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Thermal investigation and stereochemical studies of some cyclic ligand complexes of nickel(II), copper(II), zinc(II) and cadmium(II) in the solid state.
Part 1

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Abstract

Nickel(II), copper(II), zinc(II), and cadmium(II) complexes of *N*-methylmorpholine (Mmorph) and *N*,*N*′-dimethylpiperazine (DMP), with the compositions [Ni(Mmorph)Cl_2], [$2CuCl_2 \cdot 3$Morph], [Zn(Mmorph)Cl_2], [Ni(DMP)Cl_2], [Cu(DMP)Cl_2] · H_2O, [Zn(DMP)-Cl_2] and [Cd(DMP)Cl_2], have been synthesized in order to carry out thermal investigations (TGA and DTA) and to study stereochemical changes during their thermal decomposition. Attempts to prepare a methylmorpholine complex of $CdCl_2$ failed. Some intermediate complexes were isolated by the temperature arrest technique. Configurational and conformational changes were studied from elemental and thermal analyses, IR spectral data, and magnetic moment measurements. All the complexes of methylmorpholine and dimethylpiperazine appeared to be tetrahedral, except [$2CuCl_2 \cdot 3$Morph] which is octahedral and dimeric. The activation energy E_a^*, and the enthalpy ΔH and entropy ΔS changes for the dehydration and decomposition reactions were evaluated with some standard equations and are compared. The order of stability of the complexes with respect to the activation energy is also discussed. A linear correlation is found between E_a^* and ΔS for the dehydration and decomposition reactions of the complexes.

INTRODUCTION

Acyclic ligands having oxygen or nitrogen donor atoms in their structures can act as good chelating agents for transition and non-transition metal ions [1–3]. However, works on cyclic ligand complexes are still very rare [4–7] and there has been little thermal investigation of cyclic ligand complexes in the solid state [8, 9]. The main aim of the present work is to synthesize some cyclic ligand (six-membered ring) complexes of nickel(II), copper(II), zinc(II), and cadmium(II) and to study their stereochemical changes during thermal decomposition. The purpose of selecting these cyclic ligands was

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also to determine the effect of stability of the complexes formed by two (same or different) donor centres in the same molecule. Some workers [10–12] have determined activation energy values for the decomposition reactions of simple salts by using different equations. We have also applied different equations for the evaluation of the activation energy, and the values are compared and discussed. Prior to heating, methylmorpholine in the complexes [Ni(Mmorph)Cl_2] and [Zn(Mmorph)Cl_2], and dimethyl-piperazine in [Zn(DMP)Cl_2] and [Cd(DMP)Cl_2], function as bidentate chelates and exist in the boat form [4, 5–7, 13]. Dimethylpieperazine in the complexes [Ni(DMP)Cl_2] and [Cu(DMP)Cl_2] · H_2O functions as a bridging bidentate (chair form) [5], but methylmorpholine in [2CuCl_2 · 3Morph] functions as a bidentate chelate as well as a bridging bidentate ligand [4, 5, 8]. If these complexes are heated under non-isothermal conditions, they decompose via stable and unstable intermediates in which the cyclic ligand may function as a bridging bidentate ligand (chair form). This type of conformational change in the ligand (boat form → chair form) has been confirmed by IR spectral data. In these complexes the chloride ion might function as a terminal unidentate ligand or as a bridging ligand [14]. Parameters such as E_a^*, ΔH and ΔS for the decomposition reactions of the complexes in the solid state have been evaluated and compared.

EXPERIMENTAL

Materials and methods

The metal chlorides were of AnalaR grade and were used as received. Methylmorpholine (Fluka, Switzerland) and *N,N′*-dimethylpiperazine (Aldrich Co., USA) were used as received. Ethanol and diethyl ether were dried using standard procedures [15].

Preparation of the complexes

The metal chloride complexes with methylmorpholine and dimethylpiperazine were synthesized as follows. For [Ni(Mmorph)Cl_2], ligand (approx. 5 mmol) in dry ethanol (40 cm^3) was added with constant stirring to a solution of freshly prepared nickel chloride (approx 5 mmol) in dry ethanol (50 cm^3) and kept overnight. The green complex was collected by filtration under suction, washed carefully with ethanol and diethyl ether, and dried over fused calcium chloride in a desiccator; yield, approx. 80%.

The same procedure was used to synthesize the complexes [2CuCl_2 · 3Morph], [Zn(Mmorph)Cl_2], [Ni(DMP)Cl_2], [Cu(DMP)Cl_2] · H_2O, [Zn(DMP)Cl_2] and [Cd(DMP)Cl_2].

Nickel, copper, zinc and cadmium were estimated gravimetrically using standard procedures [16] and carbon, hydrogen and nitrogen were determined using a Carlo Erba 1106 elemental analyser. Results of elemental analyses are given in Table 1. Thermal investigations were carried out on a

TABLE 1

Analytical data (calculated values in parentheses) and effective magnetic moment values of cyclic ligand [a] complexes of Ni(II), Cu(II), Zn(II) and Cd(II)

No.	Complex [a]	Colour	Analysis/%				μ_{eff}/(BM)
			Metal	Carbon	Nitrogen	Hydrogen	
1a	[$NiL'Cl_2$]	Green	25.44 (25.40)	26.00 (26.00)	6.05 (6.06)	4.75 (4.76)	3.01
2a	[$2CuCl_2 \cdot 3L'$]	Deep green	22.20 (22.21)	31.47 (31.46)	7.40 (7.34)	5.80 (5.76)	2.30
2b	[$2CuCl_2 \cdot 2L'$]	Light chocolate	47.18 (47.22)	44.50 (44.59)	10.31 (10.40)	8.17 (8.16)	2.27
3a	[$ZnL'Cl_2$]	White	27.50 (27.54)	25.27 (25.27)	5.80 (5.89)	4.60 (4.63)	–
4a	[NiL^*Cl_2]	Green	24.00 (24.09)	29.50 (29.54)	11.49 (11.48)	5.75 (5.74)	3.48
5a	[CuL^*Cl_2] $\cdot H_2O$	Light green	23.80 (23.83)	27.00 (27.01)	10.45 (10.50)	6.05 (6.00)	2.03
6a	[ZnL^*Cl_2]	White	26.10 (26.11)	28.61 (28.75)	11.10 (11.18)	5.50 (5.59)	–
7a	[CdL^*Cl_2]	White	37.70 (37.79)	24.10 (24.20)	9.35 (9.41)	4.60 (4.70)	–

[a] L′, *N*-methylmorpholine (Mmorph); L*, *N*,*N*′-dimethylpiperazine (DMP).

Shimadzu thermal analyser DT-30 (Japan) under a dynamic nitrogen atmosphere with a heating rate of 10°C min^{-1}, using α-alumina as a standard reference substance. The E_a^* values were determined from the TGA curves using the equations of Horowitz and Metzger [17], Coats and Redfern [18], and Freeman and Carroll [19], and from the DTA curves using the equation of Borchardt and Daniels [20]. The enthalpy change, ΔH was evaluated using the relation $\Delta H = KA$, where K is the heat transfer coefficient (the calibration constant or cell constant); the cell used was a platinum crucible and its constant K was evaluated from the data obtained using indium metal as a calibrant. A is the total area under the particular DTA peak measured using a compensating planimeter with the Fuji Corona 027 optical tracer. The enthalpy change ΔS was calculated using the relation [21] $\Delta S = \Delta H / T_m$, where T_m is the DTA peak temperature in kelvin. IR spectra were recorded using Perkin-Elmer models 363, 597, 783 and 843, with KBr/CsI discs. The effective magnetic moments were evaluated from the results of magnetic susceptibility measurements using an EG and G PAR 155 vibrating sample magnetometer. Solid residues obtained after pyrolysis were identified by qualitative analysis [22].

RESULTS AND DISCUSSION

The $[\mathrm{Ni(Mmorph)Cl_2}]$ (**1a**), $[\mathrm{Zn(Mmorph)Cl_2}]$ (**3a**), $[\mathrm{Zn(DMP)Cl_2}]$ (**6a**), and $[\mathrm{Cd(DMP)Cl_2}]$ (**7a**) complexes were expected to be monomeric. On heating, complexes **1a**, **3a** and **7a** are converted into metal chlorides via the respective intermediates $[\mathrm{Ni(Mmorph)_{0.5}Cl_2}]$ (**1b**), $[\mathrm{Zn(Mmorph)_{0.5}Cl_2}]$ (**3b**) and $[\mathrm{Cd(DMP)_{0.5}Cl_2}]$ (**7b**), by losing one half of the cyclic ligand as

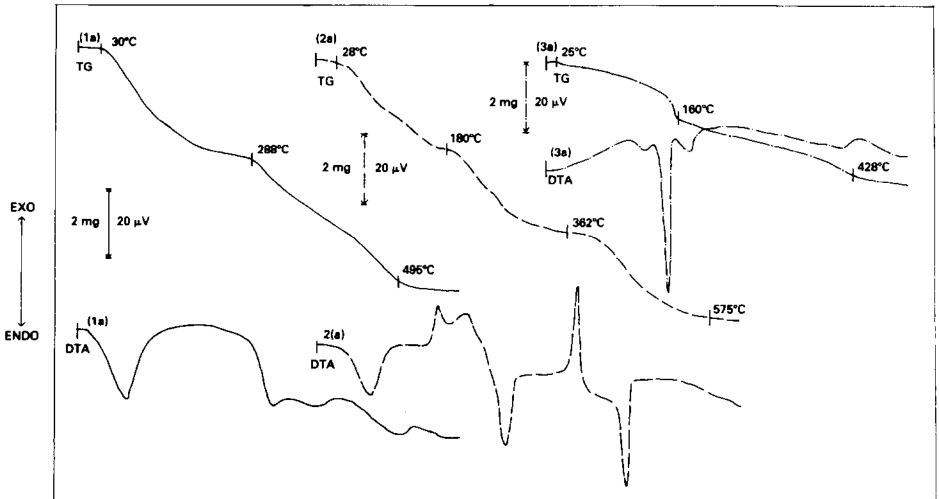

Fig. 1. Thermal curves: (——), $[\mathrm{Ni(Morph)Cl_2}]$ (**1a**) sample mass 15.0 mg; (— — —), $[\mathrm{2CuCl_2 \cdot 3Morph}]$ (**2a**) sample mass 14.0 mg; and (— · — · —), $[\mathrm{Zn(Morph)Cl_2}]$ (**3a**) sample mass 7.5 mg.

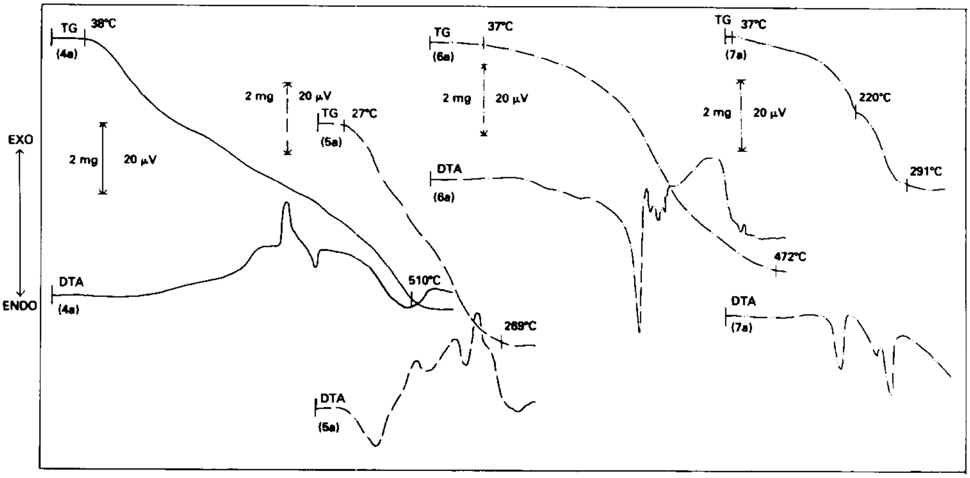

Fig. 2. Thermal curves: (——), [Ni(DMP)Cl_2] (**4a**) sample mass 15.5 mg; (— — —), [Cu(DMP)Cl_2] (**5a**) sample mass 13.1 mg; (— · — · —), [Zn(DMP)Cl_2] sample mass 14.3 mg; and (— · · — · · —), [Cd(DMP)Cl_2] (**7a**) sample mass 10.8 mg.

reflected in the TGA curves (Figs. 1 and 2); the corresponding DTA peaks are given in Table 2. These intermediate complexes could not be isolated. The complex **6a** decomposes into zinc chloride in a single step by loosing one molecule of the cyclic ligand in the range 37–472°C, as shown in the TGA curve (Fig. 2). The thermodynamic parameters, E_a^*, ΔH and ΔS, for the decomposition reactions of the complexes **1a**, **3a**, **6a** and **7a** are given in Table 2.

Before heating, the cyclic ligand in all the complexes functions as a bidentate chelate (boat form), as indicated by the greater number of infrared-active bands in the region of 700–1400 cm^{-1} with respect to the free ligand which exists in the chair form [4, 5, 8]. All the complexes are expected to be tetrahedral. The green colour and the effective magnetic moment ($\mu_{eff} = 3.01$ BM) also suggest that complex **1a** has a tetrahedral structure. The probable decomposition reactions are summarized in Fig. 3.

The complex [$2CuCl_2 \cdot 3$Morph] (**2a**) has not been reported before. On heating, **2a** undergoes decomposition with loss of one molecule of the cyclic ligand in the range 28–180°C, as reflected in the TGA curve (Fig. 1 and Table 2). After losing one molecule of cyclic ligand, the complex **2b** decomposes into $CuCl_2$ via the intermediate [$2CuCl_2 \cdot$ Morph] (**2c**) in the temperature ranges 181–362°C and 363–575°C. The corresponding DTA peaks appear at 161, 207, 379°C (exothermic) and 52, 270, 440°C (endothermic) respectively. Values of E_a^*, ΔH and ΔS for the conversions **2a** → **2b**, **2b** → **2c**, and **2c** → $2CuCl_2$ are given in Table 2.

Complex **2a** is expected to be dimeric with an octahedral structure, in which the cyclic ligand functions as a bidentate chelate as well as a bridging bidentate ligand, as shown by the IR spectral bands given in Table 3

TABLE 2

Thermal parameters of *N*-methylmorpholine (L′) and *N,N*′-dimethylpiperazine (L″) complexes of Ni(II), Cu(II), Zn(II) and Cd(II)

No.	Decomposition reactions	TG temp. range/°C	DTA peak temp./°C		E_a/kJ mol^{-1} [a]				Enthalpy change ΔH/ kJ mol^{-1}	Entropy change ΔS/ J K^{-1} mol^{-1}
			Exo.	Endo.	TG			DTA		
					H.M.	C.R.	F.C.			
1a	$[NiL'Cl_2] \rightarrow [NiL'_{0.5}Cl_2]$	30–288	–	72	13	2	2	70	52	150
1b	$[NiL'_{0.5}Cl_2] \rightarrow NiCl_2$	289–495	–	309	56	27	31	–	–	–
2a	$[2CuCl_2 \cdot 3L'] \rightarrow [2CuCl_2 \cdot 2L']$	28–180	161	52 [b]	88	58	54	65	14	43
2b	$[2CuCl_2 \cdot 2L'] \rightarrow [2CuCl_2 \cdot L']$	181–362	207 [b]	270	31	12	12	80	53	110
2c	$[2CuCl_2 \cdot L'] \rightarrow 2CuCl_2$	363–575	379	440 [b]	149	89	88	271	38	53
3a	$[ZnL'Cl_2] \rightarrow [ZnL'_{0.5}Cl_2]$	25–160	–	153	28	17	18	187	47	110
3b	$[ZnL'_{0.5}Cl_2] \rightarrow ZnCl_2$	161–428	–	200	33	14	19	–	–	–
4a	$[NiL''Cl_2] \rightarrow NiCl_2$	38–510	255 289 331 [b]	70	20	10	9	–	–	–
5a	$[CuL''Cl_2] \cdot H_2O \rightarrow CuCl_2$	27–269	140 201 234 [b]	65	23	15	16	–	–	–
6a	$[ZnL''Cl_2] \rightarrow ZnCl_2$	37–472	–	140 280 [b] 309	43	24	23	–	–	–
7a	$[CdL''Cl_2] \rightarrow [CdL''_{0.5}Cl_2]$	37–220	–	200	33	20	12	212	7	14
b	$[CdL''_{0.5}Cl_2] \rightarrow CdCl_2$	221–291	–	259 280 [b]	168	42	40	137	21	37

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[a] H.M., Horowitz and Metzger; C.R., Coats and Redfern; F.C., Freeman and Carroll. [b] DTA peak temperature used for the evaluation of ΔS.

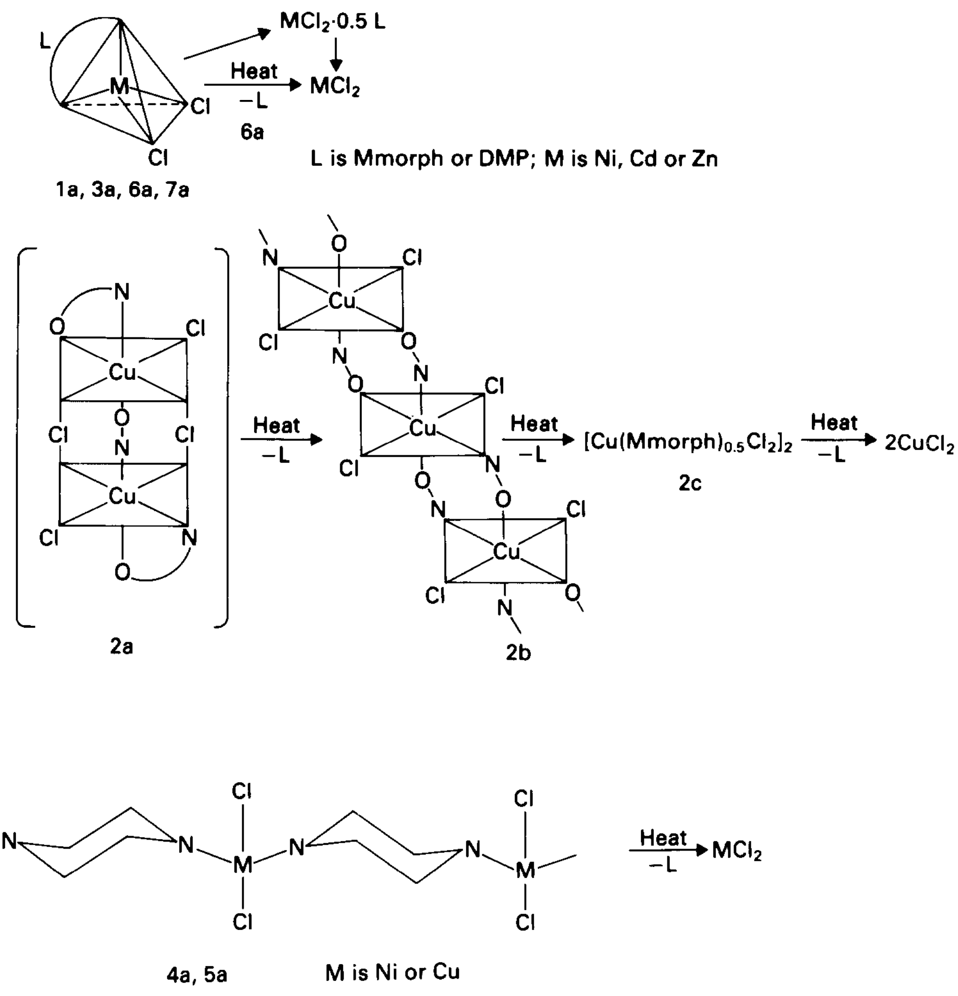

Fig. 3.

[8, 9, 22]. The chloride ion functions as a bridging bidentate as well as terminal unidentate [14]. The intermediate complex, **2b**, was isolated. In **2b**, the cyclic ligand functions as a bridging bidentate chelate (chair form) having a polymeric structure (Fig. 3). The magnetic moment values (Table 1) of **2a** and **2b** indicate that the complexes are octahedral. The probable thermochemical decomposition reactions are given in Fig. 3.

On heating [Ni(DMP)Cl_2] (**4a**) and [Cu(DMP)Cl_2] · H_2O (**5a**), the complexes are converted into the metal chloride in a single step in the ranges 38–510°C and 27–269°C, as reflected in the TGA curves. The nature of the DTA peaks and the thermodynamic parameters of the decomposition reactions are given in Table 2 and Fig. 2.

In both the complexes **4a** and **5a**, the ligand functions as a bridging bidentate ligand (chair form), as the number of IR-active bands is more or

TABLE 3

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

No.	Complex	ν(NH) + ν(OH)	$\nu(CH_2)$	∂(NH) + ∂(HOH)	$\partial(CH_2)$	τ (NH) + ρ_W(NH) + $\tau(CH_2)$	ν(CN) + ν(C–C) + ν_a(COC)	$\rho_r(CH_2)$ + ν_S(COC)	ν(M–N) + ν(M–O)	ν(M–Cl)
1a	[NiL′Cl_2]	3300(sbr)	2810(w)	1630(w)	1480(s)	1380(w)	1140(vw)	880(s)	460(s)	280(s)
		3200(br)	2745(w)	1620(s)	1460(sh)	1375(s)	1080(s)	860(w)	380(s)	260(sh)
		3180(s)		1600(sh)	1430(w)	1360(sh)	1060(w)	845(ms)	360(sh)	215(ms)
				1580(s)		1290(s)	1010(s)	732(w)	320(w)	
				1560(w)		1262(vw)	1000(sh)			
						1240(w)	935(w)			
						1200(ms)				
2a	[2CuCl_2 · 3L′]	3457(sh)	2746(w)	1693(s)	1493(s)	1386(s)	1070(s)	849(s)	454(ms)	292(s)
		3352(br)	2352(w)	1643(vs)	1461(w)	1371(s)	1028(s)	821(s)	431(ms)	263(s)
		3338(sbr)	2338(s)	1630(vs)	1428(ms)	1336(vw)	987(s)	725(s)	418(sh)	240(ms)
		3200(s)	2329(s)	1622(w)	1401(s)	1308(s)	949(w)	713(sh)	405(s)	232(ms)
		3105(ms)		1613(sh)		1271(ms)	915(ms)		396(s)	220(w)
				1555(v)		1242(sh)	895(sh)		348(ms)	
						1200(w)				
2b	[2CuCl_2 · 2L′]	3400(br)	2740(s)	1680(s)	1480(s)	1366(ms)	1060(s)	840(ms)	430(ms)	245(s)
		3340(sbr)	2713(sh)	1671(sh)	1431(w)	1340(sh)	1020(s)	830(sh)	400(w)	230(sh)
		3200(s)	2340(s)	1660(ms)	1400(ms)	1321(ms)	948(ms)	800(w)	385(ms)	215(s)
			2300(ms)	1650(vw)	1392(sh)	1295(s)	940(sh)	790(w)		
								775(ms)		
3a	[ZnL′Cl_2]	3390(s)	2880(w)	1660(s)	1440(w)	1360(s)	1110(vs)	840(ms)	460(s)	295(s)
		3200(br)	2840(s)	1650(w)	1390(s)	1350(sh)	1100(ms)	830(sh)	400(w)	280(s)
		3162(ms)	2750(s)			1300(s)	1040(ms)	815(w)	345(w)	250(w)

			2680(w) 2360(s)			1280(ms) 1250(w) 1220(vw)	1010(s) 980(ms) 942(w)	760(w)		
4a	[NiL″Cl$_2$]	3400(s) 3380(sbr) 3240(s) 3200(sh) 3172(ms)	2690(w) 2380(w) 2370(vw)	1700(w) 1680(w) 1670(vw) 1660(sh) 1650(s) 1620(w)	1460(s) 1430(s) 1385(w)	1340(w) 1290(w) 1247(ms) 1000(s) 1097(sh)	1140(s) 1080(s)	880(s) 860(s)	460(s) 380(s) 365(sh) 345(sh) 320(s)	300(s) 290(s) 280(s)
5a	[CuL″Cl$_2$] · H$_2$O	3452(ms) 3350(ms) 3200(br) 3050(ms) 3020(sh)	2955(w) 2860(w) 2800(vw) 2720(vw)	1660(br) 1650(w) 1600(s)	1460(sh) 1454(vs) 1413(w)	1385(w) 1367(ms) 1298(w) 1279(s) 1197(w)	1949(w) 1135(s) 1102(ms) 1070(w) 1058(s) 1010(s)	894(s) 819(s)	455(s) 440(sh) 420(w) 400(w)	320(s) 300(s) 245(w)
6a	[ZnL″Cl$_2$]	3480(sbr) 3380(w) 3340(s)	2900(w) 2861(br) 2720(s)	1680(w) 1660(w) 1645(vw)	1480(s) 1460(s) 1435(ms)	1395(sh) 1370(s) 1255(w) 1180(ms) 1150(w) 1110(w)	1040(s) 960(s) 955(sh) 930(w) 925(w)	800(ms) 760(sh) 740(sh) 715(vs) 700(w)	450(w) 420(s) 415(sh) 390(s)	300(s) 270(s) 250(s)
7a	[CdL″Cl$_2$]	3400(vs) 3350(w) 3100(w) 3020(s)	2900(w) 2860(w) 2780(s)	1675(w) 1620(s) 1600(sh)	1475(sh) 1460(sh) 1440(s) 1415(sh)	1380(s) 1362(s) 1340(s) 1302(ms) 1290(sh) 1240(w) 1120(w) 1100(s)	1098(s) 1080(w) 1040(w) 1019(s) 990(vs) 970(ms)	820(vs) 760(sh) 745(sh) 735(vs)	460(sh) 450(s) 420(ms)	320(s) 310(as) 300(s)

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[a] Sbr, strong broad; ms, medium strong; br, broad; w, weak; vw, very weak; sh, shoulder; vs, very strong; s, strong. [b] L′, methylmorpholine (Mmorph); L″, dimethylpiperazine (DMP).

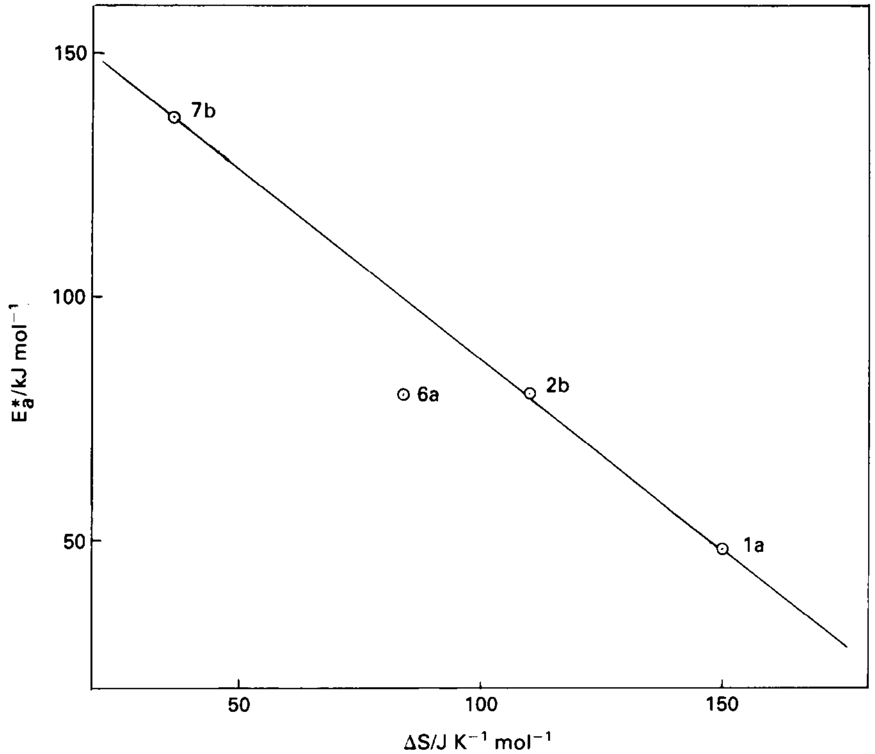

Fig. 4. Plots of E_a^* vs. ΔS for the conversions: $[Ni(Morph)Cl_2] \rightarrow [Ni(Morph)_{0.5}Cl_2]$ (**1a**); $[2CuCl_2 \cdot 2Morph] \rightarrow [2CuCl_2 \cdot Morph]$ (**2b**); $[Zn(DMP)Cl_2] \rightarrow ZnCl_2$ (**6a**); and $[Cd(DMP)_{0.5}Cl_2] \rightarrow CdCl_2$ (**7b**).

less the same as that of the free ligand [5]. The effective magnetic moment values for **4a** and **5a** also suggest tetrahedral structures (Table 1) [8, 9].

The activation energy values reported by some workers [10–12] using the Horowitz and Metzger equation for the decomposition reactions of simple salts are higher with respect to the values evaluated by the Freeman–Carroll and Coats–Redfern equations. In the present study the same observation is noticed in most of the cases (Table 2).

If we consider the order of stability with respect to activation energy, the following trend can be observed for *N*,*N*′-dimethylpiperazine complexes: Ni(II) < Cu(II) < Zn(II). But no systematic trend is apparent for *N*-methylmorpholine complexes.

Furthermore, a linear correlation is obtained on plotting the values of E_a^* against ΔS (Fig. 4) for the decomposition of the complexes, which shows that a system having a higher entropy change ΔS will require less energy E_a^* for its thermal decomposition.

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