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Thermal Investigation and Stereochemical Studies of some Cyclic Diamine Complexes of Nickel(II) in the Solid State

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Abstract

Nickel(II) complexes of piperazine (pipz) and *N*-methylpiperazine (*N*-Mepipz) have been prepared. These complexes having the composition $[NiL_2(NCSe)_2]\cdot 2H_2O$ (L = pipz and *N*-Mepipz) appear to possess O_h symmetry and have been characterized by elemental analyses, IR spectral and magnetic moment data, conductivity measurement and thermal analyses in the solid state. An attempt to prepare the *N,N'*-dimethylpiperazine complex of nickel(II) failed. Stereochemical studies have been made with the help of IR spectral and magnetic moment data. Thermodynamic parameters like activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS) for each step of the dehydration and decomposition reactions of the complexes are evaluated by using some standard methods. Probable mechanistic paths of decomposition reactions have been proposed. The order of stability of the complexes (with respect to DTA peak temperatures) follows the trend pipz > *N*-Mepipz. A linear correlation between E_a^* and ΔS for the decomposition reactions of the complexes has been found.

Introduction

Works on acyclic diamine complexes are well known in the literature but works on cyclic diamine complexes are fewer [1, 2]. Recently, we reported the thermal investigation and stereochemical studies of some cyclic diamine complexes of nickel(II), zinc(II), and cadmium(II) in the solid state [3] in which only thiocyanato complexes were studied. Our present paper reports the thermal and stereochemical studies of selenocyanato complexes of nickel(II) which were not reported earlier [4–13]. It is observed that these complexes might be dimeric [3, 14]; the cyclic ligands function as bidentate chelating agents (boat form) [2, 3, 15, 16] and selenocyanate functions as a bridging bidentate ligand (see Table II) [17] in addition to its existence as ions outside the coordination sphere as supported by molar conductance data [18]. Some thermodynamic parameters like E_a^*, ΔH and ΔS for the dehydration and decomposition reactions of the complexes in the solid state have been calculated (Table I) and some useful conclusions like thermal stability and effect of *N*-alkylation of the ligand upon the complexes have been drawn.

Experimental

Materials and Methods

AR grade nickel(II) chloride hexahydrate and potassium selenocyanate were used as received. Piperazine obtained from Merck (F.R.G.), *N*-methylpiperazine and *N,N'*-dimethylpiperazine from Fluka AG, Switzerland were used as received. Diethylether and ethanol were dried using standard procedures [19]. AR grade dimethyl sulphoxide was used as received.

Preparation of the Complexes $[NiL_2(NCSe)_2]\cdot 2H_2O$ *(L = pipz or N-Mepipz)*

Nickel selenocyanate in solution was prepared by treating a solution of the crystalline nickel(II) chloride (*ca.* 3 mmol) in 30 cm^3 of dry ethanol with a solution of potassium selenocyanate (*ca.* 6 mmol) in the same solvent (30 cm^3) and separating the precipitate of potassium chloride by filtration. The filtrate containing nickel selenocyanate was immediately treated with 20 cm^3 of dry ethanolic solution of the ligand (*ca.* 6 mmol) when a bluish precipitate of the complex appeared. The complex was collected by filtration in suction, washed with dry ethanol followed by a little dry ether and dried over fused calcium chloride in a desiccator. (Yield ~ 70%).

Nickel was estimated gravimetrically using a standard procedure [20]. C, H and N were determined on a Perkin-Elmer 240 C elemental analyser. *Anal.* Found: Ni, 12.11; C, 25.00; H, 5.01; N, 17.56. Calc. for $[Ni(pipz)_2(NCSe)_2]\cdot 2H_2O$: Ni, 12.32; C, 25.18; H, 5.04; N, 17.62%. Found: Ni, 11.54; C, 28.51; H, 5.51; N, 16.52. Calc. for $[Ni(N\text{-}Mepipz)_2(NCSe)_2]\cdot 2H_2O$: Ni, 11.63; C, 28.54; H, 5.55; N, 16.65%.

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TABLE I. Thermal Parameters of Cyclic Diamine Complexes of Ni(II)[a]

		Decomposition reaction	Temperature range (℃)	DTA peak temperature (℃)		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)	$[NiL_2(NCSe)_2]\cdot 2H_2O \rightarrow [NiL_2(NCSe)_2]$	30–180	110		23.08	40.03	60.95	159.27
	(b)	$[NiL_2(NCSe)_2] \rightarrow [NiL(NCSe)_2]$	180–204	195		330.27		27.38	57.69
	(c)	$[NiL(NCSe)_2] \rightarrow Ni(SeCN)_2$	204–360		344	33.62	53.17	995.20	1612.65
2	(a)	$[NiL'_2(NCSe)_2]\cdot 2H_2O \rightarrow [NiL'_2(NCSe)_2]$	100–135	125		131.49	150.28	42.90	107.79
	(b)	$[NiL'_2(NCSe)_2] \rightarrow [NiL'(NCSe)_2]$	135–156	152		474.06	257.09	18.87	44.40
	(c)	$[NiL'(NCSe)_2] \rightarrow Ni(SeCN)_2$	156–260		185, 245	100.77	199.97	38.80	74.90[b]

[a] L = piperazine, L′ = *N*-methylpiperazine. [b] 245 ℃ (518 K) is used.

TABLE II. IR Spectral Data[a] (cm^{-1}) of Ni(II) Cyclic Diamine Complexes

Compound[b]	$\nu(NH_2)$ + $\nu(OH)$	$\nu(CH_2)$	$\nu(CN)$	$\delta(NH_2)$ + $\delta(HOH)$	$\delta(CH_2)$	$\rho_\omega(CH_2)$	$\tau(NH_2)$ + $\rho_\omega(NH_2)$ + $\tau(CH_2)$	$\nu(C-N)$ + $\nu(C-C)$ (Skeleton)	$\rho_r(CH_2)$ + $\rho_r(NH_2)$	$\nu(CSe)$[c]	$\nu(MN)$[c] + $\nu(MSe)$	$\delta(NCSe)$
(1a) $[NiL_2(NCSe)_2]\cdot 2H_2O$	3400(br)	2970(s)	2340(w)	1660(sh)	1450(s)	1385(vw)	1330(w)	1090(vs)	900(sh)	700(sh)	520(br)	430(w)
	3200(vs)	2942(s)	2120(vs)	1650(s)	1430(s)	1370(vw)	1290(vw)	1010(s)	870(vs)	640(br)	470(sh)	370(w)
		2860(w)	2020(sh)	1610(s)	1400(sh)	1350(vw)	1250(w)	990(vs)	820(vw)	520(br)		290(sh)
				1500(w)			1180(vw)		750(sh)			255(w)
							1120(sh)					230(sh)
							1115(sh)					210(m)
(2a) $[NiL'_2(NCSe)_2]\cdot 2H_2O$	3420(vs)	2980(w)	2240(br, sp)	1670(s)	1450(vs)	1380(w)	1330(sh)	1100(vs)	870(w)	710(w)	510(sh)	450(m)
	3260(w)	2900(sh)	2210(w)	1640(sh)	1440(w)	1370(vs)	1320(m)	1040(s)	810(vw)	650(ms)	500(s)	435(sh)
		2880(vw)	2100(vs)	1560(vw)	1420(vs)		1300(m)	1020(vs)	780(vs)	610(w)	480(sh)	410(vs)
		2840(sh)	2060(sh)		1400(sh)		1280(s)	1015(sh)		600(sh)		365(w)
		2820(w)					1205(w)	990(vs)		510(sh)		305(w)
		2790(sh)					1190(vs)	915(ms)		500(s)		285(sh)
		2740(vw)					1180(m)					270(sh)
							1145(vs)					260(m)
												220(m)

[a] vs = very strong, s = strong, ms = medium strong, m = medium, br = broad, w = weak, vw = very weak, sh = shoulder and sp = splitted. [b] L = piperazine, L′ = *N*-methylpiperazine. [c] Some overlapping spectral bands are given.

The thermal investigation (TG and DTA) was carried out on Shimadzu DT-30 thermal analyser under nitrogen atmosphere with the heating rate of 10 °C min^{-1} for the piperazine complex and 5 °C min^{-1} for the *N*-methylpiperazine complex using α-Al_2O_3 as a standard. Indium metal was used as a calibrant for the evaluation of enthalpy changes. Infrared spectra were recorded with a Perkin-Elmer 783 IR spectrometer in KBr medium. The effective magnetic moments were evaluated from the values of magnetic susceptibilities measured with an EG and G PAR 155 vibrating sample magnetometer at room temperature. Conductivity measurements of the complexes were done in DMSO at a concentration of 10^{-3} M at 22 °C with the Conductivity Bridge 305, Systronics (India), using a dip-type cell.

Results and Discussion

[Ni(pipz)$_2$(NCSe)$_2$]·2H$_2$O (1a)

Complex **1a** was not reported earlier. It has a very light blue colour and its lattice water was confirmed by the appearance of IR spectral bands at 3400, 3200 and 1660, 1650, 1610 cm^{-1} for ν(OH) and δ(HOH) respectively (Table II). Further, the weight loss in the TG curve of **1a** in the temperature range 30–180 °C and the endothermic peak in the DTA curve at 110 °C (Fig. 1) correspond to two molecules of lattice water (Table I). The anhydrous complex $[Ni(pipz)_2(NCSe)_2]$ (**1b**) is converted into $Ni(SeCN)_2$ under non-isothermal conditions via the formation of an intermediate $[Ni(pipz)(NCSe)_2]$ (**1c**) in two steps 1(b) and 1(c) in the ranges 180–204 and 204–360 °C respectively (Table I and Fig. 1). The DTA curve of complex **1a** shows an endothermic peak at 195 °C for step 1(b) and another exothermic peak at 344 °C for step 1(c). Intermediate complexes **1b** and **1c** were very unstable and could not be isolated.

E_a* has been evaluated from the TG curve by using the equation of Horowitz and Metzger [21] and from the DTA curve using that of Borchardt and Daniels [22]. The values of E_a* for the conversions of the complexes **1a** → **1b**, **1b** → **1c** and **1c** → $Ni(SeCN)_2$ from the TG and DTA** curves are 23.08 (40.03), 330.27 and 33.62 (53.17) kJ mol^{-1} respectively (Table I).

ΔH has been evaluated from the DTA curves using the relation, $\Delta H = KA$, where K is the heat transfer coefficient (cell constant, here the cell is a platinum crucible) and A is the total area under the particular DTA curve [22, 23]. Values of ΔH for the steps 1(a), 1(b) and 1(c) are 60.95, 27.38 and 995.20 kJ mol^{-1} respectively. ΔS has been calculated from the relation, $\Delta S = \Delta H/T_m$, where T_m is the DTA peak temperature in kelvin [24]. ΔS values for the steps 1(a), 1(b) and 1(c) are found to be 159.27, 57.69 and 1612.65 J K^{-1} mol^{-1} respectively.

The bluish colour and the value of the magnetic moment (μ_{eff} = 3.36 BM) of **1a** show that this complex has an octahedral configuration. In this

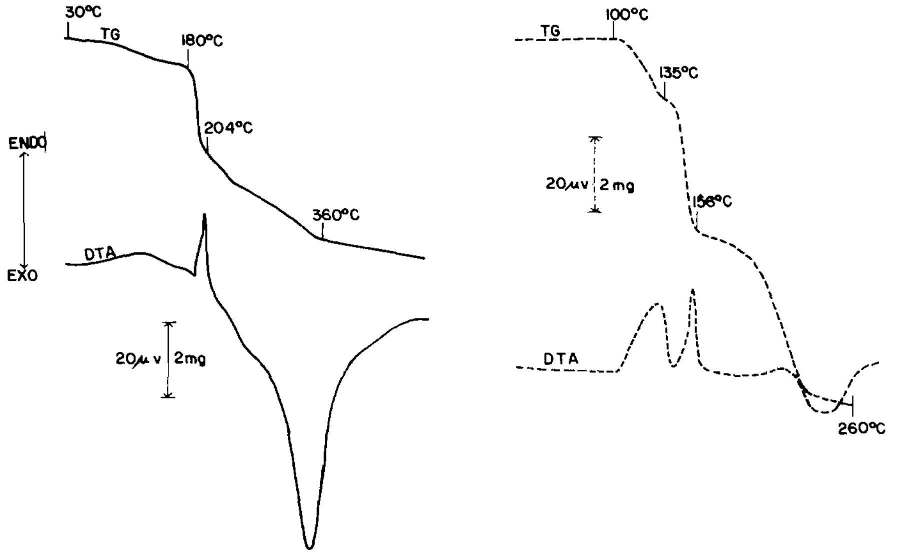
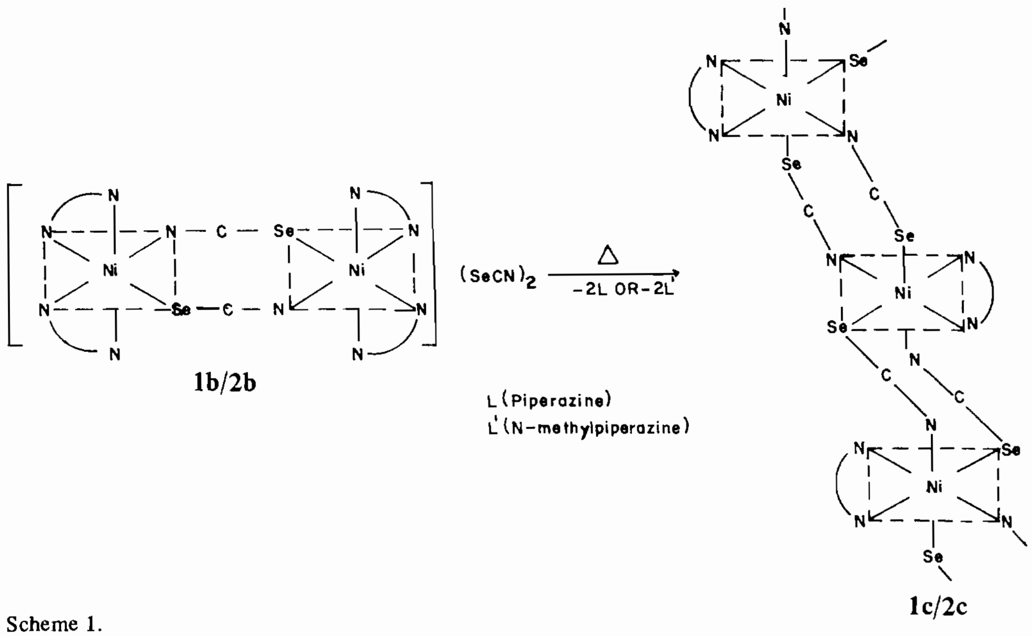


Fig. 1. Thermal curves of $[Ni(pipz)_2(NCSe)_2]\cdot 2H_2O$ (——), sample mass 12.40 mg and $[Ni(N\text{-}Mepipz)_2(NCSe)_2]\cdot 2H_2O$ (– – –), sample mass 19.50 mg.

**Values of E_a* from the DTA curve are given in parentheses.



Scheme 1.

complex, piperazine (ligand) may exist in the boat form which is evidenced by the increase in the number of IR bands between 700–1400 cm^{-1} (Table II) with respect to the number of IR bands of the free ligand which exists in the chair form [2, 25, 26]. In this case, selenocyanate may function as a bridging bidentate ligand as shown by the IR bands (Table II) [17] and the molar conductance value of the complex (Λ_m = 235.16 ohm^{-1} cm^2 mol^{-1} at 22 °C) indicates the existence of two selenocyanate ions outside the coordination sphere [18]. From the thermal investigation, IR spectral studies and the molar conductance value it may be expected that **1a** exists in the dimeric form like that of [Ni(pipz)$_2$(NCS)$_2$] [3, 14]. The probable path of decomposition of complex **1b** to **1c** is given in Scheme 1.

*[Ni(N-Mepipz)$_2$(NCSe)$_2$]·2H$_2$O (**2a**)*

Complex **2a** was not reported earlier. It is blue in colour and has two molecules of lattice water which are confirmed by the appearance of IR spectral bands at 3420, 3260 and 1670 cm^{-1} of ν(OH) and δ(HOH) respectively. Further, the presence of two molecules of lattice water is also shown by the corresponding weight loss in the TG curve of this complex in the range 100–135 °C and an endothermic peak in the corresponding DTA curve at 125 °C (Fig. 1 and Table I). The anhydrous complex [Ni(N-Mepipz)$_2$(NCSe)$_2$] (**2b**) is converted into Ni(SeCN)$_2$ by heating, via the formation of an intermediate complex [Ni(N-Mepipz)(NCSe)$_2$] (**2c**) in the steps 2(b) and 2(c) in the temperature ranges 135–156 and 156–260 °C respectively (Fig. 1 and Table I). During the transformation of **2a** into the complexes **2b** and **2c**, the corresponding DTA curve shows one endothermic peak at 152 °C for step 2(b) and two other exothermic peaks at 185 and 245 °C (prominent) for step 2(c) (Fig. 1). The intermediate complexes **2b** and **2c** could not be isolated.

E_a* values for the transformations of the complexes **2a** → **2b**, **2b** → **2c** and **2c** → Ni(SeCN)$_2$ from the TG and DTA** curves are 131.49 (150.28), 474.06 (257.09) and 100.77 (199.97) kJ mol^{-1} respectively. ΔH values for the steps 2(a), 2(b) and 2(c) are 42.90, 18.87 and 38.80 kJ mol^{-1} respectively while ΔS values are 107.79, 44.40 and 74.90 J K^{-1} mol^{-1} respectively (Table I).

Complex **2a** has the octahedral configuration as shown by the blue colour and the value of the magnetic moment (μ_{eff} = 3.14 BM). It may exist in the dimeric form like complex **1a** [14, 27, 28]. IR spectral data show that the ligand (N-Mepipz) functions as a bidentate chelating agent and exists in the boat form as in **1a** while selenocyanate functions as a bridging bidentate ligand. The molar conductance value (Λ_m = 225 ohm^{-1} cm^2 mol^{-1}) also shows that the two selenocyanate ions are present outside the coordination sphere as in **1a**.

The probable structures of **2b** and **2c** are given in Scheme 1.

In the DTA curves of **1a** and **2a**, there appears one endotherm each, with the peak at 195 and 152 °C respectively, for the liberation of the first molecule of the ligand. Further, each endotherm covers a smaller area as compared with that of the liberation of the second molecule of the cyclic ligand (Fig. 1). The reduction of the area of the first endotherm (steps 1(b) and 2(b)) might be due to the liberation

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**Values are in parentheses.

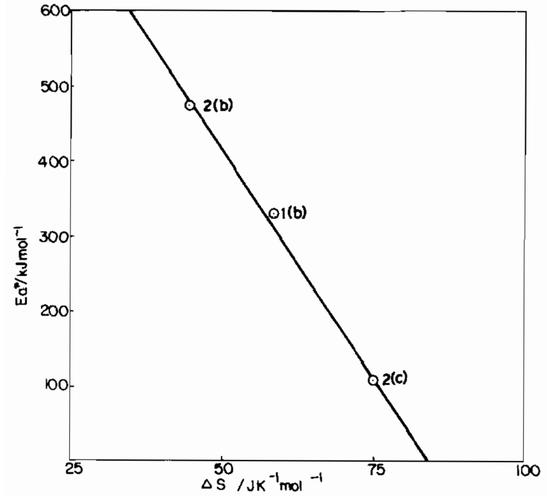

Fig. 2. Plots of E_a* *vs.* ΔS for the conversion of [Ni(*N*-Mepipz)$_2$(NCSe)$_2$] → [Ni(*N*-Mepipz)(NCSe)$_2$] 2(b), [Ni(pipz)$_2$(NCSe)$_2$] → [Ni(pipz)(NCSe)$_2$] 1(b) and [Ni(*N*-Mepipz)(NCSe)$_2$] → Ni(SeCN)$_2$ (2c).

of much heat (dissociation energy) for the escaping of the first ligand molecule from the complex.

If the DTA peak temperatures are compared, the order of stability of the complexes follows the trend pipz > *N*-Mepipz (Table I), though *N*-alkylation increases the basicity of the cyclic ligand stability decreases here due to steric effect [29, 30].

A linear correlation is observed when values of E_a* *versus* ΔS for the decomposition reactions of piperazine and *N*-methylpiperazine complexes are plotted (Fig. 2). It is seen that a system having a higher entropy change will require less activation energy for its thermal decomposition [24].

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