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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

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Abstract

Nickel(II), zinc(II) and cadmium(II) complexes of piperazine (pipz), *N*-methylpiperazine (mpipz) and 1,4-diazacycloheptane (dach) with the compositions $[Ni(pipz)(DCA)_2(H_2O)_2]$, $[Ni(dach)_2(DCA)_2]$, $[M(pipz)_2(DCA)_2]$ (M = Zn or Cd), $[M(dach)_2(DCA)_2]\cdot H_2O$ (M = Zn or Cd) and $[Cd(mpipz)_2(DCA)_2]$, where DCA = dichloroacetate, have been synthesised. Attempts to prepare *N*-methylpiperazine complexes of nickel(II) and zinc(II) and *NN'*-dimethylpiperazine complexes of all three 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^*) and enthalpy (ΔH) and entropy changes (ΔS) for the dehydration and decomposition reactions of these complexes show that the order of stability of the complexes (with respect to E_a^*) follows the trend pipz > mpipz > 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 their thermal decomposition. In addition to six-membered cyclic diamine ligands, we have studied a seven-membered cyclic diamine to see

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whether the 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 point.

Before heating, the cyclic diamines function as bidentate chelating agents (boat form) [3–9] and the dichloroacetate ion as a unidentate agent [10]. On non-isothermal heating, the complexes first become dehydrated (in some cases) and then decompose via stable intermediates in which the cyclic diamine ligands may function as bridging bidentate (chair form) [3–7,11,12] ligands and the dichloroacetate ion might act as a bridging bidentate ligand (in all the intermediates) as well as a unidentate ligand in the mpipz and dach complexes of Cd(II). This kind of conformational change of the cyclic ligand (boat form → chair form) and the nature of the change of coordination of dichloroacetate ion (unidentate to chelate or bridging bidentate) have been confirmed by IR spectral data. Such parameters as E_a^*, ΔH and ΔS for the dehydration and decomposition reactions of the complexes in the solid state have been calculated.

EXPERIMENTAL

Materials and methods

Metal carbonates were of A.R. grade and used as received. Metal dichloroacetates were freshly prepared by neutralising dichloroacetic acid with an excess of metal carbonate and subsequent crystallisation from the filtrates obtained. Piperazine obtained from Merck (Germany), and *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 [13].

Preparation of the complexes

$[Ni(pipz)(DCA)_2(H_2O)_2]$

The ligand (ca. 6 mmol) in dry ethanol (20 cm^3) was added with constant stirring to a dry ethanolic solution (ca. 50 cm^3) containing freshly prepared nickel dichloroacetate (ca. 3 mmol). The bluish green nickel complex was collected by filtration, washed carefully with dry diethyl ether, and dried over fused calcium chloride in a desiccator. Yield ca. 70%. The complexes $[Ni(dach)_2(DCA)_2]$, $[Zn(pipz)_2(DCA)_2]$, $[Zn(dach)_2(DCA)_2] \cdot H_2O$, $[CdL_2(DCA)_2]$ (L = pipz or mpipz) and $[Cd(dach)_2(DCA)_2] \cdot H_2O$ were prepared similarly; yields ca. 60–70%.

Nickel, zinc and cadmium were estimated gravimetrically by standard procedures [14], and C, H, and N by using Perkin–Elmer 240C and Carlo Erba 1106 elemental analysers. Elemental analyses are reported in Table 1. Thermal investigation (TGA and DTA) was carried out on a Shimadzu

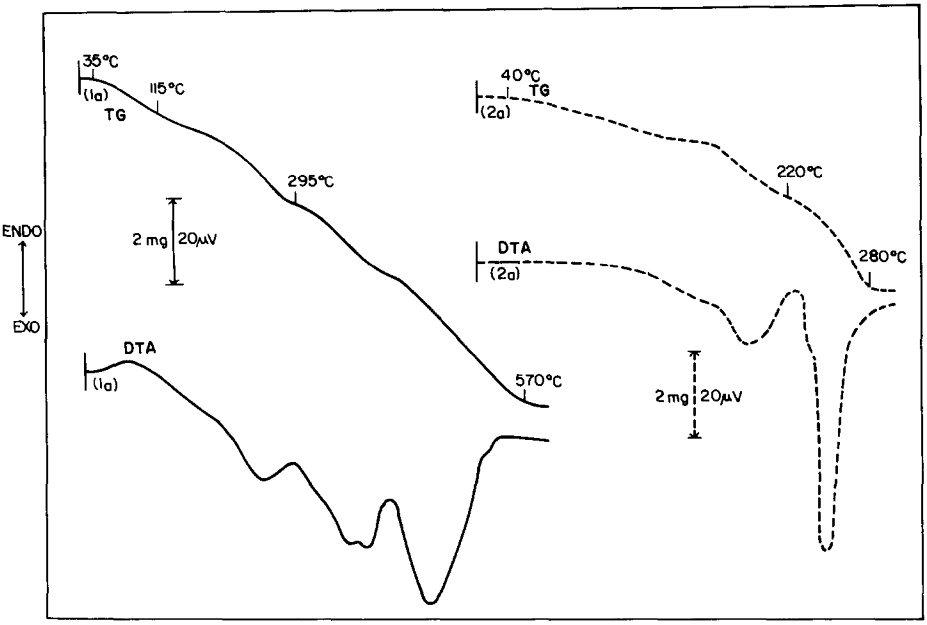


Fig. 1. Thermal curves of [Ni(pipz)(DCA)$_2$(H$_2$O)$_2$] (**1a**) (———), sample mass 10.80 mg; and [Ni(dach)$_2$(DCA)$_2$] (**2a**) (— — —), sample mass 12.18 mg.

DT-30 thermal analyser under a nitrogen atmosphere with a heating rate of 10°C min^{-1} and α-alumina as a standard. 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&G PAR 155 vibrating sample magnetometer at room temperature. Conductivity measurements of the complexes were made in dimethyl sulphoxide at a concentration of 10^{-3} M at room temperature with a conductivity bridge 305 (Systronics, India), using a dip-type cell. Solid residues obtained after pyrolysis were identified by qualitative analyses.

RESULTS AND DISCUSSION

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

This bluish complex has not been reported earlier. It contains two molecules of coordinated water, as confirmed by IR spectral bands at 3400 and 3280 cm^{-1} [ν(OH)] and 1660 and 1630 cm^{-1} [δ(HOH)] (Table 3). Further, the weight loss in the TG curve of **1a** in the range 35–105°C and the endothermic DTA peak at 70°C (Fig. 1) correspond to two molecules of water. The anhydrous complex [Ni(pipz)(DCA)$_2$] (**1b**) is converted into Ni(DCA)$_2$ in the range 115–295°C. The corresponding DTA curve shows an exothermic peak at 205°C. Activation energy has been evaluated from the TGA curves using the equation of Horowitz and Metzger [15] and from the DTA curves by the equation of Borchardt and Daniels [16]. The ΔH values were evaluated from DTA curves using the relation [16] $\Delta H = KA$, where K is the heat transfer coefficient (cell constant or calibration constant) and A is the total area under the particular DTA curve. The ΔS values were evaluated from the relation $\Delta S = \Delta H/T_m$, where T_m is the DTA peak temperature in K [17]. In complex **1a** the cyclic ligand functions as a chelate and exists in the boat form [3–9] whereas the dichloroacetate acts as a unidentate ligand [10,17,18] ($\Delta\nu = 245$ cm^{-1}, Table 3). The bluish colour of the complex and its magnetic moment value indicate an octahedral structure (Scheme 1).

*[Ni(dach)$_2$(DCA)$_2$] (**2a**)*

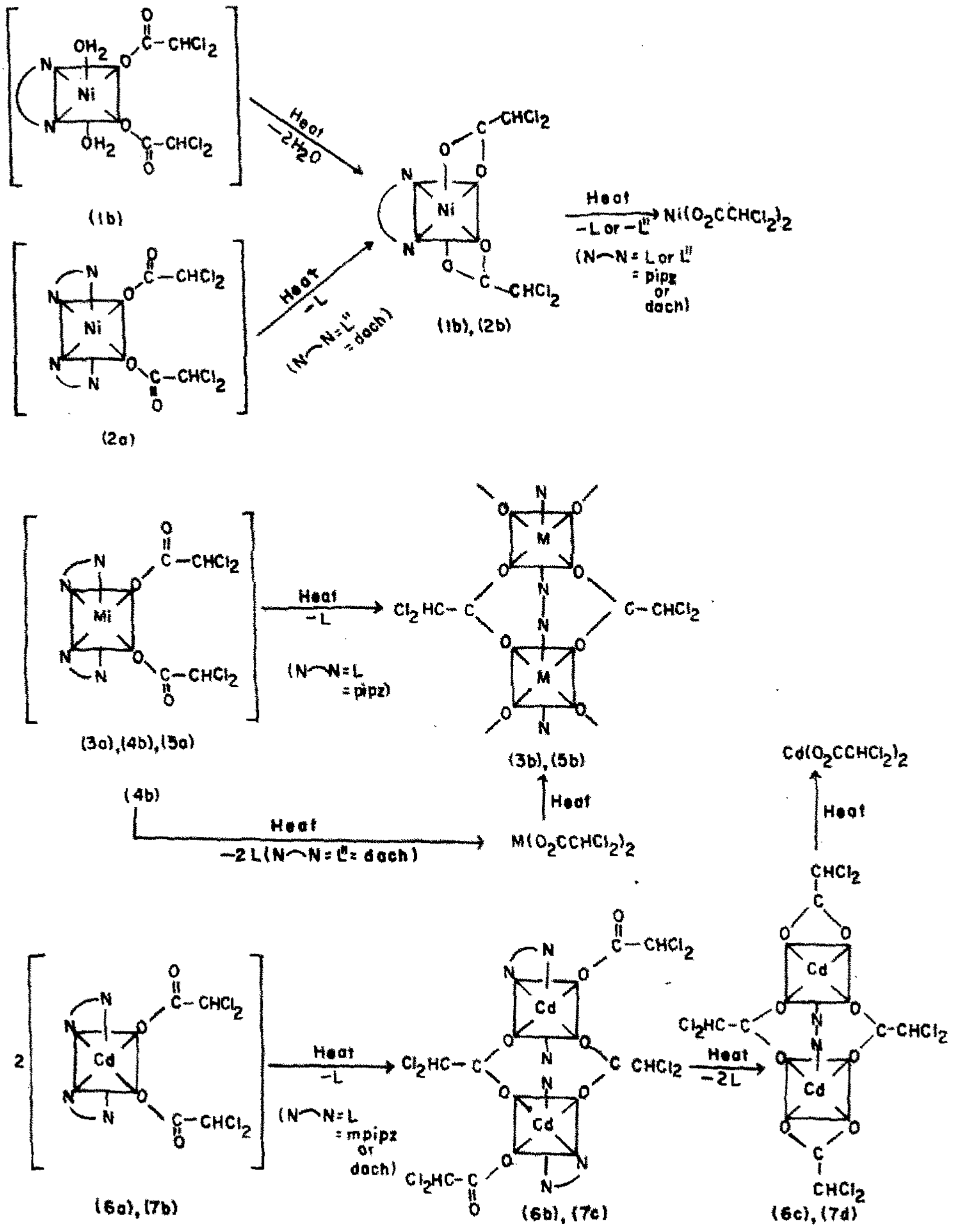
This complex has not been reported earlier. It is greenish yellow in colour. Complex **2a** decomposes to Ni(DCA)$_2$ via the formation of the intermediate [Ni(dach)(DCA)$_2$] (**2b**) in two steps in the ranges 40–220 and 220–280°C. The corresponding DTA curve shows two exotherms and peaks appear at 195 and 245°C respectively (Fig. 1). The values of E_a^*, ΔH and ΔS are given in Table 2.

The cyclic ligand in **2a** acts as a chelate and exists in the boat form [3–9]. Dichloroacetate might function as a unidentate ligand [10,17,18] ($\Delta\nu = 240$ cm^{-1}, Table 3). Complex **2a** has an octahedral structure as indicated by the value of its magnetic moment (Table 1 and Scheme 1).

In the intermediate complex **2b** the cyclic ligand appears to act as a chelate and exists in the boat form [3–9], and dichloroacetate acts as a bidentate ligand [10]. The decomposition path and the structure of the complexes **2a** and **2b** are given in Scheme 1.

*[Zn(pipz)$_2$(DCA)$_2$] (**3a**) and [Zn(dach)$_2$(DCA)$_2$] · H$_2$O (**4a**)*

These complexes have not been reported earlier. Thermal investigation has confirmed that lattice water in **4a** (Table 2) is lost in the range 35–80°C. The decomposition of [Zn(pipz)$_2$(DCA)$_2$] (**3a**) into Zn(DCA)$_2$ takes place via the formation of [Zn(pipz)(DCA)$_2$] (**3b**) in two steps in the ranges 150–230 and 230–360°C (Fig. 2 and Table 2). The intermediate complex **3b** could be isolated by keeping the rate of heating at 1°C min^{-1} in the desired temperature range. The complex [Zn(dach)$_2$(DCA)$_2$] (**4b**) is converted into Zn(DCA)$_2$ in a single step in the range 80–360°C.



Scheme 1.

The structures of the complexes **3a** and **4a** are shown in Scheme 1. The cyclic ligands function as chelates in the boat conformation [3–9] and dichloroacetate may act as a unidentate ligand [10,17,18] (Table 3). The IR spectra of **3b** (Table 3) shows that piperazine functions as a bridging ligand and exists in the chair form [3–7,12] and that dichloroacetate acts as a bridging bidentate ligand [6–10] (see Table 3 and Scheme 1).

TABLE 1

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

	Complex	Colour	Analysis (%)				μ_{eff} (B.M.)
			Metal	C	H	N	
1a	$[NiL(DCA)_2(H_2O)_2]$	Bluish green	13.01 (13.44)	21.65 (21.98)	3.00 (2.75)	6.21 (6.41)	3.21
2a	$[NiL''_2(DCA)_2]$	Greenish yellow	10.98 (11.40)	32.97 (32.64)	5.52 (5.05)	11.36 (10.88)	3.34
3a	$[ZnL_2(DCA)_2]$	White	12.85 (13.25)	28.97 (29.18)	4.21 (4.46)	5.71 (5.67)	
3b	$[ZnL(DCA)_2]$	White	15.91 (16.05)	23.63 (23.56)	2.77 (2.95)	6.25 (6.87)	
4a	$[ZnL''_2(DCA)_2]\cdot H_2O$	White	11.91 (12.12)	31.71 (31.14)	4.96 (4.82)	10.47 (10.38)	
5a	$[CdL_2(DCA)_2]$	White	20.50 (20.79)	30.81 (31.08)	4.02 (4.07)	10.11 (10.36)	
5b	$[CdL(DCA)_2]$	White	24.22 (24.74)	21.25 (21.13)	2.59 (2.64)	6.05 (6.16)	
6a	$[CdL'_2(DCA)_2]$	White	19.56 (19.77)	28.25 (29.56)	4.53 (4.57)	9.63 (9.85)	
7a	$[CdL''_2(DCA)_2]\cdot H_2O$	White	19.05 (19.17)	28.71 (28.64)	4.64 (4.77)	9.32 (9.55)	

[a] L = piperazine (pipz), L′ = *N*-methylpiperazine (mpipz), and L″ = 1,4-diazacycloheptane (dach).

TABLE 2

Thermal parameters of dichloroacetato-cyclic diamine [pipz(L)/mpipz(L′)/dach(L″)] complexes of Ni(II), Zn(II) and Cd(II)

	Decomposition reactions	Temperature range (°C)	DTA peak temp (°C)		E_a^* (kJ mol^{-1})		Enthalpy change ΔH (kJ mol^{-1})	Entropy change ΔS (J K^{-1} mol^{-1})
			Endo	Exo	TG	DTA		
1(a)	$[NiL(DCA)_2(H_2O)_2] \rightarrow [NiL(DCA)_2]$	35–115	70	–	33	26	40	118
(b)	$[NiL(DCA)_2] \rightarrow Ni(DCA)_2$	115–295	–	205		99	109	229
(c)	$Ni(DCA)_2 \rightarrow NiCl_2$	295–570	–	350, 380, 450 [a]		–	197	272
2(a)	$[NiL''_2(DCA)_2] \rightarrow [NiL''(DCA)_2]$	40–220	–	195	14	–	106	227
(b)	$[NiL''(DCA)_2] \rightarrow Ni(DCA)_2$	220–280	–	245	107	238	182	352
3(a)	$[ZnL_2(DCA)_2] \rightarrow [ZnL(DCA)_2]$	150–230	–	200	42	35	158	334
(b)	$[ZnL(DCA)_2] \rightarrow Zn(DCA)_2$	230–360	–	325 (broad)	58	–	–	–
(c)	$Zn(DCA)_2 \rightarrow ZnCl_2$	360–590	–	470, 554 (broad)	78	–	455	–
4(a)	$[ZnL''_2(DCA)_2]\cdot H_2O \rightarrow [ZnL''_2(DCA)_2]$	35– 80	55	–	8	–	46	143
(b)	$[ZnL''_2(DCA)_2] \rightarrow Zn(DCA)_2$	80–360	–	358	12	–	311	493
(c)	$Zn(DCA)_2 \rightarrow ZnCl_2$	360–550	–	475			663	887
5(a)	$[CdL_2(DCA)_2] \rightarrow [CdL(DCA)_2]$	115–180	–	153	136	190	192	451
(b)	$[CdL(DCA)_2] \rightarrow Cd(DCA)_2$	180–330	–	270	29	–	62	115
(c)	$Cd(DCA)_2 \rightarrow CdCl_2$	330–560	–	480	–	–	743	987
6(a)	$[CdL'_2(DCA)_2] \rightarrow [CdL'_{1.5}(DCA)_2]$	80–115	–	100	8	–	111	299
(b)	$[CdL'_{1.5}(DCA)_2] \rightarrow [CdL'_{0.5}(DCA)_2]$	130–170	–	160	15	–	74	171
(c)	$[CdL'_{0.5}(DCA)_2] \rightarrow Cd(DCA)_2$	170–220	–	203	16	–	10	21
7(a)	$[CdL''_2(DCA)_2]\cdot H_2O \rightarrow [CdL''_2(DCA)_2]$	55–120	80	–	8	–	35	101
(b)	$[CdL''_2(DCA)_2] \rightarrow [CdL''_{1.5}(DCA)_2]$	120–185	–	135	15	–	31	76
(c)	$[CdL''_{1.5}(DCA)_2] \rightarrow [CdL''_{0.5}(DCA)_2]$	185–230	–	190	22	–	31	67
(d)	$[CdL''_{0.5}(DCA)_2] \rightarrow Cd(DCA)_2$	230–395	–	258 (less prominent)	27	–	355	464
(e)	$Cd(DCA)_2 \rightarrow CdCl_2$	395–560	–	491, 525	–	–	–	–

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

TABLE 3

IR spectral data (cm^{-1}) for dichloroacetato (DCA)–cyclic diamine (L = pipz/L′ = mpipz/L″ = dach) complexes of Ni(II), Zn(II) and Cd(II)

	Complex	ν(NH) + ν(CH)	$\nu(CH_2)$	δ(NH) + δ(HOH) + $\nu_{as}(CO_2^-)$	$\delta(CH_2)$ + $\nu_s(CO_2^-)$	$\Delta\nu$	$\rho_\omega(CH_2)$	τ(NH) + ρ_ω(NH) + $\tau(CH_2)$	Stretching vibrations of skeleton ν(C–N) + ν(C–C)	$\rho_r(CH_2)$	$\delta(CO_2^-)$ + ν(C–Cl)	ρ_r(NH) + [b] $\rho_r(CH_2)$ + ν(M–N)	ν(M–O)
(1a)	$[NiL(DCA)_2(H_2O)_2]$	3400(sbr) 3280(sh)	3000(wbr) 2880(sh)	1660(sh) $\underline{1630}$(sbr) 1500(vw)	1460(w) 1450(sh) 1400(sh) $\underline{1385(s)}$	245	1360(sh)	1225(wbr) 1180(sh)	1100(wbr) 1085(sh) 1050(vw) 1015(sh) 1000(wbr)	950(vw) 880(w)	825(w) 790(wbr) [a] 720(mbr) [a]	675(wbr) [a] 600(sh)	490(vw) 430(wbr) [a] 290(vw)
(2a)	$[NiL''_2(DCA)_2]$	3420(sbr)	3000(sbr) 2880(wbr) 2800(w)	1700(sh) $\underline{1625}$(sbr) 1580(sh) 1560(sh) 1540(sh)	1470(sh) 1455(w) 1430(m) $\underline{1385(vs)}$	240	1370(sh)	1330(w) 1315(w) 1275(vw) 1260(vw) 1235(vw) 1220(vw) 1200(sh) 1180(vw) 1160(vw) 1150(vw) 1125(vw)	1100(vw) 1075(m) 1060(m) 1050(sh) 1020(w) 1005(w) 980(sh) 970(w)	955(w) 940(w) 930(vw) 910(vw) 895(m) 880(w) 860(sh)	850(vw) 820(w) 795(w) 765(m) 740(vw) 730(sh) 715(w)	630(vw) 530(vw)	495(vw) 390(vw) 350(vw) 315(vw)
(3a)	$[ZnL_2(DCA)_2]$	3440(mbr) 3150(s)	3040(w) 3010(w) 2970(m) 2940(w) 2870(w)	$\underline{1670}$(vs) $\underline{1630}$(vs) 1500(vw)	1460(w) 1440(ms) 1435(sh) 1390(sh) $\underline{1380}$(vs)	290 (250)	1360(sh) 1340(w)	1270(w) 1260(w) 1230(w) 1225(ms) 1210(m) 1205(w) 1180(ms) 1125(vw)	1085(m) 1035(m) 1005(sh) 1000(m)	900(m) 890(sh) 880(ms)	835(m) 825(m) 775(ms) 720(sh) 710(s)	675(m) 655(ms) 600(sh) 525(sh) 520(w)	400(vw) 315(vw) 270(w)

(3b)	$[ZnL(DCA)_2]$	3480(sbr) 3100(m)	3020(m) 2960(w) 2920(w) 2800(vw)	1700(vw) 1620(sbr) 1560(w) 1520(vw)	1490(vw) 1450(s) 1430(ms) 1400(ms)	170	1370(vw) 1340(w)	1300(vw) 1190(w) 1150(vw)	1080(m) 1020(w)	920(w) 870(w)	700(w)	670(vw) 610(m) 550(w) 500(vw)	450(w) 370(vw)
(4a)	$[ZnL''_2(DCA)_2]\cdot H_2O$	3420(sbr)	2980(vw) 2960(w) 2920(w) 2890(vw)	1650(sh) 1620(vsbr) 1555(w) 1505(w)	1490(sh) 1470(m) 1450(vw) 1440(vw) 1420(vs)	200	1350(vw)	1330(ms) 1320(sh) 1300(sh) 1275(w) 1240(w) 1210(w) 1150(w) 1135(vw)	1075(ms) 1065(ms) 1055(sh) 1020(m) 970(m)	915(m) 900(m) 875(w)	820(vw) 800(w) 770(m) 740(vw)	630(w) 600(sh) 590(vw) 550(vw) 525(vw) 500(w)	400(w) 310(m) 285(m)
(5a)	$[CdL_2(DCA)_2]$	3420(mbr) 3270(m) 3190(m)	3000(sh) 2970(w) 2940(vw) 2880(vw)	1630(vsbr)	1470(sh) 1455(sh) 1450(w) 1420(w) 1400(sh) 1380(vs)	250	1350(sh)	1330(ms) 1320(sh) 1280(vw) 1255(w) 1215(sh) 1200(s) 1185(sh) 1120(sh)	1095(s) 1060(sh) 1040(vw) 1020(ms) 1010(w) 1000(w)	920(w) 875(s)	810(s) 780(sh) 755(sh) 735(s)	680(vw) 645(w) 520(w)	470(vw) 430(vw) 370(w) 330(w) 270(w)
(5b)	$[CdL(DCA)_2]$	3440(sbr) 3120(w)	3020(m) 2980(w) 2800(w)	1640(sh) 1610(s) 1570(sh) 1550(sh) 1505(vw)	1450(s) 1400(ms)	160	1380(sh)	1330(vw) 1300(vw) 1190(w) 1140(vw)	1080(ms) 1050(w) 1000(w)	920(vw) 870(w)	810(vw) 700(vw)	650(vw) 600(w) 550(w) 500(w)	460(m) 350(vw) 300(vw)
(6a)	$[CdL'_2(DCA)_2]$	3340(mbr) 3210(m)	2950(w) 2920(m) 2820(w) 2790(w)	1630(sbr)	1440(w) 1430(s) 1415(m)	200	1365(vw) 1350(w)	1305(vw) 1280(w) 1265(m) 1170(m) 1125(s)	1090(m) 1020(w) 1005(m) 980(vs)	890(w) 855(ms)	820(vw) 760(w) 700(wbr)	620(vw) 580(vw) 525(wbr)	420(w) 375(w) 300(vw)

TABLE 3 (continued)

Complex	ν(NH) + ν(CH)	$\nu(CH_2)$	δ(NH) + δ(HOH) + $\nu_{as}(CO_2^-)$	$\delta(CH_2)$ + $\nu_s(CO_2^-)$	$\Delta\nu$	$\rho_\omega(CH_2)$	τ(NH) + ρ_ω(NH) + $\tau(CH_2)$	Stretching vibrations of skeleton ν(C–N) + ν(C–C)	$\rho_r(CH_2)$	$\delta(CO_2^-)$ + ν(C–Cl)	ρ_r(NH) + $\rho_r(CH_2)$ + ν(M–N) [b]	ν(M–O)
(7a) $[CdL_2''(DCA)_2]\cdot H_2O$	3440(mbr)	2980(mbr)	1600(vsbr)	1465(m)	190	1370(wbr)	1320(m)	1070(m)	950(sh)	830(sh)	670(vw)	485(w)
		2800(vw)		1410(s)			1310(sh)	1050(w)	915(w)	810(sh)	630(w)	390(w)
							1275(sh)	1015(w)	900(m)	800(m)	580(vw)	
							1240(sh)	1000(sh)	870(m)	760(m)	540(wbr)	
							1215(w)	960(m)		720(w)		
							1150(w)					
							1310(vw)					

Key: v = very, s = strong, m = medium, br = broad, w = weak, sh = shoulder.

[a] Frequencies overlap with those of coordinated water molecule [790 (720) cm^{-1} $\rho_r(H_2O)$, 675 (600) cm^{-1} $\rho_\omega(H_2O)$, and 430 cm^{-1} ν(M–O) in M–OH_2].

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

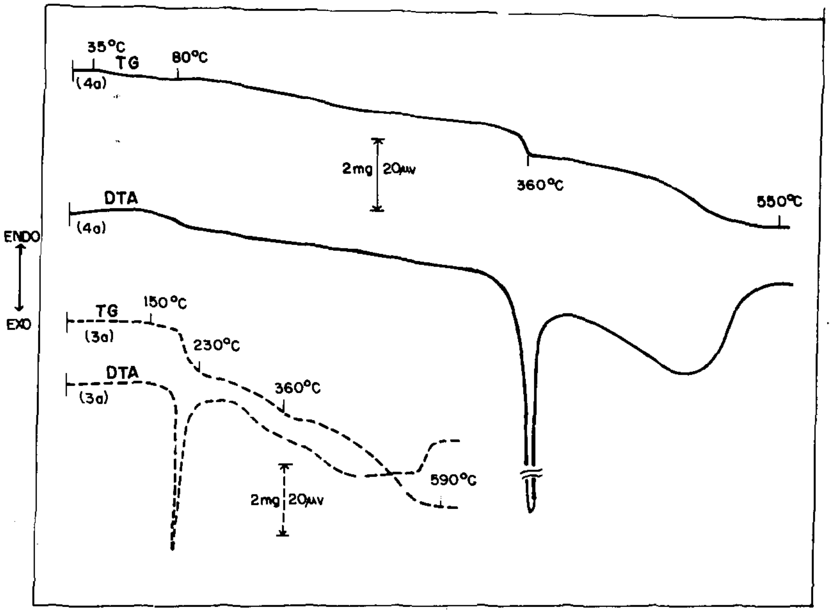


Fig. 2. Thermal curves of [Zn(pipz)$_2$(DCA)$_2$] (**3a**) (———), sample mass 7.2 mg; and [Zn(dach)$_2$(DCA)$_2$]·H_2O (**4a**) (— — —), sample mass 5.8 mg.

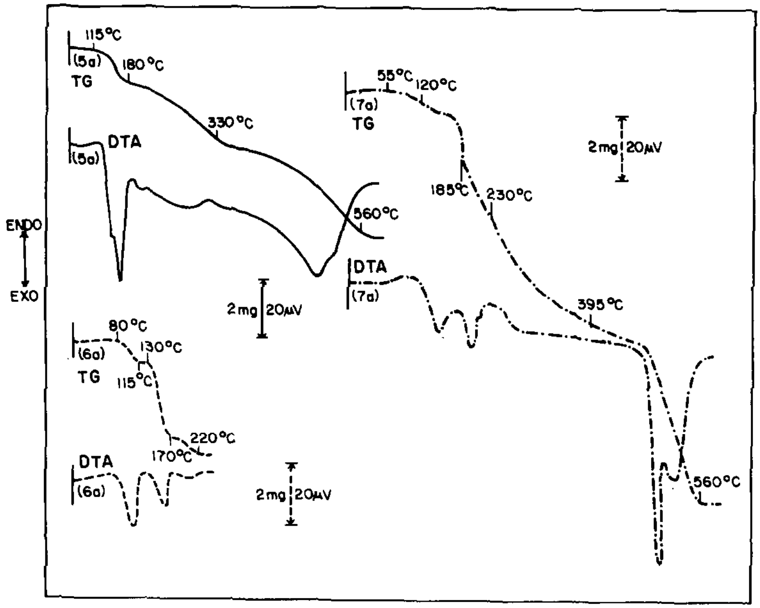


Fig. 3. Thermal curves of [Cd(pipz)$_2$(DCA)$_2$] (**5a**) (———), sample mass 8.5 mg; [Cd(mpipz)$_2$(DCA)$_2$] (**6a**) (— — —), sample mass 8.86 mg; and [Cd(dach)$_2$(DCA)$_2$]·H_2O (**7a**) (–·–·–), sample mass 18.9 mg.

[Cd(pipz)$_2$(DCA)$_2$] *(**5a**)*, *[Cd(mpipz)$_2$(DCA)$_2$]* *(**6a**) and [Cd(dach)$_2$(DCA)$_2$]* $\cdot$ *H_2O (**7a**)*

These complexes have not been reported earlier. The complexes **5a**, **6a** and **7a** are converted into Cd(DCA)$_2$ via the formation of the intermediate in two or multiple steps (Fig. 3) as shown in Table 2 and in the Scheme.

In the complexes **5a**, **6a** and **7b**, the cyclic ligands function as chelates and exist in the boat conformation, and dichloroacetate may act as a unidentate ligand, as confirmed by the IR spectra (Table 3 and Scheme). However, in the intermediate complex [Cd(pipz)(DCA)$_2$] (**5b**) the cyclic ligand piperazine and dichloroacetate function as bidentate and bridging ligands (Table 3 and Scheme). The probable structures of the complexes are shown in the Scheme.

In most cases, after the loss of the cyclic ligand, the M(DCA)$_2$ (M = Ni(II), Zn(II) or Cd(II)) decomposes to the metal chloride [19,20].

If we consider the activation energy, the order of stability of the complexes follows the trend pipz > mpipz > dach (Table 2). A linear correlation is observed upon plotting the values of E_a^* versus ΔS for the decomposition reactions of the complexes. A system having a higher entropy change will require less energy, E_a^*, for its thermal decomposition [3]. Further, the increase of the antisymmetric and decrease of the symmetric frequencies of COO$^-$ of the acetate could be accounted for by the electron withdrawing effect of chlorine [17] upon COO$^-$ in dichloroacetate.

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