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THERMAL INVESTIGATION AND STEREOCHEMICAL STUDIES OF SOME CYCLIC LIGAND COMPLEXES OF COPPER(II) AND CADMIUM(II) IN THE SOLID STATE

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ABSTRACT

Copper(II) and cadmium(II) complexes of morpholine (morph), thioxane (thiox), and dithiane (dith) with the compositions $[CuCl_2(morph)]$, $[CuBr_2(morph)_2(H_2O)_2]$, $[CuCl_2(thiox)_2(H_2O)_2]$, $[CuBr_2(thiox)_2]\cdot 2H_2O$, $[CuCl_2(dith)]\cdot 2H_2O$, $[CuBr_2(dith)_2]\cdot 2H_2O$, $[2CdCl_2(morph)_3]$, $[CdBr_2(morph)_2]$, $[2Cd(SCN)_2(morph)_3]$, $[CdCl_2(thiox)(H_2O)_2]$, $[CdBr_2(thiox)_2]$, $[Cd(SCN)_2(thiox)_2]\cdot H_2O$, and $[CdBr_2(dith)]$ have been synthesized. Attempts to prepare dithiane complexes of $CdCl_2$ and $Cd(SCN)_2$ failed. Some intermediate complexes were isolated by the temperature arrest technique (pyrolysis). Configurational and conformational changes have been studied by elemental analysis, IR and far-IR spectra, magnetic moment measurements, and thermal analysis. Most of the complexes of morpholine, thioxane and dithiane appear to be octahedral except $[CuCl_2(morph)]$, $[Cd(SCN)_2(thiox)_2]\cdot H_2O$, and $[CdBr_2(dith)]$ which are tetrahedral. Activation energies (E_a^*), enthalpy change (ΔH) and entropy change (ΔS) for the dehydration and decomposition reactions are calculated. A linear correlation is found between E_a^* and ΔS for the decomposition reactions of the complexes.

INTRODUCTION

Acyclic ligands having nitrogen, oxygen, and sulphur donor atoms in their structures can act as good chelating agents for the transition and nontransition metal ions [1–3]. However work on cyclic ligand complexes is still very sparse [4–11]. There has been little thermal investigation of cyclic ligand complexes in the solid state [12–15]. The main aim of our work is to synthesize some cyclic ligand (six membered ring) complexes of copper(II) and cadmium(II) and study the stereochemical changes during thermal decomposition. The purpose of selecting the above mentioned cyclic ligands was also to see the effect of the stability of the complexes formed by two (same or different) donor centres in the same molecule but we have failed to

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draw any definite conclusions regarding this. Before heating, thioxane in the complexes $[CuBr_2(thiox)_2] \cdot 2H_2O$ and $[CdCl_2(thiox)(H_2O)_2]$, morpholine in $[2CdCl_2(morph)_3]$, $[CuCl_2(morph)]$, $[CdBr_2(morph)_2]$ and $[2Cd(SCN)_2(morph)_3]$ and dithiane in $[CdBr_2(dith)]$ function as bidentate chelating agents (boat form) [12]. Morpholine in the complexes $[CuBr_2(morph)_2(H_2O)_2]$, and thioxane in $[CuCl_2(thiox)_2(H_2O)_2]$ and $[Cd(SCN)_2(thiox)_2]$ function as unidentate ligands and exist in the chair form [5,7,9,16]. Dithiane in $[CuX_2(dith)] \cdot 2H_2O$ (X = Cl or Br) and thioxane in $[CdBr_2(thiox)_2]$ are bridging and bidentate (chair form) [16]. If these complexes are heated under non-isothermal conditions they decompose via stable intermediates in which the cyclic ligand may function as a bridging bidentate ligand (chair form). This type of conformational change of the ligand (boat form → chair form) has been confirmed by IR and far-IR spectral data. Chloride, bromide and thiocyanate ion might function in these complexes as a terminal unidentate or as a bridging ligand [17]. Parameters such as $E_a^\star$, ΔH and ΔS for the dehydration step and decomposition reactions of the complexes in the solid state have been evaluated.

EXPERIMENTAL

Materials and methods

All metal salts (chlorides of Cu(II), and Cd(II)) were of AR grade and used as received. Metal bromides were freshly prepared by neutralizing concentrated hydrobromic acid (AR grade) with corresponding metal carbonates (AR grade) and subsequent crystallization from the filtrates obtained. Metal thiocyanates were freshly prepared by mixing ethanolic solutions of metal salts with potassium thiocyanate and subsequent crystallization from the filtrates obtained. Morpholine obtained from E. Merck (India), thioxane and dithiane (Aldrich Co., U.S.A.) were used as received. Ethanol and diethyl ether were dried using standard procedures [18].

Preparation of the complexes

$[CuCl_2(morph)]$. The ligand (ca. 6 mmol) in dry ethanol (30 cm^3) was added with constant stirring to a dry ethanolic solution (40 cm^3) containing copper(II) chloride (ca. 3 mmol). The bluish copper complex was collected by filtration, washed carefully with dry ether and dried over fused calcium chloride in a desiccator. Yield ca. 70%.

Complexes $[CuBr_2(morph)_2(H_2O)_2]$, $[CuCl_2(thiox)_2(H_2O)_2]$, $[CuBr_2(Thiox)_2] \cdot 2H_2O$, $[CuCl_2(dith)] \cdot 2H_2O$, $[CuBr_2(dith)] \cdot 2H_2O$, $[2CdCl_2(morph)_3]$, $[CdBr_2(morph)_2]$, $[2Cd(SCN)_2(morph)_3]$, $[CdCl_2(thiox)(H_2O)_2]$,

TABLE 1

Analytical data (calculated values in parentheses) of morpholine (morph), thioxane (thiox) and dithiane (dith) complexes of Cu(II) and Cd(II)

No.	Complex	Colour	Analysis (%)				μ_{eff} (B.M.)
			Metal	Carbon	Hydrogen	Nitrogen	
1a	$[CuCl_2(morph)]$	Light brown	28.54(28.66)	21.35(21.67)	4.01(4.06)	6.25(6.32)	1.82
2a	$[CuBr_2(morph)_2(H_2O)_2]$	Light green	14.69(14.64)	22.05(22.14)	5.00(5.07)	6.35(6.46)	1.52
2c	$[CuBr_2(morph)]$	Brown	20.40(20.45)	15.49(15.46)	2.81(2.90)	4.50(4.51)	1.80
3a	$[CuCl_2(thiox)_2(H_2O)_2]$	Green	16.87(16.77)	25.21(25.36)	5.26(5.28)		1.92
3b	$[CuCl_2(thiox)]$	Yellowish	25.50(25.55)	19.12(19.32)	3.10(3.22)		1.82
4a	$[CuBr_2(thiox)_2]\cdot 2H_2O$	Brown	13.50(13.58)	20.40(20.53)	4.29(4.27)		1.65
5a	$[CuCl_2(dith)]\cdot 2H_2O$	Black	21.80(21.85)	16.48(16.52)	4.16(4.13)		1.66
6a	$[CuBr_2(dith)]\cdot 2H_2O$	Brown	16.67(16.73)	12.69(12.64)	13.00(13.16)		1.46
7a	$[2CdCl_2(morph)_3]$	White	35.70(35.80)	22.80(22.94)	4.21(4.30)	6.60(6.69)	
7b	$[2CdCl_2(morph)]$	White	49.43(49.53)	10.48(10.58)	1.79(1.98)	3.18(3.08)	
8a	$[CdBr_2(morph)_2]$	White	25.29(25.17)	21.42(21.50)	4.20(4.03)	5.91(6.02)	
8b	$[CdBr_2(morph)]$	White	31.20(31.27)	13.39(13.36)	2.42(2.50)	3.98(3.90)	
9a	$[2Cd(SCN)_2(morph)_3]$	White	31.10(31.32)	26.79(26.75)	3.70(3.76)	13.45(13.63)	
9b	$[2Cd(SCN)_2(morph)_2]$	Cream	35.69(35.64)	22.80(22.83)	2.85 (2.80)	13.39(13.32)	
10a	$[CdCl_2(thiox)(H_2O)_2]$	White	34.71(34.75)	14.80(14.84)	3.70(3.71)		
11a	$[CdBr_2(thiox)_2]$	White	23.30(23.39)	19.91(19.81)	3.26(3.33)		
12a	$[Cd(SCN)_2(thiox)_2]H_2O$	White	24.70(24.73)	26.35(26.41)	3.90(3.96)		
13a	$[CdBr_2(dith)]$	White	28.58(28.64)	12.08(12.23)	2.00(2.03)		

TABLE 2

Thermal parameters of morpholine (morph), thioxane (thiox) and dithiane (dith) complexes of Cu(II) and Cd(II)

No.	Decomposition reaction	TG temp. 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		
1a	$[CuCl_2(morph)] \xrightarrow[transition]{phase} [CuCl_2(morph)]$		45				22	70
1b	$[CuCl_2(morph)] \rightarrow CuCl_2$	95–328		155	21	133	40	94
2a	$[CuBr_2(morph)_2(H_2O)_2] \rightarrow [CuBr_2(morph)_2]$	40–136	65		27	18	27	81
2b	$[CuBr_2(morph)_2] \rightarrow [CuBr_2(morph)]$	136–327		138 [a] 285	21	171	43	105
2c	$[CuBr_2(morph)] \rightarrow CuBr_2$	327–404		328 350 [a]	180	65	57	92
3a	$[CuCl_2(thiox)_2(H_2O)_2] \rightarrow [CuCl_2(thiox)]$	88–145	142		128	145	152	364
3b	$[CuCl_2(thiox)] \rightarrow CuCl_2$	145–198	190		132	254	377	
4a	$[CuBr_2(thiox)_2] \cdot 2H_2O \rightarrow [CuBr_2(thiox)_2]$	86–120			125			
4b	$[CuBr_2(thiox)_2] \rightarrow [CuBr_2(thiox)]$	120–140	138		253	86	124	299
4c	$[CuBr_2(thiox)] \rightarrow CuBr_2$	140–191			92			
5a	$[CuCl_2(dith)] \cdot 2H_2O \rightarrow [CuCl_2(dith)_{0.5}]$	122–205	200		104	120	77	162
5b	$[CuCl_2(dith)_{0.5}] \rightarrow CuCl_2$	205–230	228		142	37	39	78
6a	$[CuBr_2(dith)] \cdot 2H_2O \rightarrow [CuBr_2(dith)]$	40–189	185		18	240	21	47
6b	$[CuBr_2(dith)] \rightarrow [CuBr_2(dith)_{0.5}]$	190–268	250		144	254	55	107
6c	$[CuBr_2(dith)_{0.5}] \rightarrow CuBr_2$	269–315	285		180	230	21	38
7a	$[2CdCl_2(morph)_3] \rightarrow [2CdCl_2(morph)]$	150–220	190		104	87	102	220
7b	$[2CdCl_2(morph)] \rightarrow 2CdCl_2$	220–280	278		179	254	50	91
8a	$[CdBr_2(morph)_2] \rightarrow [CdBr_2(morph)]$	60–172	167		68	116	63	143
8b	$[CdBr_2(morph)] \rightarrow CdBr_2$	172–250	241		123	215	97	190
9a	$[2Cd(SCN)_2(morph)_3] \rightarrow [2Cd(SCN)_2(morph)_2]$	45–160	154		33	79	67	159
9b	$[2Cd(SCN)_2(morph)_2] \rightarrow [2Cd(SCN)_2(morph)]$	160–237	191		81	97	75	161
9c	$[2Cd(SCN)_2(morph)] \rightarrow 2Cd(SCN)_2$	237–300		243	136	107	97	188
10a	$[CdCl_2(thiox)(H_2O)_2] \rightarrow [CdCl_2(thiox)]$	95–115	110		118	59	43	113
10b	$[CdCl_2(thiox)] \rightarrow CdCl_2$	115–209	130 [a] 190		56	32	43	107
11a	$[CdBr_2(thiox)_2] \rightarrow [CdBr_2(thiox)]$	40–120	115		42	132	67	173
11b	$[CdBr_2(thiox)] \rightarrow CdBr_2$	120–172	145		124	126	67	160
12a	$[Cd(SCN)_2(thiox)_2] \cdot H_2O \rightarrow [Cd(SCN)_2(thiox)_2]$	60–110	95		76	75	54	148
12b	$[Cd(SCN)_2(thiox)_2] \rightarrow Cd(SCN)_2$	112–243	210		55	123	296	
13a	$[CdBr_2(dith)] \rightarrow CdBr_2$	140–226	215		101	118	54	110

[a] Temperature used for the calculation of ΔS.

$[CdBr_2(thiox)_2]$, $[Cd(SCN)_2(thiox)_2] \cdot H_2O$ and $[CdBr_2(dith)]$ were synthesized similarly.

Copper and cadmium were estimated gravimetrically by standard procedures [19]; C, H and N were determined using a Carlo Erba 1106 elemental analyzer. Elemental analyses are given in Table 1. Thermal investigations (TGA and DTA) were carried out using a Shimadzu DT-30 thermal analyzer under 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. IR and far-IR spectra were recorded with Perkin-Elmer 234, 363, 597, and 783 spectrometers in KBr (or CsI) and polythene discs. The effective magnetic moments were evaluated at room temperature from magnetic susceptibility measurements with an EG and G PAR vibrating sample magnetometer.

RESULTS AND DISCUSSION

*$[CuCl_2(morph)]$ (**1a**) and $[CdBr_2(dith)]$ (**13a**)*

These complexes were reported earlier [5,20,21] and the cyclic ligands were found to be in the chair form. On heating, we found that complex **1a** shows a phase transition with an endothermic DTA peak at 45 ° C. Complexes **1b** and **13a** both lose one cyclic ligand and convert into their metal halides as reflected in the TGA curves in the ranges 95–328 and 140–226 ° C and the corresponding DTA peaks appear at 155 ° C (exotherm) and 215 ° C (endotherm, Fig. 1) respectively. The parameter E_a^* has been evaluated from the TGA curves using the equation of Horowitz and Metzger [22] and from the DTA curve using the equation of Borchardt and Daniels [23]. The values for the conversion of the complex **1b** into $CuCl_2$ after phase transition and **13a** into $CdBr_2$ from TGA are 21 and 101 kJ mol^{-1} and from DTA curves are 133 and 118 kJ mol^{-1} respectively. ΔH values for the conversions of **1b** into $CuCl_2$ and **13a** into $CdBr_2$ were found to be 40 and 54 kJ mol^{-1} and ΔS values evaluated from $\Delta H/T_m$ (where T_m is the DTA peak temperature in kelvin [24]) were 94 and 110 J K^{-1} mol^{-1} respectively. Enthalpy and entropy changes for the phase transition were 22 kJ mol^{-1} and 70 J K^{-1} mol^{-1} respectively (Table 2).

In both the complexes **1a** and **13a** the ligands function as chelating agents in the boat form [12], as shown by the appearance of more IR bands between 700 and 1300 cm^{-1} (Table 3) than for the ligand which exists in the chair form [5,9,16,21] and expected to be in tetrahedral structure as indicated by the value of its magnetic moment (for **1a**) (Table 1, Scheme 1). In both the complexes halogens function as unidentate ligands.

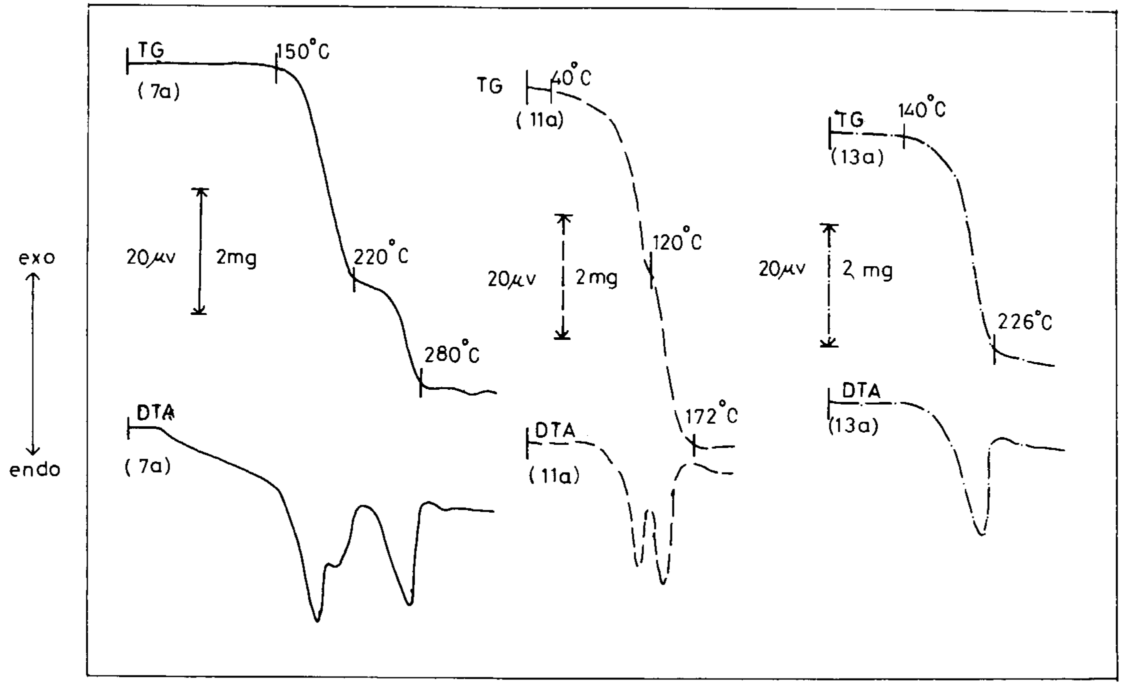

Fig. 1. Thermal curves of [$2CdCl_2(morph)_3$] (**7a**) (———), sample mass 11.9 mg; [$CdBr_2(thiox)_2$] (**11a**) (— — —), sample mass 13.4 mg; and [$CdBr_2(dith)$] (**13a**) (·—·—·), sample mass 11.5 mg.

TABLE 3

IR spectral data (cm^{-1}) for Cu(II) and Cd(II) cyclic ligand complexes

Complex	ν(NH) ^{a} + ν(OH)	ν(CH$_2$)	ν(CN)	δ(NH) + δ(HOH)	δ(CH$_2$)	ρ_ω(CH$_2$)	τ(NH) + ρ_ω(NH) + τ(CH$_2$)	ν(CN) + ν(C–C) + ν_a(C–O–C)	ρ_r(CH$_2$) + ν_s(C–O–C)	ρ_r(HOH) + ν(CS)	ρ_r(NH) + ν(C–S–C)	ρ_ω(HOH)	νN(NCS)
1a	3340(vs) 3215(w) 3125(s)	2930(vh) 2865(vw) 2780(ms)			1450(vs) 1420(vs)	1392(s) 1370(s) 1352(s)	1350(s) 1306(vs) 1280(sh) 1253(ms) 1226(ms) 1200(sh)	1108(sh) 989(w)	950(w) 908(sh) 895(vs) 880(vs) 870(vs) 850(w)		660(w) 600(s)		
2a	3400(br) 3230(s) 3220(sh) 3190(sh)	2970(w) 2890(w)		1640(s) 1620(s) 1614(w)	1455(w) 1400(w)	1360(vw)	1320(vw) 1260(s) 1200(ms)	1120(vs) 1100(ms) 1070(w) 1040(ms)	885(vs)	825(w) 810(s)	660(w)	540(s) 520(w) 510(s)	
2b	3170(s) 3040(vb)	2850(vw) 2720(w)		1650(w)	1450(s) 1445(sh)	1380(s) 1375(sh)	1350(vw) 1320(w) 1315(sh) 1305(w) 1290(s) 1200(w)	1185(s) 1100(vs) 1065(sh) 1040(s) 1025(w) 1010(w)	905(w) 875(sh) 865(vs) 845(w) 830(w) 815(w)		690(w) 680(w) 670(vw) 630(w) 620(vw)		
2c	3250(s)	2750(w) 2690(w)		1650(br)	1400(s) 1383(sh)	1385(w) 1360(sh)	1330(s) 1315(w) 1290(w) 1280(s) 1260(ms)	1165(s) 1150(w) 1132(w) 1115(w) 1075(s) 1047(w)	870(s) 850(w) 850(w) 810(ms)		675(w) 640(w) 640(w)		
3a	3400(br)	2980(w) 2970(w) 2935(vs) 2910(ms) 2895(sh) 2860(vs)		1635(s) 1614(w)	1450(s) 1405(vs)	1360(w) 1350(vs)	1315(vs) 1300(sh) 1270(vs) 1250(vs) 1208(vs)	1170(vs) 1150(vs) 1100(vs) 1040(vs) 1005(vs)	995(w) 990(vs) 970(vs) 945(s)	825(ms) 818(s)	660(w) 656(s)	566(s)	
3b		2850(br)			1440(br)	1395(s)	1325(w) 1320(w) 1305(w) 1280(s) 1270(s)	1180(w) 1155(w) 1087(s) 1050(s) 1010(w)	960(sh) 955(s) 920(w) 870(vw) 820(s)		660(w) 647(w) 610(vw)		

TABLE 3 (continued)

Complex	ν(NH) [a] + ν(OH)	$\nu(CH_2)$	ν(CN)	δ(NH) + δ(HOH)	$\delta(CH_2)$	$\rho_\omega(CH_2)$	τ(NH) + ρ_ω(NH) + $\tau(CH_2)$	ν(CN) + ν(C–C) + ν_a(C–O–C)	$\rho_r(CH_2)$ + ν_s(C–O–C)	ρ_r(HOH) + ν(CS)	ρ_r(NH) + ν(C–S–C)	ρ_ω(HOH)	νN(NCS)
4a	3400(br)	2960(w)		1630(s)	1450(s)	1379(ms)	1339(ms)	1176(vs)	1000(vs)		663(vs)		
		2942(sh)		1620(w)	1445(w)		1313(w)	1146(s)	986(s)		650(w)		
		2921(vw)			1430(ms)			1085(vs)	964(s)		640(ms)		
		2900(ms)			1400(ms)			1040(s)	952(sh)		560(ms)		
		2882(sh)							943(sh)				
		2860(s)							820(ms)				
									812(sh)				
5a	3400(br)	3000(vw)		1635(w)	1404(s)	1385(sh)	1315(ms)	1150(ms)	995(sh)		656(w)		
		2976(w)		1614(br)		1381(s)	1304(sh)	1098(vs)	991(vs)		566(s)		
		2930(vw)				1359(vw)	1279(sh)	1045(s)	969(vs)				
						1351(vw)	1272(s)	1002(vs)	945(w)				
							1250(w)		825(w)				
							1206(ms)						
6a	3440(br)	2990(s)		1620(br)	1398(w)	1386(sh)	1280(s)	1151(s)	998(sh)		667(vw)		
		2960(w)				1380(ms)	1270(w)	1145(vw)	889(ms)		652(w)		
		2840(w)					1260(w)	1140(w)	875(s)				
7a	3220(s)	2960(sh)			1450(sh)	1370(w)	1260(ms)	1125(s)	902(w)		650(sh)		
	3200(sh)	2940(w)			1445(ms)	1340(sh)	1230(w)	1110(sh)	877(vs)		640(s)		
		2920(w)			1425(s)	1320(w)	1205(sh)	1100(ms)	865(sh)				
		2850(s)			1420(sh)		1200(s)	1060(ms)	850(w)				
					1400(w)			1040(s)	840(w)				
								1030(sh)	830(w)				
								1005(s)					
7b	3240(vs)	2970(w)			1460(vw)	1350(wv)	1250(s)	1090(s)	893(w)		650(w)		
	3200(w)	2940(w)			1440(w)	1320(vw)	1170(w)	1080(sh)	870(vs)		620(w)		
		2900(w)			1430(s)	1300(w)		1000(w)	830(w)		550(w)		
		2840(vw)			1422(sh)			975(w)	815(s)				
8a	3260(s)	2980(sh)			1450(sh)	1388(s)	1300(s)	1180(w)	987(vs)		630(s)		
		2960(ms)			1430(vs)	1360(w)	1292(sh)	1160(s)	890(ms)				
		2930(ms)			1420(sh)	1340(sh)	1245(vs)	1110(vs)	870(vs)				
		2900(w)			1405(ms)			1090(vs)	824(s)				
								1038(ms)	810(s)				
								1025(ms)					
								1015(sh)					

8b	3260(w)	2960(w) 2930(w) 2900(sh) 2890(s) 2850(w)			1440(sh) 1420(ms) 1407(sh)	1385(vw) 1350(vw) 1310(vw)	1280(vw) 1245(vs) 1190(vw)	1155(w) 1100(ms) 1087(vs) 1080(sh) 1018(ms)	970(ms) 960(sh) 890(s) 865(vs) 810(s)		630(s)		
9a	3220(s)	2980(w) 2960(w) 2938(s) 2915(w) 2850(w) 2830(sh)	2120(ms) 2050(sh)		1450(sh) 1440(sh) 1427(s)	1385(w) 1355(vw) 1310(vw)	1298(vw) 1250(s)	1110(vs) 1090(ms) 1085(ms) 1030(w) 1026(s) 1011(vw)	985(ms) 938(vw) 910(vw) 890(ms) 874(vs)	818(s) 780(s) 768(w)	625(w)		480(s) 470(w)
9b	3240(w)	2980(vw) 2940(vw) 2859(vw)	2180(vw) 2100(vs)		1450(vw) 1430(vw)	1320(vw) 1305(vw)	1260(w) 1170(s)	1030(s) 1040(w) 1030(w)	990(w) 980(vw) 945(vw) 900(w) 850(vs)	824(w) 780(vw)	640(vw)		500(vw) 475(vw) 460(vw) 440(vw)
10a	3450(br) 3425(w)	2944(w) 2912(w) 2849(w)		1630(w) 1620(w)	1450(w) 1412(w)	1355(s) 1312(w)	1279(ms) 1263(w) 1205(w) 1195(sh)	1160(w) 1085(s) 1039(w)	992(w) 980(w) 975(sh) 965(vw) 960(w)	819(w) 809(s)	660(ms) 650(w) 641(sh)	546(w) 505(br)	
11a		2950(w) 2920(w) 2855(w)			1443(vw) 1410(w)	1355(vs) 1315(w)	1280(s) 1209(vw)	1099(vs) 1040(vw) 999(s) 959(w)	835(sh) 818(s) 808(w)		654(w) 650(w)		
12a	3410(br)	2940(w) 2932(w) 2800(vw)	2050(s)	1635(w) 1625(br)	1440(w)	1320(br) 1300(w)		1150(w) 1115(w) 1106(w) 1015(vw)	940(br)	855(w) 845(s) 838(sh)	654(w) 548(w)		490(w) 465(s) 425(w)
13a	–	2996(w) 2970(vw) 2920(w) 2850(w)			1465(w) 1443(w) 1416(sh) 1400(s)	1392(vs) 1365(s)	1284(s) 1275(w) 1262(sh) 1250(s)	1151(vs) 1138(s) 1074(w) 1050(w) 1024(w) 1000(s) 985(w)	962(w)		660(s) 655(sh) 640(w) 630(w)		

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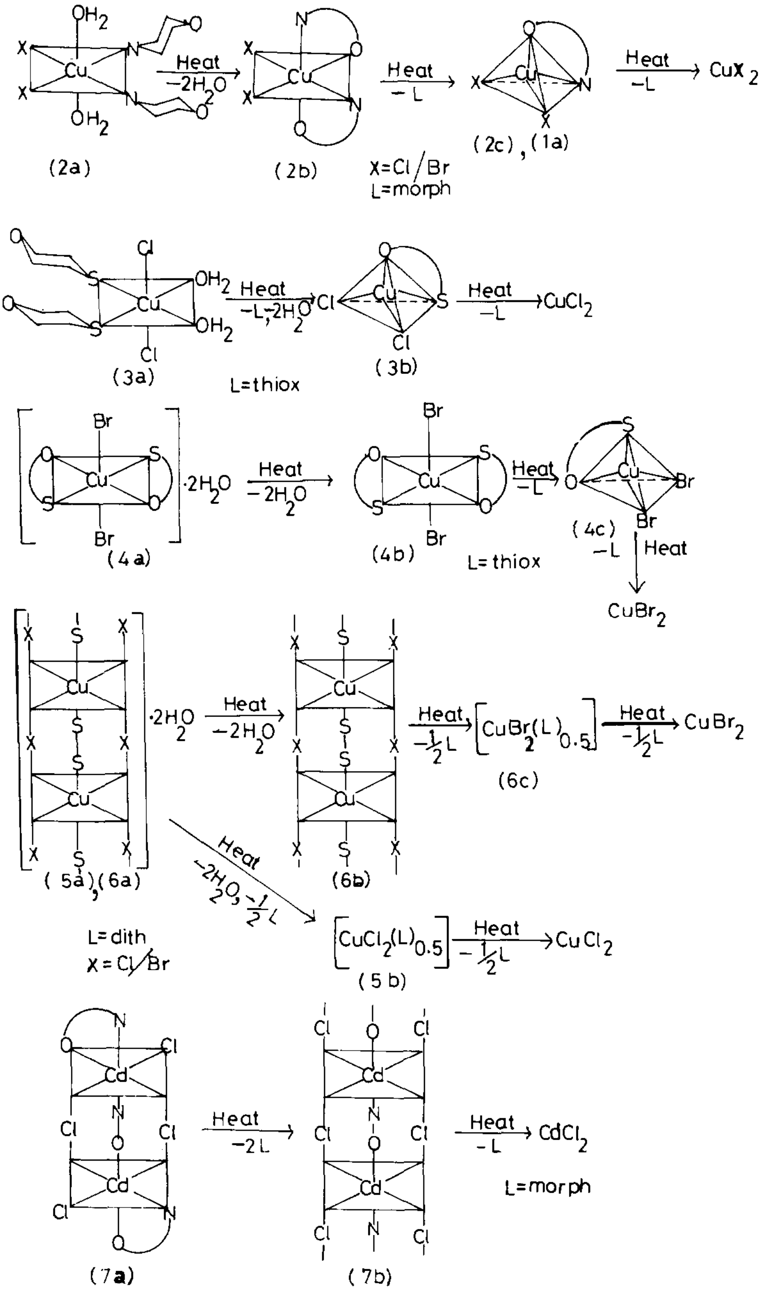
[a] Complexes containing H_2O molecule bands for ν(NH) and δ(NH) overlapped with ν(OH) and δ(HOH) respectively.

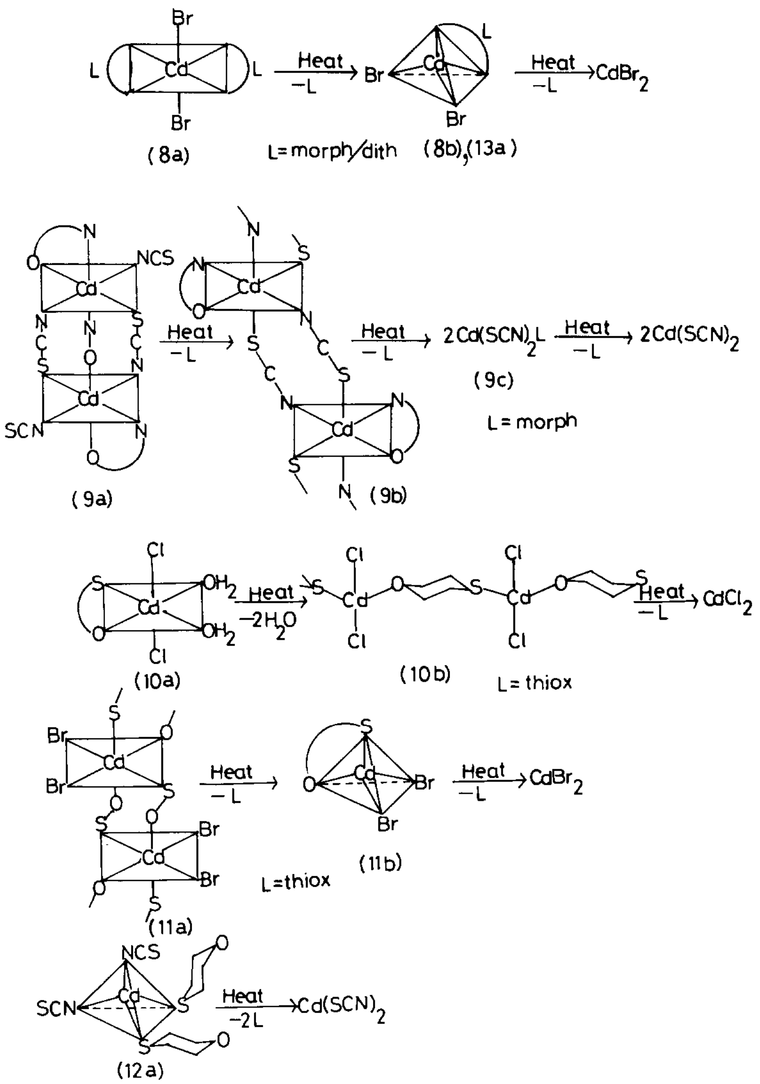
Abbreviations: vs, very strong; s, strong; ms, medium strong; br, broad; w, weak; vw, very weak; sh, shoulder.



Scheme 1.

$[CuBr_2(morph)_2(H_2O)_2]$ (2a) and $[CuCl_2(thiox)_2(H_2O)_2]$ (3a)

These complexes have been reported earlier [5,7]. The presence of coordinated water molecules was confirmed by IR bands at 3400 cm^{-1} (ν(OH));



Scheme 1 (continued).

1640, 1635 and 1614 cm^{-1} (δ(HOH)); 825 cm^{-1} [ρ_γ(HOH)]; 566, 540 and 510 cm^{-1} (ρ_ω(HOH)); 425 and 419 cm^{-1} (ν(Cu–O)) in (Cu–OH_2) [17]. Further the weight loss in TGA curves for **2a** and **3a** in the ranges 40–136 °C and 88–145 °C along with endothermic peaks at 65 and 142 °C (Table 2 and Fig. 2) respectively correspond to two molecules of coordinated water (with also one ligand for **3a**). Complex **2b** is again converted into $CuBr_2$ via formation of [$CuBr_2$(morph)] (**2c**) in the ranges 136–327 and 327–404 °C showing endothermic DTA peaks at 138, 285 °C and 328, 350 °C respectively. Complex [$CuCl_2$(thiox)] (**3b**) is converted into $CuCl_2$ in the range 145–198 °C with an endothermic DTA peak at 190 °C (Fig. 2). IR and far-IR data (Tables 3 and 4) show that ligands in the complexes **2a** and **3a** function as unidentate and coordinate through nitrogen and sulphur respectively and exist in the chair form [5,9,25]. Values of effective magnetic moments (Table 1) indicate that the complexes **2a** and **3a** are octahedral.

The intermediate complexes **2b**, **2c** and **3b** could be isolated at around 136, 327 and 145 °C respectively by keeping the heating rate at 0.5 °C min^{-1} in the respective temperature range. In the complexes **2b**, **2c** and **3b**, the cyclic ligands exist in the boat form [12] as shown by the IR spectral data (Table 3) and magnetic moments indicate the complex **2b** is octahedral, whilst **2c** and **3b** have tetrahedral structures. Structures are shown in Scheme 1. Value of $E_a^\star$, ΔH and ΔS are given in Table 2.

*[CuBr$_2$(thiox)$_2$] · 2H$_2$O (**4a**), [CdBr$_2$(morph)$_2$] (**8a**) and [CdBr$_2$(thiox)$_2$] (**11a**)*

Complexes **4a** and **11a** have not previously been reported. Complex **8a** was reported earlier [5]. Our thermal investigation has confirmed that the lattice water in **4a** is lost in range 86–120 °C (Table 2). The decomposition reactions of **4b**, **8a** and **11a** into their corresponding metal halides take place in two steps via the intermediates [CuBr_2(thiox)] (**4c**), [CdBr_2(morph)] (**8b**), and [CdBr_2(thiox)] (**11b**) as reflected by the mass loss in TGA curves and endothermic peaks in DTA curves (Fig. 1 and Table 2).

In complexes **4a**, **4b**, **8a**, **8b** and **11b**, both morpholine and thioxane function as bidentate chelates (boat form) [12] as indicated by the IR spectral bands (Table 3). In complex **11a**, the ligand exists as bridging bidentate [16] (chair form) (Table 3) and is probably polymeric as shown in Scheme 1. Complexes **4a**, **4b**, **8a** and **11a** are octahedral and **4c**, **8b** and **11b** have tetrahedral structures as shown in Scheme 1 (magnetic moment values for **4a**, **4b** and **4c** are given in Table 1). Values of $E_a^\star$, ΔH and ΔS for dehydration and decomposition reactions are given in Table 2.

*[CuCl$_2$(dith)] · 2H$_2$O (**5a**) and [CuBr$_2$(dith)] · 2H$_2$O (**6a**)*

These complexes were reported earlier [7,21]. Thermal investigation has confirmed that the lattice water in **5a** and **6a** is lost in the ranges 122–205 and 40–189 °C respectively. The anhydrous complex [$\text{CuCl}_2(\text{dith})_{0.5}$] **5b** decomposes into CuCl_2 in a single step and [CuBr_2(dith)] (**6b**) into CuBr_2 (Fig. 2) via the intermediate [$\text{CuBr}_2(\text{dith})_{0.5}$] (**6c**) as shown in Table 2 and Scheme 1. In complex **5a**, dithiane is in the chair form [7,12,16,21] and halogens are bridging bidentate [1,17] as indicated by IR and far-IR bands (Tables 3 and 4). They are probably polymeric [12] as shown in Scheme 1.

*[2CdCl$_2$(morph)$_3$] (**7a**) and [2Cd(SCN)$_2$(morph)$_3$] (**9a**)*

Both the complexes **7a** and **9a** are expected to be dimeric [12,25] (as shown in Scheme 1). On heating, **7a** decomposes into metal chloride (Fig. 1)

TABLE 4

Far-IR spectral data [a] (cm^{-1}) for Cu(II) and Cd(II) cyclic ligand complexes

No.	Complex [b]	ν(M–O)	ν(M–N)	ν(M–S)	ν(M–X) [b]	δ(M–X) [b]
1a	$[CuCl_2L]$	460(s) 455(sh) 445(w)	332(w) 324(w)		300(s) 288(w) 275(sh)	195(s) 126(w)
2a	$[CuBr_2L_2(H_2O)_2]$	425(s) 419(w)	335(s) 325(w)		240(w) 225(s) 210(ms)	150(w)
2b	$[CuBr_2L_2]$	437(ms)	330(ms) 321(s)		240(s) 232(sh)	160(ms) 147(s)
2c	$[CuBr_2L]$	440(ms) 421(s)	355(ms) 348(vw) 300(w)		280(s) 270(w) 240(br)	157(ms) 140(w)
3a	$[CuCl_2L'_2(H_2O)_2]$	425(ms) 405(s)		340(ms) 330(s)	250(w) 240(w)	
3b	$[CuCl_2L']$	450(w) 432(ms)		333(ms) 319(w)	260(w) 242(w)	
4a	$[CuBr_2L'_2]\cdot 2H_2O$	560(s) 549(vw)		340(ms)	270(w) 240(ms) 210(w)	138(ms) 125(w)
5a	$[CuCl_2L'']\cdot 2H_2O$			347(ms) 330(ms)	279(ms) 268(sh)	172(w) 148(w)
6a	$[CuBr_2L'']\cdot 2H_2O$			332(ms) 321(w)	280(w) 270(ms)	172(ms) 138(w)
7a	$[2CdCl_2L_3]$	440(ms) 435(w) 420(ms)	340(s) 330(sh) 317(ms)		300(w) 280(w) 272(s) 260(ms)	165(w) 155(w) 125(ms)
7b	$[2CdCl_2L]$	450(w) 420(ms) 400(w)	325(ms) 315(w)		280(w) 250(w) 220(sh)	172(ms) 165(w)
8a	$[CdBr_2L_2]$	460(ms) 440(w)	330(ms) 323(w)		280(ms) 275(sh) 262(w)	135(w)
8b	$[CdBr_2L]$	450(ms) 430(w) 420(w)	370(w) 330(s)		245(w) 220(sh)	
9a	$[2Cd(SCN)_2L_3]$	468(w) 455(s) 435(w)	375(w) 390(w)			
9b	$[2Cd(SCN)_2L_2]$	440(ms) 425(w)	330(s)			
10a	$[CdCl_2L'(H_2O)_2]$	452(s) 442(w) 438(w)		380(ms) 352(w)	318(ms) 307(sh)	200(ms) 175(w)
11a	$[CdBr_2L'_2]$	460(ms) 450(w) 435(s)		360(w) 320(s) 310(ms)	262(ms) 245(w)	160(w) 125(w)
12a	$[Cd(SCN)_2L'_2]\cdot H_2O$			332(sh) 304(ms)		
13a	$[CdBr_2L'']$			387(w) 375(w) 330(vs)	268(ms) 244(w) 206(w)	172(ms) 148(s) 112(w)

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[a] For cyclic ligands (morpholine and thioxane) and coordinated water molecules bands for ν(M–O) overlapped with each other.

[b] X = Cl/Br.

L, morpholine; L′, thioxane; L″, dithiane; vs, very strong; s, strong; ms,medium strong; sh, shoulder; w, weak; vw, very weak.

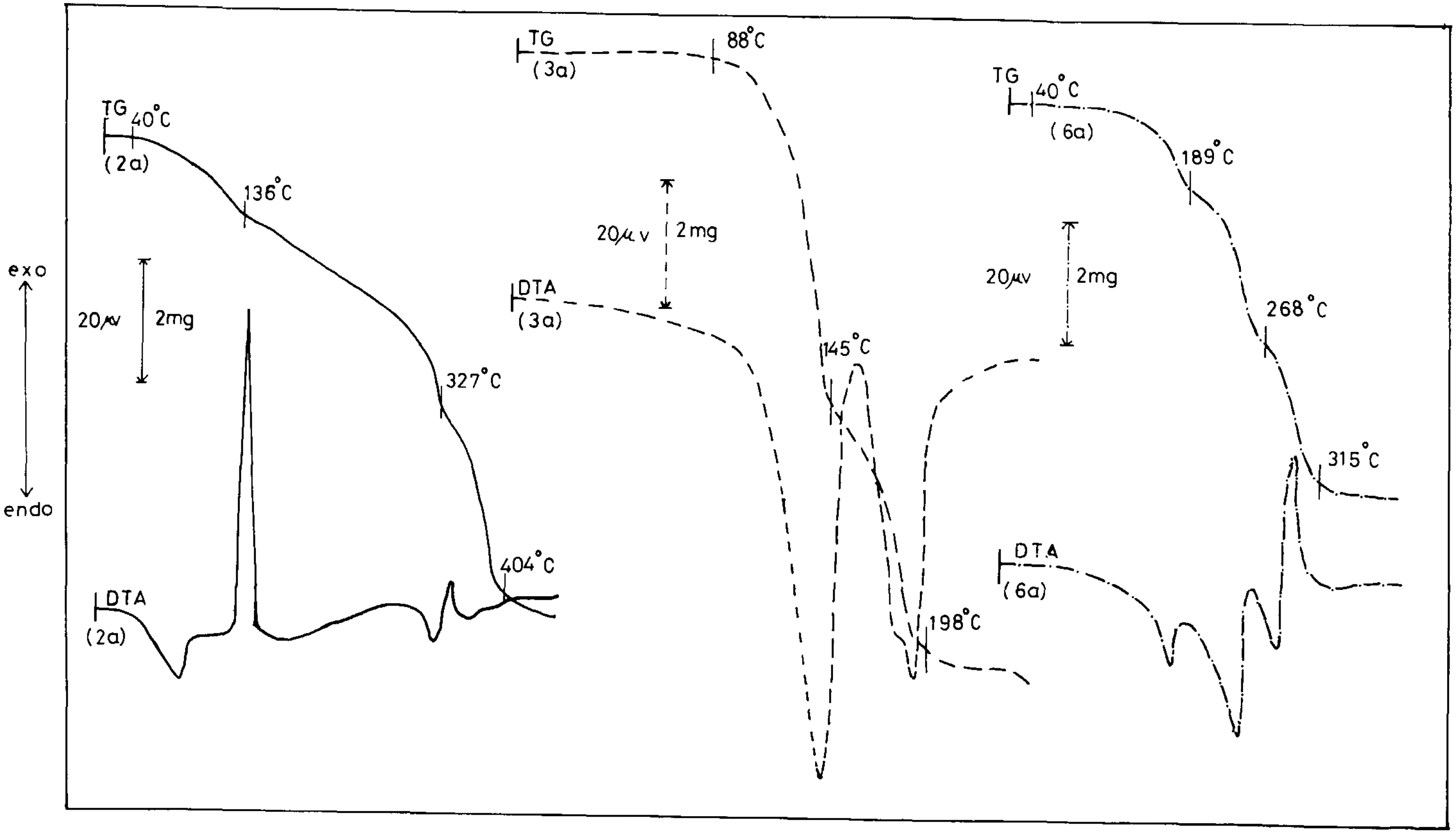

Fig. 2. Thermal curves of $[CuBr_2(morph)_2(H_2O)_2]$ (**2a**) (———), sample mass 15.7 mg; $[CuCl_2(thiox)_2(H_2O)_2]$ (**3a**) (— — —), sample mass 14.7 mg; and $[CuBr_2(dith)] \cdot 2H_2O$ (**6a**) (·—·—·), sample mass 15.2 mg.

with intermediate **7b** having a polymeric structure [17,25] and **9a** is converted into $Cd(SCN)_2$ via the two intermediates **9b** (polymeric) and **9c** as shown in Scheme 1.

In both **7a** and **9a**, the ligands are both bridging bidentate and chelating (Table 3) [12,17,25]. The thiocyanate and chloride are also both bridging bidentate and terminal unidentate [12,17,25] as shown by the very strong bands at 2120 and 2050 cm^{-1} for $\nu(CN)$; 818 and 780 cm^{-1} for $\nu(CS)$; 480 cm^{-1} for $\delta(NCS)$; 300, 280, 272 and 260 cm^{-1} for $\nu(M-Cl)$; and 165, 155 and 125 cm^{-1} for $\delta(M-Cl)$ [12,17,25] (Tables 3 and 4). Values of thermodynamic parameters are given in Table 2.

*$[CdCl_2(thiox)(H_2O)_2]$ (**10a**)*

This complex has not previously been reported. The presence of coordinated water molecules was confirmed by IR bands at 3450 and 3425 cm^{-1} ($\nu(OH)$); 1630 and 1620 cm^{-1} ($\delta(HOH)$); 470 cm^{-1} ($\rho_r(HOH)$); and 452 cm^{-1} ($\nu(Cd-O)$) in $[Cd-OH_2]$ [17]. Further, the weight loss in the TGA curve of complex **10a** in the range 95–115 °C and endothermic peak (DTA) at 110 °C (Table 2) corresponds to two molecules of coordinated water. The anhydrous complex $[CdCl_2(thiox)]$ (**10b**) is converted into $CdCl_2$ in a single step in the range 115–209 °C with two endothermic DTA peaks at 130 and 190 °C.

In the complex **10a** thioxane is in boat form [12] and in the intermediate **10b** it exists as bridging bidentate [12,16] as indicated by the IR spectral bands (Table 3). The probable path of decomposition of **10a** to $CdCl_2$ is shown in Scheme 1.

*$[Cd(SCN)_2(thiox)_2] \cdot H_2O$ (**12a**)*

This complex has not previously been reported. Our thermal investigation has confirmed that the lattice water in **12a** (Table 2) is lost in the range 60–110 °C. The decomposition of $[Cd(SCN)_2(thiox)_2]$ into metal thiocyanate takes place in a single step as found in the TGA curve in the range 112–243 °C with an endothermic DTA peak at 210 °C. In **12a**, both thioxane (in the chair form) [7,11,16] and thiocyanate are unidentate [12,25].

A linear correlation is observed upon plotting $E_a^\star$ versus ΔS for the decomposition reactions of the complexes and shows that a system having a higher entropy change will require less energy ($E_a^\star$) for its thermal decomposition.

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