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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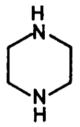
Nickel(II), zinc(II), and cadmium(II) complexes of piperazine (pipz), *N*-methylpiperazine (mpipz), and 1,4-diazacycloheptane (dach) with the compositions $[NiL_2(NCS)_2]$, $[Ni(dach)_2][SCN]_2$, $[ZnL(NCS)_2]$, $[Zn(dach)_2][SCN]_2$, $[CdL(NCS)_2]$, and $[Cd(dach)(NCS)_2]$ (L = pipz or mpipz) have been synthesised. Attempts to prepare *N,N'*-dimethylpiperazine complexes failed. Some intermediate complexes were isolated by pyrolysis. Configurational and conformational changes have been studied by elemental analyses, i.r. spectra, magnetic moment measurements, and thermal analysis. All the complexes of pipz and mpipz appear to be octahedral and those of dach to be square planar. Activation energies (E_a), enthalpy (ΔH) and entropy changes (ΔS) for the dehydration and decomposition reactions 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 nickel complexes.

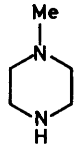
Acyclic diamines having the $N(CH_2)_nN$ grouping act as chelating agents for transition-metal ions.[1,2] Work on cyclic diamine complexes is scanty.[1,3] There has been little thermal investigation of solid cyclic diamine complexes. The main aim of our work is to synthesize some cyclic diamine (six- or seven-membered ring) complexes of transition and non-transition metals, and 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 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.

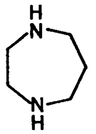
Before heating, the pipz, mpipz, and dach ligands in the Ni^{II} complexes and the dach ligand in the complexes of Zn^{II} and Cd^{II} function as bidentate chelating agents (boat form),[3–5] and in the remaining pipz and mpipz complexes of Zn^{II} and Cd^{II} the ligands are bridging and bidentate (chair form).[3,6,7] If these complexes are heated under non-isothermal conditions they decompose *via* stable intermediates in which the cyclic diamine ligands may function as bridging bidentate ligands (chair form). This kind of conformational change of the ligand (boat form ⟶ chair form) has been confirmed by the i.r. spectral data.[3,6] Thiocyanate in these complexes functions as a unidentate ligand[8] but more usually as a bridging bidentate ligand.[8–12] Parameters like 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.—All metal salts were of A.R. grade and used as received. Metal thiocyanates were freshly prepared by mixing alcoholic solutions of metal salts and potassium thiocyanate and subsequent crystallization 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.[13]


piperazine
(pipz)


N-methylpiperazine
(mpipz)


1,4-diazacycloheptane
(dach)

Preparation of the Complexes.—$[NiL_2(NCS)_2]$ (L = pipz *or* mpipz). The ligand (*ca.* 6 mmol) in dry ethanol (20 cm^3) was added with constant stirring to a dry ethanolic solution (35 cm^3) containing freshly prepared nickel thiocyanate (*ca.* 3 mmol). The blue 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 complex $[Ni(dach)_2][SCN]_2$ was prepared similarly.

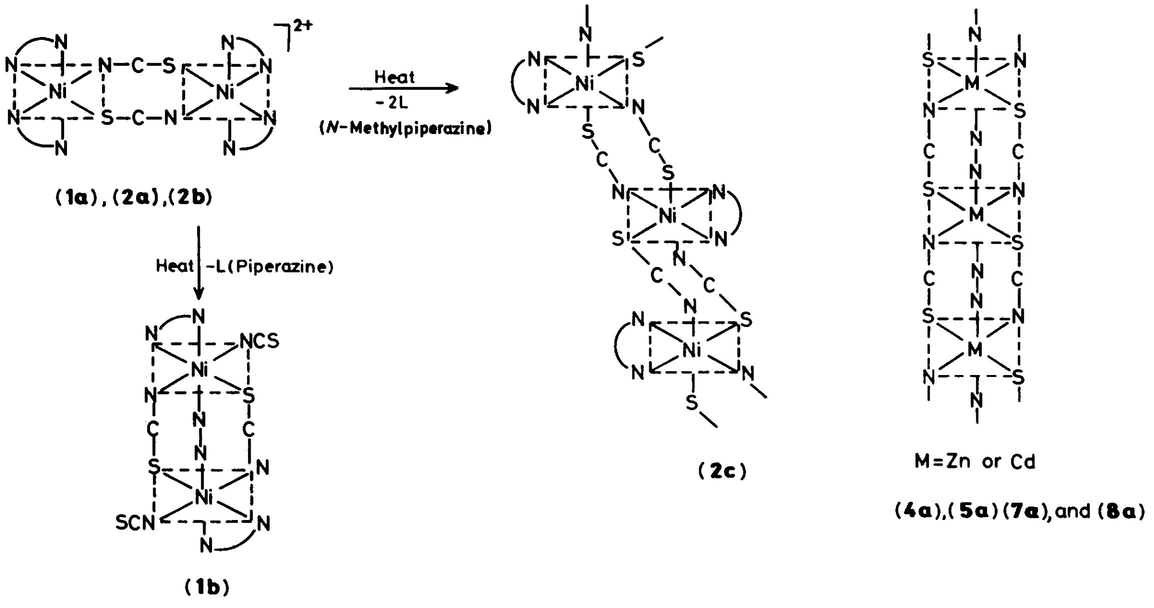
$[ZnL(NCS)_2]$ *and* $[Zn(dach)_2][SCN]_2$ (L = pipz *or* mpipz). A clear solution of freshly prepared zinc thiocyanate (*ca.* 3 mmol) in dry ethanol (35 cm^3) was treated with the ligand to give a turbid solution. An excess of the ligand in dry ethanol (20 cm^3) was then added till a clear solution was obtained. On addition of an excess of dry diethyl ether a cream precipitate of the zinc complex appeared. It was collected by filtration, washed with dry diethyl ether, and dried over fused calcium chloride in a desiccator. Yield *ca.* 40—50%.

$[CdL(NCS)_2]$ (L = pipz, mpipz, *or* dach). Freshly prepared cadmium thiocyanate (3 mmol) in dry ethanol (35 cm^3) was treated with the ligand (*ca.* 3—4 mmol in 20 cm^3 of dry ethanol) to give a white precipitate of the cadmium complex which was collected by filtration, washed with the dry ethanol followed by a little dry diethyl ether, and dried over fused calcium chloride in a desiccator. Yield *ca.* 60%.

Nickel, zinc, and cadmium were estimated gravimetrically by standard procedures,[14] C, H, and N by a Perkin-Elmer 240 C elemental analyser. Elemental analyses are given in Table 1. Thermal investigations (t.g.a. and d.t.a.) was carried out on a Shimadzu DT-30 thermal analyzer 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 Beckmann 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.

Table 1. Analytical data (calculated values in parentheses) for piperazine (L^1), *N*-methylpiperazine (L^2), and 1,4-diazacycloheptane (L^3) complexes of Ni^{II}, Zn^{II}, and Cd^{II}

		Analysis/%				
Compound	Colour	M	C	H	N	$\mu_{eff.}$
(**1a**) $[NiL^1_2(NCS)_2]$	Blue	16.9 (16.95)	34.5 (34.6)	5.80 (5.75)	24.2 (24.25)	3.26
(**1b**) $[Ni_2L^1_3(NCS)_4]$	Bluish	19.3 (19.35)	33.6 (33.6)	2.95 (2.95)	23.0 (23.05)	3.08
(**2a**) $[NiL^2_2(NCS)_2]{\cdot}2H_2O$	Bluish	14.2 (14.3)	35.1 (35.05)	6.80 (6.80)	20.4 (20.45)	3.08
(**2c**) $[Ni_2L^2_2(NCS)_4]$	Bluish	21.4 (21.35)	30.6 (30.6)	4.35 (4.35)	20.35 (20.4)	2.22
(**3a**) $[NiL^3_2][SCN]_2{\cdot}2H_2O$	Yellow	14.3 (14.3)	35.1 (35.05)	6.80 (6.80)	20.45 (20.45)	
(**4a**) $[ZnL^1(NCS)_2]{\cdot}H_2O$	White	22.8 (22.9)	25.25 (25.25)	4.20 (4.20)	19.6 (19.65)	
(**5a**) $[ZnL^2(NCS)_2]$	White	23.2 (23.2)	29.8 (29.85)	4.25 (4.25)	19.95 (19.9)	
(**6a**) $[ZnL^3_2][SCN]_2$	Cream	17.15 (17.15)	37.75 (37.75)	6.30 (6.30)	22.0 (22.05)	
(**7a**) $[CdL^1(NCS)_2]$	White	35.75 (35.75)	22.9 (22.9)	3.15 (3.20)	17.8 (17.8)	
(**8a**) $[CdL^2(NCS)_2]$	White	34.25 (34.2)	25.6 (25.6)	3.65 (3.65)	17.0 (17.05)	
(**9a**) $[CdL^3(NCS)_2]{\cdot}H_2O$	White	32.2 (32.45)	24.6 (24.25)	4.00 (4.05)	16.05 (16.15)	



Scheme.

Results and Discussion

$[Ni(pipz)_2(NCS)_2]$ (**1a**).—This complex was reported earlier by Mel'nik *et al.* [15] who found that it exists in the dimeric form. On heating, we found that it first loses one molecule of the ligand in the temperature range 200—255 °C. The corresponding d.t.a. curve shows one exotherm with a peak at 255 °C. The intermediate product $[Ni_2L_3(NCS)_4]$ (**1b**) (Scheme) is stable over the range 255—300 °C, but loses ligand in the range 300—320 °C showing two exothermic (d.t.a.) peaks at 305 and 318 °C and giving $Ni(SCN)_2$ (Figure).

The parameter E_a has been evaluated from the t.g.a. curve using Horowitz and Metzger's equation [16] and the d.t.a. curve by Borchardt and Daniels' equation.[17] The values for the conversion of complex (**1a**) into (**1b**) from the t.g.a. and d.t.a. curves are 183 and 259 kJ mol^{-1} respectively and that for the conversion of (**1b**) into $Ni(SCN)_2$ from the t.g.a. curve is 742 kJ mol^{-1}. The latter high value (Table 2) may be due to the polymeric nature[6,11,18,19] of complex (**1b**) as compared with (**1a**). For the first step, ΔH is found to be 21 kJ mol^{-1}, and ΔS, evaluated from $\Delta H/T_m$ where T_m = d.t.a. peak temperature in K,[20] is 39 J K^{-1} mol^{-1}.

In the blue dimeric complex (**1a**), the ligand functions as a chelating agent in the boat form as shown by the appearance of more i.r. bands between 700 and 1 400 cm^{-1} (Table 3) than for the free ligand which exists in the chair form.[3,6,21] Thiocyanate acts as a bridging bidentate ligand as shown by the very strong band of ν(CN) at 2 120 cm^{-1}. Complex (**1b**) has an octahedral structure as indicated by the value of its magnetic moment (Table 1) and characteristic i.r. bands showing that the ligand is both bridging bidentate and chelating (Table 3). The thiocyanate is also both bridging bidentate and terminal unidentate, as shown by the bands[4,8] at 2 140 and 2 080 cm^{-1} for ν(CN) and 480 cm^{-1} for δ(NCS). The decomposition path and structure of complexes (**1a**) and (**1b**) are given in the Scheme.

$[Ni(mpipz)_2(NCS)_2]{\cdot}2H_2O$ (**2a**).—This complex was not reported earlier. It has two molecules of lattice water as confirmed by i.r. spectral bands at 3 440, 3 260 [ν(OH)] and 1 670 cm^{-1} [δ(HOH)]. Further the weight loss in the t.g.a. curve of complex (**2a**) in the range 100—140 °C and the endothermic peak (d.t.a.) at 130 °C (Table 2) correspond to two molecules of lattice water. The complex is expected to be dimeric[12,18] like complex (**1a**). The anhydrous complex $[Ni(mpipz)_2(NCS)_2]$ (**2b**) is converted into $Ni(SCN)_2$ *via* the formation of $[Ni(mpipz)(NCS)_2]$ (**2c**) in two steps in the ranges 140—210 and 210—290 °C respectively. The corresponding d.t.a. curve

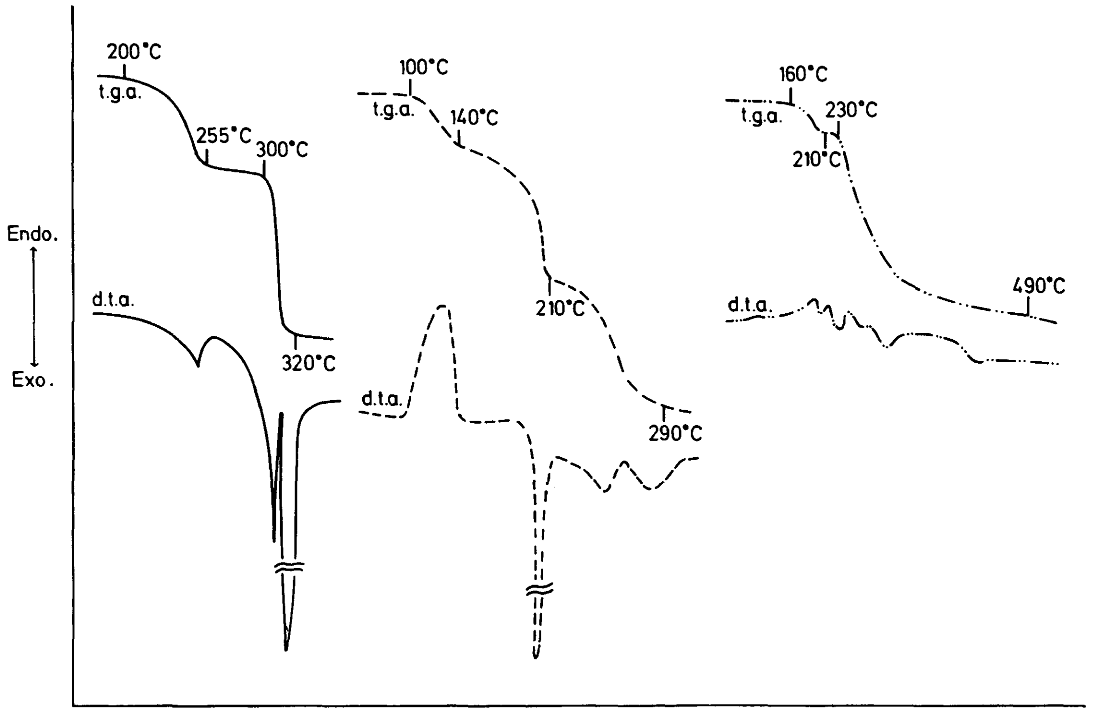


Figure. Thermal decomposition curves of 12.26 mg $[Ni(pipz)_2(NCS)_2]$ (——), 12.71 mg $[Ni(mpipz)_2(NCS)_2]\cdot 2H_2O$ (— — —), and 9.68 mg $[Ni(dach)_2][SCN]_2\cdot 2H_2O$ (— · · — · · —)

Table 2. Thermal parameters of cyclic diamine complexes of Ni^{II}, Zn^{II}, and Cd^{II} (ligands as in Table 1)

Decomposition reaction	Temperature range (°C)	Peak temperature (°C)		E_a/kJ mol^{-1}		ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
		Endo.	Exo.	t.g.a.	d.t.a.		
$[NiL^1_2(NCS)_2] \longrightarrow [NiL^1_{1.5}(NCS)_2]$	200—255		255	183	259	21	39
$[NiL^1_{1.5}(NCS)_2] \longrightarrow Ni(SCN)_2$	300—320		305, 318	742		61, 206	106, 349
$[NiL^2_2(NCS)_2]\cdot 2H_2O \longrightarrow [NiL^2_2(NCS)_2]$	100—140	130		172	144	112	278
$[NiL^2_2(NCS)_2] \longrightarrow [NiL^2(NCS)_2]$	140—210		210	82		71	147
$[NiL^2(NCS)_2] \longrightarrow Ni(SCN)_2$	210—290		250, 285	138	146	27, 46	52, 82
$[NiL^3_2][SCN]_2\cdot 2H_2O \longrightarrow [NiL^3_2][SCN]_2$	160—210	195		183			
cis-$[NiL^3_2][SCN]_2 \longrightarrow$ *trans*-$[NiL^3_2][SCN]_2$	210—230	220					
trans-$[NiL^3_2][SCN]_2 \longrightarrow Ni(SCN)_2$	230—490	247	300, 430	42			
$[ZnL^1(NCS)_2]\cdot H_2O \longrightarrow [ZnL^1(NCS)_2]$	120—220	150		18		14	
$[ZnL^1(NCS)_2] \longrightarrow Zn(SCN)_2$	240—440	280	300	75			
$[ZnL^2(NCS)_2] \longrightarrow [ZnL^2_{0.5}(NCS)_2]$	60—169	160		39	203	64	147
$[ZnL^2_{0.5}(NCS)_2] \longrightarrow Zn(SCN)_2$	169—400		250, 335	99			
$[ZnL^3_2][SCN]_2 \longrightarrow [ZnL^3(NCS)_2]$	40—227	125	170	14			
$[ZnL^3(NCS)_2] \longrightarrow Zn(SCN)_2$	227—410		255	62			
$[CdL^1(NCS)_2] \longrightarrow Cd(SCN)_2$	200—420	270	280	146			
$[CdL^2(NCS)_2] \longrightarrow [CdL^2_{0.5}(NCS)_2]$	150—260	218, 240	254	81		34	64*
$[CdL^2_{0.5}(NCS)_2] \longrightarrow Cd(SCN)_2$	260—295		285	296	186	17	30
$[CdL^3(NCS)_2]\cdot H_2O \longrightarrow [CdL^3(NCS)_2]$	140—245	236		96			
$[CdL^3(NCS)_2] \longrightarrow Cd(SCN)_2$	245—320		245	49		66	128

* For evaluation of ΔS, 527 K is considered.

shows one exothermic peak at 210 °C for the second step (Figure). In complex (**2a**) the ligand functions as a chelate and exists in the boat form [as in complex (**1a**)] while the thiocyanate acts as a bridging bidentate ligand as shown by the band[8] at 2 100 cm^{-1} (Table 3). The blue colour of the complex and its magnetic moment value indicate an octahedral structure (Scheme).

The intermediate complexes (**2b**) and (**2c**) were unstable.

Table 3. I.r. spectral data (cm^{-1}) for cyclic diamine complexes of Ni^{II}, Zn^{II}, and Cd^{II} (ligands as in Table 1)*

Compound	$\nu(NH_2)$	$\nu(CH_2)$	$\nu(CN)$	$\delta(NH_2)$	$\delta(CH_2)$	$\rho_\omega(CH_2)$	$\tau(NH_2)$ + $\rho_\omega(NH_2)$ + $\tau(CH_2)$	Stretching vibrations of skeleton $\nu(C\text{–}N)$ + $\nu(C\text{–}C)$	$\rho_\tau(CH_2)$	$\nu(CS)$	$\rho_\tau(CH_2)$ + $\nu(MN)$	$\delta(NCS)$
(1a)	3 420br 3 220s 3 200 (sh)	2 980w 2 960w 2 950 (sh) 2 940w	2 120vs	1 650br	1 455s 1 440s	1 385vs 1 350vw	1 330m 1 250w 1 130m	1 090vs 1 080 (sh) 1 020 (sh) 1 005s 990vs	940w 900w 875 (sh)	870s 800m 740vw 680w	560w	480w
(1b)	3 440br 3 240m	3 000w 2 940vw 2 920vw	2 140vs 2 080 (sh)	1 640br	1 450m 1 425m	1 390m 1 340vw	1 320w 1 250vw	1 100m 1 070s 1 015vs 995m	905w 880vs	835w 780m 720vw 650vw 600w	560w 530vw	480w
(2a)	3440vs 3260m	2 980w 2 960s 2 820 (sh) 2 810m 2 740w	2 100vs	1 670m	1 460 (sh) 1 455s 1 450m 1 440w 1 420m	1 380w 1 370m	1 300w 1 280m 1 205 (sh) 1 190vs 1 180s 1 150s	1 100s 1 040m 1 025s 1 015vw 990vs	940w 910w	870vs 785 (sh) 780s 710vw 650m	510 (sh) 500 (sh)	480w
(2b)	3 440s 3 270vw 3 250vw	2 980w 2 960s 2 900vw 2 860w 2 810m 2 780 (sh) 2 740w 2 700vw	2 130 (sh) 2 100vs	1 670br 1 520w 1 510w	1 450vs 1 440w 1 420m	1 380w 1 370m	1 320w 1 305vw 1 280m 1 200 (sh) 1 190vs 1 180s 1 150vs	1 105s 1 040m 1 025s 1 015 (sh) 990vs	940 (sh) 915m 870s	790 (sh) 780ms 710br 650m	585vw 520 (sh) 500m	475w
(2c)	3 440br 3 230m	2 960m 2 740 (sh) 2 720m 2 700 (sh)	2 170w 2 110vs	1 620br	1 460 (sh) 1 450vs 1 430w 1 420w	1 370vw 1 340vw	1 320vw 1 270w 1 210vw 1 200vw 1 180vw 1 150 (sh)	1 120s 1 105w 1 070vw 1 050vw 1 030w 1 000m	980vs 900w 880 (sh) 865vs	840vw 815vw 775m 770 (sh) 730vw 700vw 670vw 650w 620w	580w 550w 520w	480m 470w
(3a)	3 460br 3 160vs	2 950w 2 918w 2 878w	2 050vs	1 640w 1 610w 1 590br 1 550m 1 530w	1 490vw 1 460 (sh) 1 450 (sh) 1 440vs 1 430 (sh) 1 420 (sh)	1 385w 1 375w 1 360vs 1 350 (sh) 1 335vw	1 310 (sh) 1 300 (sh) 1 290vs 1 270 (sh) 1 240m 1 235 (sh) 1 220m	1 134vs 1 128 (sh) 1 115s 1 100 (sh) 1 060vs 1 020w	980vs 960 (sh) 950 (sh) 940w 920vw 900 (sh) 890ms 880 (sh) 860vw	845ms 830vw 780vs 755ms 720vw 660vw 645 (sh) 633ms	600w 550ms 540 (sh) 530w	495vw 470ms
(4a)	3 450br 3 130m	2 990vw 2 950w 2 940 (sh) 2 860w	2 100vs	1 570m	1 450vs 1 430m	1 390w 1 380w 1 360w	1 335m 1 265m 1 150vs	1 085s 1 025s 1 000w 995w	950w 895m 885 (sh)	870vs 830m 670w	565vw 550vw 525w 505vw	490 (sh) 475m
(5a)	3 450br 3 240vs	2 980s 2 940w 2 920 (sh) 2 860w 2 840vw	2 100 (sp) 2 040 (sh)	1 650w	1 460 (sh) 1 445s 1 430vs	1 375w	1 330w 1 250m	1 095vs 1 070 (sh) 1 055vs 1 010vs	940w 910w	895w 880 (sh) 875vs 770w 635w	575vw 550br	470m 460m
(6a)	3 500br 3 240vs 3 230 (sh)	2 960w 2 924m 2 920 (sh) 2 900vw 2 860w	2 100vs	1 690w 1 670vw 1 650w 1 630vw 1 610vw 1 550s 1 520m	1 465w 1 460m 1 450w 1 440ms 1 430vw 1 425vw 1 415vw	1 365m 1 345vw	1 335vw 1 325vw 1 310vw 1 290vw 1 275 (sh) 1 260vw 1 240w 1 210m 1 135vs 1 125 (sh)	1 095vs 1 080vs 1 070 (sh) 1 060vw 1 040vs 1 020 (sh)	990 (sh) 980vs 960w 930vs 910vw	860w 840vs 830 (sh) 770w 745w	590w 570vw 550vw 540w 530 (sh) 510vw	490vw 465m 455m
(7a)	3 480br 3 240s	2 980s 2 940m 2 900 (sh) 2 860m 2 840 (sh)	2 100vs 2 060 (sh)	1 670 (sh) 1 620 (sh) 1 590 (sh) 1 560br	1 445s 1 430ms	1 375w 1 345vw	1 330m 1 250ms	1 095s 1 070 (sh) 1 050s 1 010vs	990s 940w 910w	890 (sh) 885 (sh) 875s 765m 635m	550vw 520vw	470ms 455ms

Table 3 (*continued*)

Compound	ν(NH_2)	ν(CH_2)	ν(CN)	δ(NH_2)	δ(CH_2)	$\rho_\omega(CH_2)$	$\tau(NH_2)$ + $\rho_\omega(NH_2)$ + $\tau(CH_2)$	Stretching vibrations of skeleton ν(C–N) + ν(C–C)	$\rho_\tau(CH_2)$	ν(CS)	$\rho_\tau(CH_2)$ + ν(MN)	δ(NCS)
(8a)	3 460br	3 000vw	2 110vs	1 690vw	1 470m	1 370w	1 330vw	1 100m	995w	890m	530w	470w
	3 250m	2 980m	2 060 (sh)	1 670vw	1 455m	1 355vw	1 280w	1 045 (sh)	950s	840s		460 (sh)
		2 950vw		1 640vw	1 440m		1 180w	1 040w	910 (sh)	780m		
		2 930vw		1 620br	1 415w		1 145w	1 015m		770w		
		2 870vw								650w		
(9a)	3 460br	2 940m	2 075vs (sp)	1 550s	1 475 (sh)	1 370w	1 300br	1 060vw	980 (sh)	880vw	550br	475m
	3 230br	2 860w		1 520w	1 450m	1 360w	1 290 (sh)	1 050br	975 (sh)	855vw	520br	
				1 515 (sh)	1 420ms	1 340 (sh)	1 270 (sh)	1 040vw	970 (sh)	830w		
				1 490w			1 250 (sh)	1 020w	965m	800w		
							1 230w		960 (sh)	785 (sh)		
							1 145w		910vw	780w		
							1 130w		900vw			
							1 115w					
							1 110vw					

* For complexes containing H_2O molecules bands for ν(NH_2) and δ(NH_2) overlapped with ν(OH) and δ(HOH), respectively, in some cases. vs = very strong, s = strong, m = medium, br = broad, w = weak, sh = shoulder, and sp = split.

However, they could be isolated at 140 and 210 °C respectively by keeping the rate of heating at 1 °C min^{-1} in the respective temperature ranges. In both the complexes the ligand exists in the boat form[3-5] as shown by the i.r. spectral data (Table 3) and the probable structures are shown in the Scheme.

The values of E_a for the conversions **(2a)** $\longrightarrow$ **(2b)**, **(2b)** $\longrightarrow$ **(2c)**, and **(2c)** $\longrightarrow$ $Ni(SCN)_2$ are shown in Table 2. Complex **(1a)** is more stable than **(2a)**; N-alkylation* of the ligand might have been expected to increase stability due to the increased basicity but this is offset by steric effects.[22-26]

$[Ni(dach)_2][SCN]_2 \cdot 2H_2O$ **(3a)**.—This complex was not reported earlier. It is yellow, diamagnetic, and has a planar geometry. A purple complex (expected to be a tris complex[2] and existing in solution) was observed when the bluish filtrate obtained from the separation of complex **(3a)** was treated with an excess of the ligand but it could not be isolated. Complex **(3a)** has two molecules of lattice water as in **(2a)**. After dehydration it is converted into $[Ni(dach)_2][SCN]_2$ **(3b)**. The latter undergoes a transition in the range 210—230 °C (Figure) and then is converted into $Ni(SCN)_2$ in a single step between 230 and 490 °C. As the dehydration peak and the peak for *cis* $\longrightarrow$ *trans* transformation merge it is not possible to evaluate ΔH and ΔS for each step.

In complex **(3a)** the ligand (dach) functions as a chelate in the boat conformation[3,5] and as shown by the i.r. data (Table 3). I.r. evidence suggests that the complex has the *cis* configuration.[26-33] The transition at 220 °C in the d.t.a. curve where there is no weight loss in the t.g.a. curve could then correspond to a change to a *trans* structure.[34]

$[Zn(pipz)(NCS)_2] \cdot H_2O$ **(4a)** *and* $[Cd(pipz)(NCS)_2]$ **(7a)**.—These complexes were reported by Grecu *et al.*[35] Our thermal investigation has confirmed that the lattice water in **(4a)** (Tables 2 and 3) is lost in the range 120—220 °C. The decompositions of $[Zn(pipz)(NCS)_2]$ **(4b)** and $[Cd(pipz)(NSC)_2]$ **(7a)** into the corresponding metal thiocyanates take place in single steps as reflected by the t.g.a. curves in the ranges 240—440 and 200—420 °C respectively but their d.t.a. curves show multiple peaks (Table 2).

In complexes **(4a)** and **(7a)** both piperazine (in the chair form) and thiocyanate are bridging bidentate[3,6,7] as indicated by their i.r. spectral bands (Table 3). They are probably polymeric[3,6,18,19,36,37] as shown in the Scheme.

$[Zn(mpipz)(NCS)_2]$ **(5a)** *and* $[Cd(mpipz)(NCS)_2]$ **(8a)**.—These white complexes were not reported earlier. Both decompose *via* the intermediates $[ZnL_{0.5}(NCS)_2]$ **(5b)** and $[CdL_{0.5}(NCS)_2]$ **(8b)** in the ranges 60—169 and 150—260 °C in t.g.a. and their corresponding d.t.a. curves show a single endothermic peak at 160 °C, and two endothermic peaks at 218 and 240 °C and one exothermic peak at 254 °C respectively. Complexes **(5b)** and **(8b)** decompose into the corresponding metal thiocyanates in the ranges 169—400 and 260—295 °C. The structures of complexes **(5a)** and **(8a)** are probably similar to those of **(4a)** and **(7a)** (Scheme).

$[Zn(dach)_2][SCN]_2$ **(6a)** *and* $[Cd(dach)(NCS)_2] \cdot H_2O$ **(9a)**.—These complexes were not reported earlier. The former is cream while the latter is white with one molecule of lattice water. Complex **(6a)** after losing one ligand molecule in the range 40—227 °C is converted into $[Zn(dach)(NCS)_2]$ **(6b)**. Complex **(9a)** loses its water molecule in a single step (140—245 °C) and is converted into $[Cd(dach)(NCS)_2]$ **(9b)**. Complexes **(6b)** and **(9b)** decompose into their corresponding metal thiocyanates in a single step in the ranges 227—410 and 245—320 °C respectively and the corresponding d.t.a. peak (exothermic) appears at 255 and 245 °C respectively. The i.r. spectral data (Table 3) show that the ligand (dach) in complexes **(6a)** and **(9a)** acts as a bidentate chelate in the boat form.[3-5] Further, these complexes may exist in the *cis* configuration.[1,27-33] Both may be similar in structure to complex **(3a)**.

If we consider the activation energy (evaluated from the t.g.a. curves), the order of stability of the complexes follows the trend pipz > mpipz > dach (Table 2). Further, a linear correlation is observed upon plotting E_a *versus* ΔS for the decomposition reactions of the pipz and mpipz complexes of Ni^{II}. A system having a higher entropy change will require less energy, E_a, for its thermal decomposition.[20]

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* The same trend is also observed in complexes of Zn^{II} and Cd^{II} (Table 2).

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