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THERMAL INVESTIGATION AND STEREOCHEMICAL STUDIES OF SOME CYCLIC DIAMINE COMPLEXES OF NICKEL(II), ZINC(II) AND CADMIUM(II) IN THE SOLID STATE. Part V

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ABSTRACT

Nickel(II), zinc(II) and cadmium(II) complexes of piperazine (pipz), and 1,4-diazacycloheptane (dach) with the composition $[Ni(pipz)(TCA)_2(H_2O)_2]$, $[M(dach)_2(TCA)_2]$ (M = Ni or Cd), $[Zn(pipz)_2(TCA)_2]\cdot H_2O$, $[Zn(dach)_2(TCA)_2]\cdot 2H_2O$ and $[Cd(pipz)_2(TCA)_2]\cdot 2H_2O$ (where TCA represents trichloroacetate ion) have been synthesised. Attempts to prepare *N*-methylpiperazine and *N,N'*-dimethylpiperazine complexes of all the metal ions failed. Some intermediate complexes were isolated by pyrolysis. Configurational and conformational changes have been studied by elemental analyses, IR spectra, magnetic moment measurements and thermal analyses. All the complexes and the intermediates appear to be octahedral. Activation energies (E_a^*), enthalpy (ΔH) and entropy changes (ΔS) for the dehydration and decomposition reactions of the complexes have been evaluated. The order of stability of the complexes (with respect to E_a^*) follows the trend pipz > dach. A linear correlation has been found between E_a^* and ΔS for the decomposition of the complexes.

INTRODUCTION

Acyclic diamines having the $N(CH_2)N$ grouping act as chelating agents for transition metal ions [1,2]. There has been little thermal investigation of solid cyclic diamine complexes [3–6]. The main aim of our work is to synthesise some cyclic diamine (six- or seven-membered ring) complexes of transition and non-transition metals, and to study stereochemical changes during thermal decomposition. In addition to six-membered cyclic diamine ligands, we have studied a seven-membered cyclic diamine to see whether

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strain in the ligand could be reduced by introducing a methylene group between the amine functions [1] but have failed to draw any definite conclusion on this part.

Before heating, the cyclic diamines function as bidentate chelates (boat form) [3,7–9] and trichloroacetate ion as a unidentate ligand [10,11]. When these complexes were heated under non-isothermal conditions, the complexes first became dehydrated (in some cases) and then decomposed to trichloroacetate via some intermediates in which the cyclic ligands might function as chelate (boat form), bridging bidentate (chair form) or both, while trichloroacetate would act as a chelate, bridging bidentate or monodentate ligand. Before heating, the cyclic ligands as well as trichloroacetate (unidentate) appear to coordinate with the central metal ion at *cis* positions as indicated by two or more IR bands of $\rho_r(CH)_2$ [12] for the *cis* isomer but one band for the *trans* isomer. Parameters such as E_a^*, ΔH and ΔS for the dehydration and decomposition reactions of the complexes in the solid state have been calculated [13,14].

EXPERIMENTAL

Materials and methods

Metal carbonates of A.R. grade were used as received. Metal trichloroacetates were freshly prepared by neutralising trichloroacetic acid with an excess of metal carbonate followed by crystallisation from the filtrates obtained. Piperazine obtained from Merck (Germany), *N*-methylpiperazine, *N*,*N*′-dimethylpiperazine, and 1,4-diazacycloheptane obtained from Fluka (Switzerland) were used as received. Diethyl ether and ethanol were dried by standard procedures [15].

Preparation of the complexes

$[Ni(pipz)(TCA)_2(H_2O)_2]$. The ligand (ca. 4 mmol) in dry ethanol (20 cm^3) was treated with constant stirring of a dry ethanolic solution (50 cm^3) of freshly prepared nickel trichloroacetate (2 mmol). A bluish green precipitate of the complex appeared after addition of dry diethyl ether and was dried over silica gel in a desiccator. Yield was ca. 50%.

$[Ni(dach)(TCA)_2]$, $[Zn(pipz)_2(TCA)_2] \cdot H_2O$, $[Zn(dach)_2(TCA)_2] \cdot 2H_2O$, $[Cd(pipz)_2(TCA)_2] \cdot 2H_2O$ and $[Cd(dach)_2(TCA)_2]$ were similarly prepared. Yields were ca. 50–60% in most cases. Nickel, zinc and cadmium were estimated gravimetrically by standard procedures [16]; C, H, and N were estimated using Perkin–Elmer 240C and Carlo Erba 1106 elemental analysers. Elemental analyses are given in Table 1. Thermal investigation was carried out on a Shimadzu DT-30 thermal analyser under a nitrogen

TABLE 1

Analytical (calculated values in parentheses) and magnetic moment data of trichloroacetato-cyclic diamine [a] complexes of Ni(II), Zn(II) and Cd(II)

Complex	Colour	Analysis (%)				μ_{eff} (B.M.)
		M	C	H	N	
(1a) $[NiL(TCA)_2(H_2O)_2]$	Bluish green	11.42 (11.61)	18.54 (18.98)	3.02 (2.77)	6.00 (5.54.)	3.15
(2a) $[NiL''_2(TCA)_2]$	Yellowish green	9.68 (10.06)	29.31 (28.78)	4.36 (4.11)	10.02 (9.59)	3.20
(3a) $[ZnL_2(TCA)_2]\cdot H_2O$	White	10.64 (11.27)	28.54 (28.94)	4.05 (4.47)	9.95 (9.64)	
(3c) $[ZnL(TCA)_2]$	White	13.71 (13.73)	20.10 (20.15)	2.01 (2.10)	5.69 (5.88)	
(4a) $[ZnL''_2(TCA)_2]\cdot 2H_2O$	White	9.84 (10.44)	27.00 (26.80)	4.42 (4.47)	9.32 (8.93)	
(5a) $[CdL_2(TCA)_2]\cdot 2H_2O$	White	17.11 (17.42)	22.15 (22.31)	3.65 (3.72)	8.54 (8.68)	
(5c) $[CdL(TCA)_2]$	White	21.41 (21.46)	18.31 (18.33)	1.90 (1.91)	5.31 (5.35)	
(6a) $[CdL''_2(TCA)_2]$	White	17.57 (17.63)	26.41 (26.36)	3.82 (3.77)	8.92 (8.79)	

[a] L, piperazine (pipz); L'', 1,4-diazacycloheptane (dach).

TABLE 2

IR spectral data [a] (cm^{-1}) for trichloroacetato (TCA)-cyclic diamine (L = pipz/L'' = dach) complexes of Ni(II), Zn(II) and Cd(II)

Complex	ν(NH) + ν(OH)	$\nu(CH_2)$	δ(NH) + δ(HOH) + $\nu_{as}(CO_2^-)$	$\delta(CH_2)$ + $\nu_s(CO_2^-)$	$\Delta\nu$	$\rho_w(CH_2)$	τ(NH) + ρ_w(NH) + $\tau(CH_2)$	Stretching vibrations of skeleton ν(C–N) + ν(C–C)	$\rho_t(CH_2)$	$\delta(CO_2^-)$ + ν(C–Cl)	ρ_r(NH) [b] + $\rho_r(CH_2)$ + ν(M–N)	ν(M–O)
(1a) $[NiL(TCA)_2(H_2O)_2]$	3360(vsbr) 3200(s)	2940(w) 2840(vw)	1730(sh) 1685(sh) *1630*(sbr) 1500(sh)	*1440*(vsbr) *1390*(vsbr)	190 (*240*)	1350(sh)	1270(m) 1190(vw) 1170(vw) 1150(vw)	1080(w) 1055(vw) 1035(vw) 1000(vw) 980(w) 970(sh)	900(vw) 870(sh)	840(w) 800(w) [c] 730(sh) [c]	650(mbr) [c]	460(w) [c] 380(wbr) 270(w)
(2a) $[NiL''_2(TCA)_2]$	3440(mbr) 3130(vs)	2970(vw) 2940(w) 2890(w) 2850(sh)	1670(sh) *1660*(vs) 1620(vw) 1560(vw) 1540(*vw*) 1505(vw)	1480(w) 1470(sh) 1460(m) 1445(vw) *1380*(*vw*) 1360(ms) *1320*(vs)	340	1380(vw) 1360(ms)	1310(sh) 1280(sh) 1250(w) 1230(vw) 1150(*w*) 1130(w)	1070(ms) 1000(sh) 990(m) 980(sh)	930(w) 910(vw) 880(vw) 870(vw)	850(ms) 835(s) 790(w) 740(vs) 720(*vw*)	685(s) 645(w) 540(vw)	430,420 (w,sp) 310(vw) 290(w)
(3a) $[ZnL_2(TCA)_2]$ $\cdot H_2O$	3440(mbr) 3200(vw)	3030(sh) 2980(w) 2920(sh) 2860(vw) 2820(vw)	1685(sh) 1670(sh) *1660*(vs) 1630(ms) 1600(sh)	1460(ms) 1450(sh) 1390(w) 1360(sh) *1330*(vs)	330	1390(w) 1360(sh)	1210(vw) 1150(vw) 1120(vw)	1090(w) 1020(vw) 980(vw)	930(vw) 870(w)	845(s) 750(s)	680(s) 600(m)	475(vw) 450(vw) 430(sh) 320(w) 300(vw) 290(vw)

(3c) $[ZnL(TCA)_2]$	3480(ms) 3240(s)	2980(w) 2860(sh)	1690(sh) 1680(sh) *1635*(vs) 1610(sh)	*1450*(s) 1430(sh)	185	1370(vw)	1320(vw) 1300(vw) 1270(w) 1250(w) 1200(vw)	1100(ms) 1020(ms) 1000(ms)	870(ms)	810(vw)	640(w) 600(w) 570(vw) 550(vw)	470(w) 420(sh) 365(vw)
(4a) $[ZnL''_2(TCA)_2]$ $\cdot 2H_2O$	3420(mbr) 3240(vw)	2940(wbr) 2880(sh)	*1655*(s) 1560(s)	1490(ms) *1420*(s)	235	1380(vw)	1340(vw) 1320(vw) 1290(vw) 1230 (vw) 1135(w)	1050(mbr) 990(vw)	930(m) 910(sh) 875(vw) 855(sh)	805(s) 760(w)	650(mbr) 630(m) 600(sh) 570(mbr)	460(wbr) 390(wbr) 285(w)
(5a) $[CdL_2(TCA)_2]$ $\cdot 2H_2O$	3440(wvbr) 3240(m) 3200(m)	2960(w) 2940(vw) 2890(vw)	1670(sh) *1650*(vs) 1520(vw)	1475(vw) 1460(vw) 1450(w) 1370(sh) 1350(sh) *1340*(s)	310	1370(sh) 1350(sh)	1320(sh) 1280(vw) 1255(vw) 1220(w) 1190(vw) 1160(vw)	1090(w) 1050(vw) 1040(vw) 1020(vw) 980(vw)	940(vw) 890(sh) 880(ms)	840(ms) 830(sh) 750(ms)	680(s) 650(vw)	470(vw) 370(vw) 325(vw) 290(vw)
(5c) $[CdL(TCA)_2]$	3500(mbr) 3220(ms)	3060(mbr) 2860(sh) 2800(sh)	*1640*(vs) 1560(sh) 1540(sh)	1460(sh) *1450*(s) 1430(sh) 1400(sh)	190	1370(vw) 1350(vw)	1320(vw) 1300(sh) 1270(w) 1230(vw) 1200(vw) 1130(vw)	1040(sh) 1000(m)	920(vw) 870(m)	820(vw)	650(vw) 600(w) 570(vw)	470(w) 430(sh) 350(vw)
(6a) $[CdL''_2(TCA)_2]$	3420(mbr) 3200(w)	2940(vw) 2860(vw)	1680(sh) *1670*(vs) 1640(sh) 1550(w) 1530(w)	1450(msbr) 1360(sh) 1350(sh) *1320*(s)	350	1360(sh) 1350(sh)	1270(vw) 1250(vw) 1220(vw) 1130(vw)	1105(mw) 1085(w) 1030(vw) 1000(w) 975(vw)	920(vw) 860(sh)	840(m) 830(sh) 805(sh) 740(m) 705(vw)	680(m) 600(vw) 510(vw)	450(vw) 380(w) 350(vw) 320(vw)

[a] v, very; s, strong; m, medium; br, broad; w, weak; sh, shoulder; sp, split.

[b] Frequencies above 650 cm^{-1} are overlapping with those of $\delta(CO_2^-)$ and $\nu(C-Cl)$.

[c] Frequencies are overlapped with those of coordinated water molecule [800(730) cm^{-1} $\rho_t(H_2O)$, 650 cm^{-1} $\rho_w(H_2O)$ and 460 cm^{-1} $\nu(M-O)$ in $M-OH_2$].

TABLE 3

Thermal parameters of trichloroacetato-cyclic diamine [pipz(L)/dach(L'')] complexes of Ni(II), Zn(II) and Cd(II)

Decomposition reaction		Temperature range (°C)	DTA peak temp. (°C)		E_a^* (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
			endo	exo	TG	DTA		
1 (a) $[NiL(TCA)_2(H_2O)_2]$	$\rightarrow [NiL(TCA)_2]$	35–100	85		44	40	130	363
(b) $[NiL(TCA)_2]$	$\rightarrow Ni(TCA)_2$	100–195		180	68	74	58	129
(c) $Ni(TCA)_2$	$\rightarrow NiCl_2$	195–580		275, 450	114			
2 (a) $[NiL''_2(TCA)_2]$	$\rightarrow Ni(TCA)_2$	70–127		122	200 66 [b]		6	16
(b) $Ni(TCA)_2$	$\rightarrow NiCl_2$	127–357		155, 200, 245	223			
3 (a) $[ZnL_2(TCA)_2]\cdot H_2O$	$\rightarrow [ZnL_2(TCA)_2]$	50–122	70		23		11	34
(b) $[ZnL_2(TCA)_2]$	$\rightarrow Zn(TCA)_2$	122–150	130, 150 [a]		47		72	172
(c) $Zn(TCA)_2$	$\rightarrow ZnCl_2$	150–610		330	135			
4 (a) $[ZnL''_2(TCA)_2]\cdot 2H_2O$	$\rightarrow [ZnL''_{1.5}(TCA)_2]$	40–160	65		19	46	55	163
(b) $[ZnL''_{1.5}(TCA)_2]$	$\rightarrow Zn(TCA)_2$	160–210	185		26	86	93	205
(c) $Zn(TCA)_2$	$\rightarrow ZnCl_2$	210–545		385	28	30		
5 (a) $[CdL_2(TCA)_2]\cdot 2H_2O$	$\rightarrow [CdL_2(TCA)_2]$	55–135	90		10	46	81	224
(b) $[CdL_2(TCA)_2]$	$\rightarrow Cd(TCA)_2$	135–150		145	20		146	350
(c) $Cd(TCA)_2$	$\rightarrow CdCl_2$	150–590		330, 505 [a]	15			
6 (a) $[CdL''_2(TCA)_2]$	$\rightarrow [CdL''(TCA)_2]$	50–110		108	8		47	123
(b) $[CdL''(TCA)_2]$	$\rightarrow Cd(TCA)_2$	110–290	260		17		81	153
(c) $Cd(TCA)_2$	$\rightarrow CdCl_2$	290–600		440				

[a] DTA peak temperature used for the evaluation of entropy change.

[b] Value evaluated by Coats and Redfern method [20].

atmosphere with a heating rate of 10 °C min^{-1} and α-alumina as a standard. The particle size of the samples was within 150–200 mesh. Indium metal was used as a calibrant for the evaluation of enthalpy changes. Infrared spectra were recorded with Beckman IR 20A and Perkin–Elmer 783 spectrometers in KBr as a medium. The effective magnetic moments were evaluated from magnetic susceptibility measurements with an EG and G PAR 155 vibrating sample magnetometer at room temperature. Solid pyrolised products were identified by qualitative analyses.

RESULTS AND DISCUSSION

[Ni(pipz)(TCA)$_2$(H$_2$O)$_2$] (1a)

This complex has not been previously reported. The presence of coordinated water molecules was confirmed by its IR bands at 800 (730) cm^{-1} [$\rho_r(H_2O)$], 650 cm^{-1} [$\rho_w(H_2O)$], and 460 cm^{-1} [ν(M–O) in M–OH_2] (Table 2). Further, the mass loss in TG curve of the complex (1a) in the range 35–100 °C and an endothermic peak at 85 °C (Table 3) correspond to two molecules of water. The anhydrous complex [Ni(pipz)(TCA)$_2$] (**1b**) is converted into Ni(TCA)$_2$ in the range 100–195 °C (Fig. 1 and Table 3). Values of thermodynamic parameters are given in Table 3.

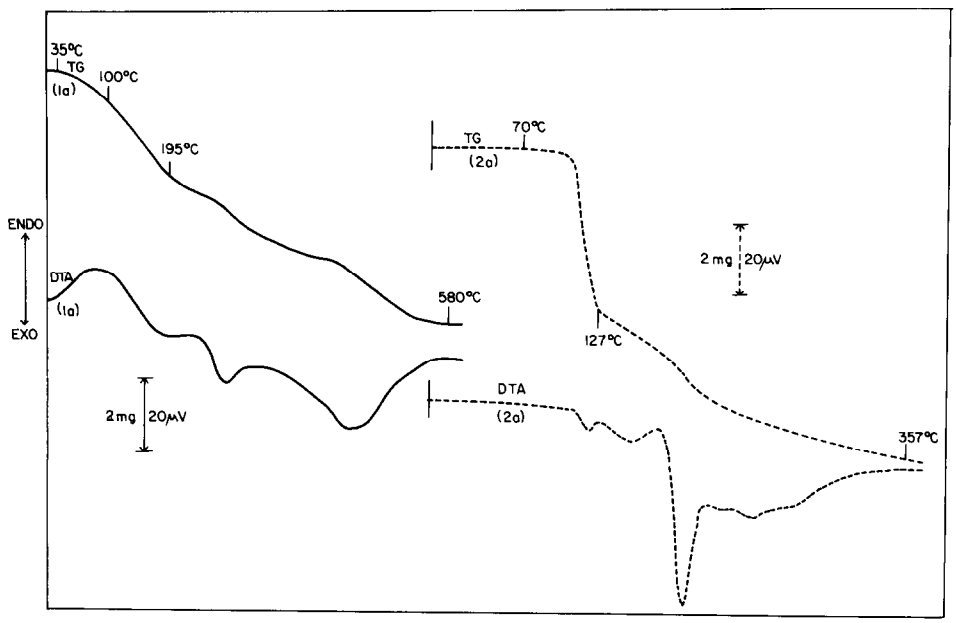
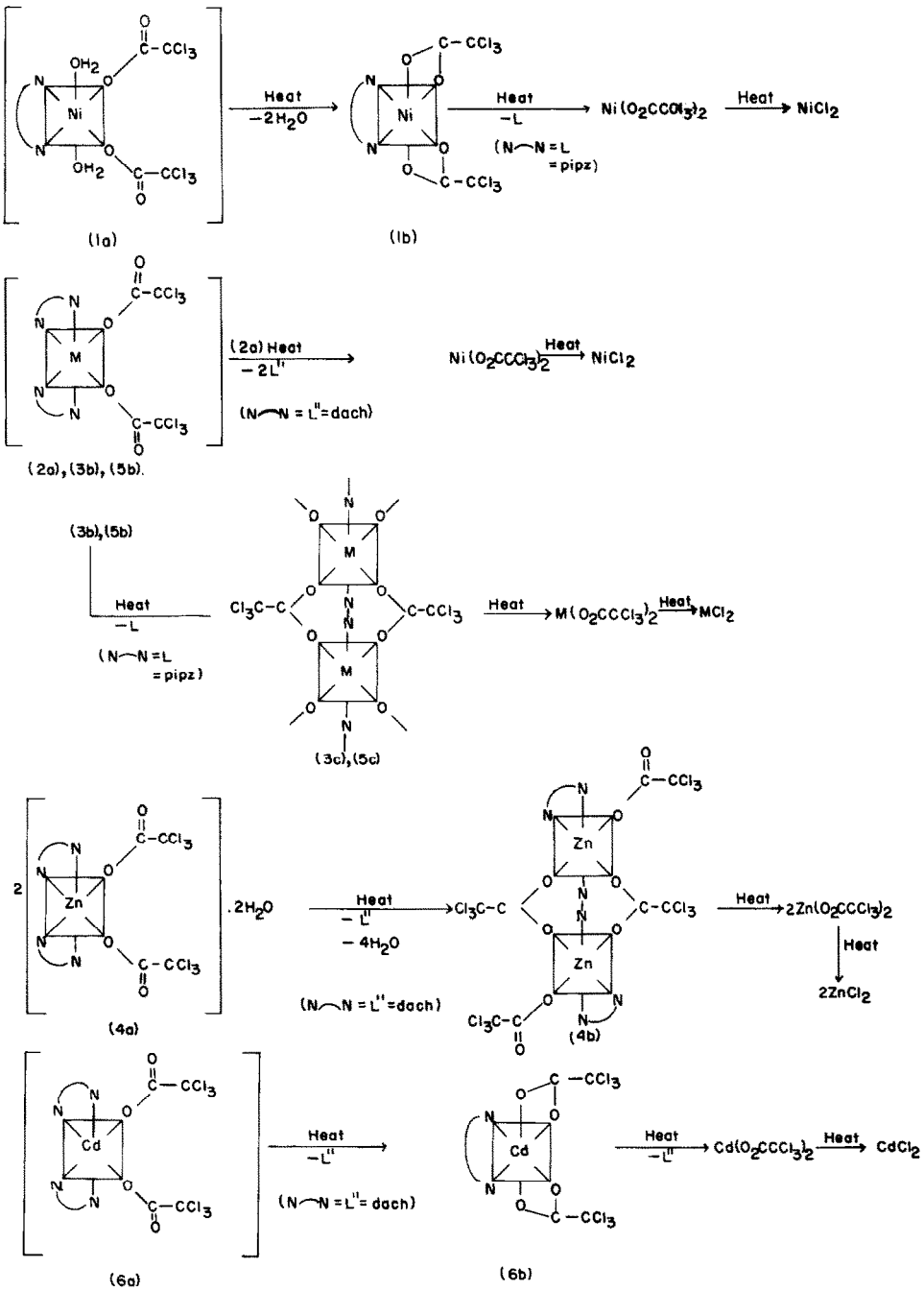


Fig. 1. Thermal curves of [Ni(pipz)(TCA)$_2$(H$_2$O)$_2$] (**1a**) (———), sample mass 11.20 mg, and [Ni(dach)$_2$(TCA)$_2$] (**2a**) (------), sample mass 12.90 mg.


Heat
−2H2O
Heat
−L
(N⌒N = L = pipz)
Heat
(1a)
(1b)
(2a) Heat
− 2L''
(N⌒N = L''=dach)
(2a), (3b), (5b).
(3b), (5b)
(3c), (5c)
(4a)
.2H2O
− L''
− 4H2O
(4b)
2ZnCl2
(6a)
(6b)

Scheme 1.

The bluish green colour and the magnetic moment value (3.15 B.M.) indicate an octahedral structure (Scheme 1). In the complex (**1a**), the cyclic ligand functions as a bidentate chelate and exists in the boat form [1,3–6] (Table 2) and the trichloroacetate (TCA) acts as unidentate ligand (Table 2). The decomposition path and structure of the complexes (**1a**) and (**1b**) are shown in Scheme 1.

$[Ni(dach)_2(TCA)_2]$ (2a)

This complex has not been reported before. On heating, complex (**2a**) loses two molecules of cyclic ligands in the range 70–127 °C and is converted into $Ni(TCA)_2$. The values of thermodynamic parameters are given in Table 3. The cyclic ligand in (**2a**) functions as chelate and exists in the boat form while trichloroacetate would act as a unidentate ligand [4–7] (Table 2).

Complex (**2a**) has octahedral configuration (Scheme 1). The probable path of decomposition of the complexes (**2a**) is shown in Scheme 1.

$[Zn(pipz)_2(TCA)_2] \cdot H_2O$ (3a)

This complex has not been reported earlier. The presence of lattice water in (**3a**) was confirmed by IR spectra (Table 2) and the mass loss in the TG curve in the range 50–122 °C along with the endothermic peak at 70 °C in

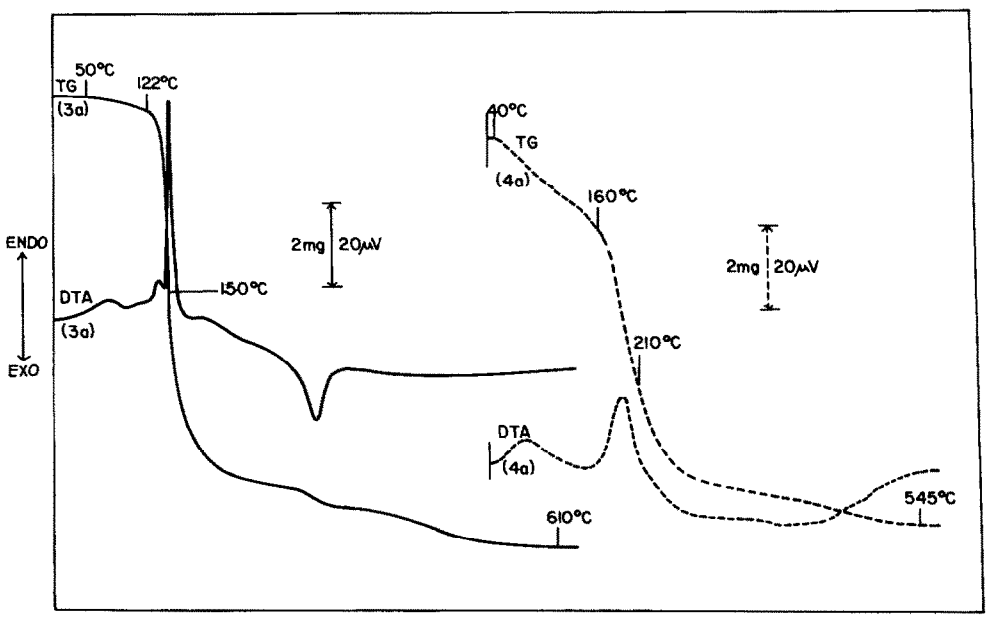


Fig. 2. Thermal curves of $[Zn(pipz)_2(TCA)_2] \cdot H_2O$ (**3a**) (———), sample mass 14.20 mg, and $[Zn(dach)_2(TCA)_2] \cdot 2H_2O$ (**4a**) (------), sample mass 16.30 mg.

the DTA curve (Fig. 2). Complex (**3b**) decomposed into $Zn(TCA)_2$ in the range 122–150 °C but the DT curve showed two peaks at 130 °C and 150 °C. The first peak at 130 °C may be assigned to the loss of the first molecule of the cyclic ligand. In the complex (**3b**) piperazine might act as bidentate chelate and exists in the boat form [1,3–7] and trichloroacetate might function as a unidentate ligand (Table 2 and Scheme 1).

Therefore (**3b**) might possess octahedral configuration. In the complex (**3c**) (not shown in Table 3), piperazine would act as a bridging bidentate ligand and exists in the chair conformation [7]. Trichloroacetate might act as a bridging bidentate ligand [10] (Table 2) and its $\Delta\nu$ value (185 cm^{-1}) is slightly higher because of the presence of CCl_3 in CCl_3COO^-. Thus (**3c**) might have an octahedral configuration. The decomposition path and structure of the complexes are given in Scheme 1.

*$[Zn(dach)_2(TCA)_2] \cdot 2H_2O$ (**4a**)*

This complex has not previously been reported. On pyrolysis the complex (**4a**) was converted into $Zn(TCA)_2$ via the formation of the intermediate $[Zn(dach)_{1.5}(TCA)_2]$ (**4b**) in the range 40–160 °C and 160–210 °C (Fig. 2). Values of E_a^*, ΔH and ΔS for the conversion of (**4a**) → (**4b**) and (**4b**) → $Zn(TCA)_2$ are given in Table 3. In the complex (**4a**), the cyclic ligand functions as a bidentate chelate and exists in the boat form [1,3–7] (Table 2). Trichloroacetate might function as a unidentate ligand (Table 2). Complex (**4a**) might have an octahedral structure and exists in the *cis* configuration as more than one $\rho_r(CH_2)$ band [12] appears in the spectra (Table 2). The probable path of reactions is shown in Scheme 1.

*$[Cd(pipz)_2(TCA)_2] \cdot 2H_2O$ (**5a**) and $[Cd(dach)_2(TCA)_2]$ (**6a**)*

These complexes have not been reported earlier. On pyrolysis (**5a**) underwent dehydration and formed the complex $[Cd(pipz)_2\ (TCA)_2]$ (**5b**) in the range 55–135 °C (Fig. 3). The complex (**5b**) is converted into $Cd(TCA)_2$ in a single step in the range 135–150 °C with an exothermic peak at 145 °C. The complex (**6a**) is converted into $Cd(TCA)_2$ in two steps via the formation of the intermediate $[Cd(dach)(TCA)_2]$ (**6b**) in the ranges 50–110 °C and 110–290 °C (Fig. 3). In the case of the decomposition of (**5b**), though there is no indication of a break in the TG curve, an intermediate complex $[Cd(pipz)(TCA)_2]$ (**5c**) could be isolated at around 140 °C by the temperature arrest technique.

In the complexes (**5b**) and (**6b**), the cyclic ligands function as chelate and exist in the boat conformation; trichloroacetate acts as a unidentate ligand (Table 2 and Scheme 1). Accordingly, complexes (**5b**) and (**6a**) have octahedral configuration. In the intermediate complex (**5c**), cyclic ligand and trichloroacetate are bridging and bidentate. In the intermediate (**6b**), cyclic

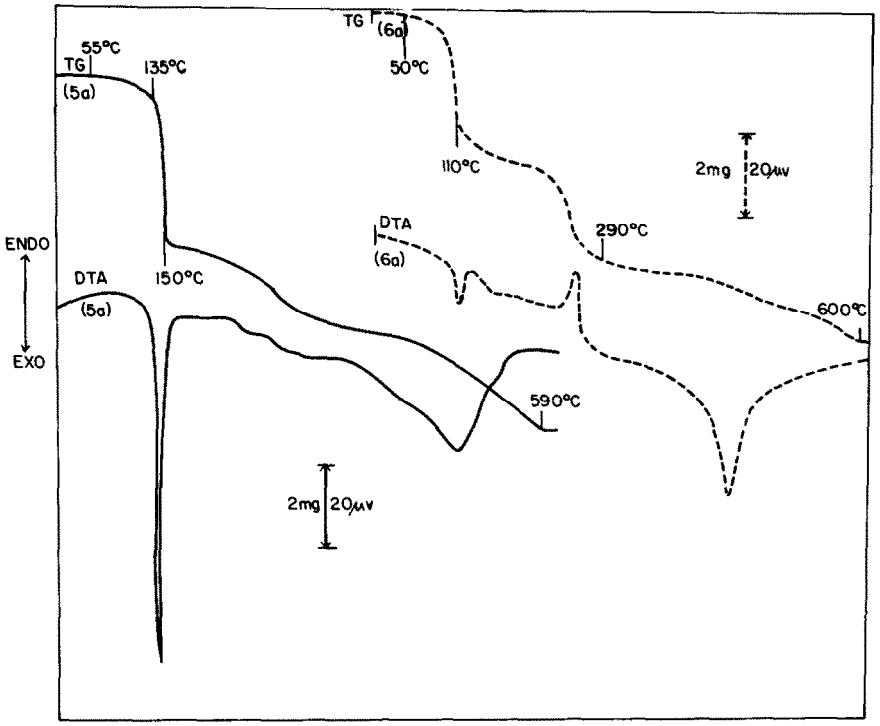


Fig. 3. Thermal curves of $[Cd(pipz)_2(TCA)_2]\cdot 2H_2O$ (**5a**) (———), sample mass 11.40, and $[Cd(dach)_2(TCA)_2]$ (**6a**) (------), sample mass 7.80.

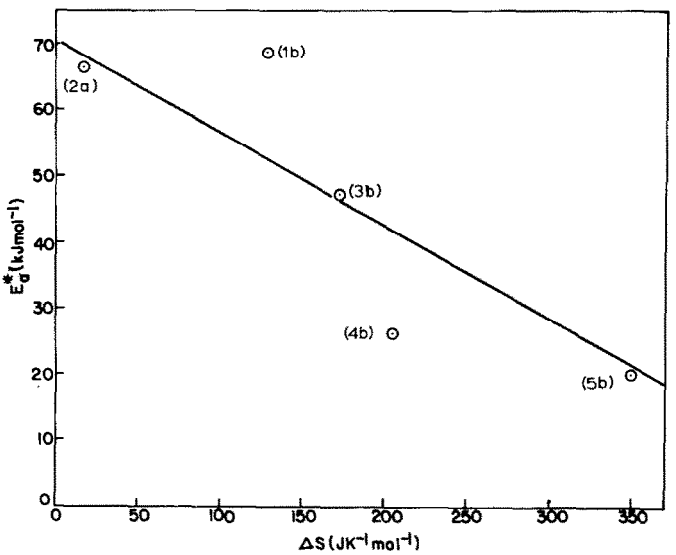


Fig. 4. Plots of the values of E_a^* versus ΔS for the conversions: $[Ni(pipz)(TCA)_2] \rightarrow Ni(TCA)_2$ (**1b**), $[Ni(dach)_2(TCA)_2] \rightarrow Ni(TCA)_2$ (**2a**), $[Zn(pipz)_2(TCA)_2] \rightarrow Zn(TCA)_2$ (**3b**), $[Zn(dach)_{1.5}(TCA)_2] \rightarrow Zn(TCA)_2$ (**4b**), and $[Cd(pipz)_2(TCA)_2] \rightarrow Cd(TCA)_2$ (**5b**).

ligand is in boat conformation and the trichloroacetate functions as chelate. The probable path of decomposition is shown in Scheme 1.

In all the complexes after the loss of cyclic ligand(s) the metal trichloacetates decomposed into metal chlorides in one or two steps as indicated by the peak(s) of the DTA curves (Table 3). The formation of metal chlorides has also been reported earlier [17,18].

If we consider the activation energy (evaluated from TG curves), the order of stability of the complexes follows the trend pipz > dach. Further, a linear correlation is obtained upon plotting E_a^* versus ΔS (Fig. 4) for the decompositions of the complexes. A system having a higher entropy change will require less energy E_a^* for its thermal decomposition [19].

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