpt})\text{SO}_4$ and $\text{Cd}(\text{dpt})\text{SeO}_4$ undergo endothermic phase transition, probably due to the conformational changes of the triamine chelate rings. The complexes $\text{Cd}(\text{dpt})(\text{SCN})_2$ and $\text{Cd}(\text{aepn})(\text{SCN})_2$ melt and the molten species remain as supercooled liquid at ambient temperature for several hours. A comparison of the thermal stabilities of dien, aepn and dpt (Table 3) shows that the T_i (initial temperature of decomposition) decreases with the increase in the size of the chelate rings. A similar trend has also been found for the related nickel(II) complexes in the solid state [11].

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