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SOLID STATE THERMAL STUDIES OF NICKEL(II) DIAMINE COMPLEXES

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ABSTRACT

The complexes $[Ni(eten)_3]X_2 \cdot H_2O$ (eten = *N*-ethyl-1,2-ethanediamine; X = Cl, Br), $[Ni(eten)_3]X_2$ (X = BF_4, NO_3, $0.5SO_4$, $0.5SeO_4$), $[Ni(eten)_2X_2] \cdot 2H_2O$ (X = Cl, Br) and $[Ni(meen)_3]X_2 \cdot 2H_2O$ (meen = *N*-methyl-1,2-ethanediamine; X = $0.5SO_4$, $0.5SeO_4$) have been synthesized from solution and their thermal investigation carried out in the solid state. $[Ni(eten)_3]Br_2$, $[Ni(eten)_2X_2]$ (X = Cl, Br, $0.5SO_4$, $0.5SeO_4$), $[Ni(eten)Cl_2]$, $Ni(eten)_{0.5}Cl_2$ and $[Ni(meen)_2X_2]$ (X = $0.5SO_4$, $0.5SeO_4$) were isolated in the solid state from their corresponding parent complexes by a pyrolytic technique. Upon heating, $[Ni(eten)_2X_2]$ (X = Cl, Br) and $[Ni(eten)_3](BF_4)_2$ undergo endothermic, kinetically irreversible phase transition, whereas $[Ni(meen)_3]SeO_4$ undergoes exothermic irreversible phase transition. The phase transition phenomena are assumed to be due to conformational changes in the diamine chelate rings. All the complexes except $Ni(eten)_{0.5}Cl_2$ have octahedral geometry. $Ni(eten)_{0.5}Cl_2$ has an unusually high magnetic moment.

INTRODUCTION

Various studies of the thermally-induced isomerization as well as decomposition of nickel(II) diamine complexes have been reported [1–11]. The conformational changes we have observed for some five/six-membered diamine complexes with variation of temperature seem to have interesting solid state chemistry [5,7–11]. In a recent report on *N*-methyl-1,2-ethanediamine (meen) complexes of nickel(II) [9], we observed a substantial change in thermal behaviour as compared with that of 1,2-ethanediamine [4,5] and substituted 1,2-ethanediamine [6–9] nickel(II) complexes. For an investigation of the effect of substitution, thermal studies of *N*-ethyl-1,2-ethanediamine (eten) complexes of NiX_2 (X = Cl, Br, BF_4, NCS, NO_3, $0.5SO_4$,

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$0.5SeO_4$) may be considered as an essential complement to these results. Our earlier paper [9] did not report on thermal studies of NiX_2 ($X = 0.5SO_4$, $0.5SeO_4$) with meen. These anions (SO_4^{2-} and SeO_4^{2-}) have shown novel behaviour with other diamines [7,11]. Studies of meen complexes of $NiSO_4/SeO_4$ have therefore been included in the present work.

EXPERIMENTAL

All the chemicals employed were AnalaR grade. The diamines were purchased from Fluka and used as received. The instruments used for recording IR (at and above ambient temperature), elemental analyses, electronic spectra (mull), magnetic susceptibility, X-ray powder diffraction and thermal parameters (TG, DSC and DTA) were as described in an earlier report [9].

Preparation of the complexes

$[Ni(eten)_3]Cl_2 \cdot H_2O$ (**1**), $[Ni(eten)_3]Br_2 \cdot H_2O$ (**2**), $[Ni(eten)_3](BF_4)_2$ (**3**), $[Ni(eten)_2(NCS)_2]$ (**4**) and $[Ni(eten)_3](NO_3)_2$ (**5**) were prepared by adding eten (3–4 mmol) dropwise with stirring to the corresponding nickel(II) salts (1 mmol) in ethanolic medium. Complexes (**1**), (**2**) and (**4**) separated immediately from the mixture, as fine crystalline compounds. Complexes (**3**) and (**5**) separated out when the resulting mixtures were kept in a desiccator for ca. 48 h. All the complexes were filtered and washed with dry ethanol.

$[Ni(eten)_3]SO_4$ (**6**), $[Ni(eten)_3]SeO_4$ (**7**), $[Ni(meen)_3]SO_4 \cdot 2H_2O$ (**8**) and $[Ni(meen)_3]SeO_4 \cdot 2H_2O$ (**9**) were synthesized according to a previously reported method [12].

$[Ni(eten)_2Cl_2] \cdot 2H_2O$ (**1b**) and $[Ni(eten)_2Br_2] \cdot 2H_2O$ (**2d**) were prepared by adding eten (2 mmol) to the corresponding nickel(II) salts (1 mmol) in ethanolic medium. The complexes separated immediately, as crystalline compounds, and were then washed with ethanol.

$[Ni(eten)_2Cl_2]$ (**1a**) and $[Ni(eten)_2Cl_2]$ (**1c**) were synthesized pyrolytically in the solid state from complexes (**1**) and (**1b**), at 166 and 98°C, respectively (Table 2).

$[Ni(eten)Cl_2]$ (**1e**) and $Ni(eten)_{0.5}Cl_2$ (**1f**) were synthesized in the solid state from complexes (**1**) and (**1b**), respectively (Table 2).

$[Ni(eten)_3]Br_2$ (**2a**) and $[Ni(eten)_2Br_2]$ (**2c**) were derived from complex (**2**). Complex (**2c**) can also be synthesized from complex (**2d**) (Table 2).

$[Ni(eten)_2SO_4]$ (**6a**), $[Ni(eten)_2SeO_4]$ (**7a**), $[Ni(meen)_2SO_4]$ (**8a**) and $[Ni(meen)_2SeO_4]$ (**9c**) were isolated pyrolytically from their corresponding parent complexes using a temperature arrest technique (Table 2).

RESULTS AND DISCUSSION

Complexes of nickel(II) chloride

The complex $[Ni(eten)_3]Cl_2 \cdot H_2O$ (**1**) appears, from magnetic and electronic spectral data, to have octahedral geometry (Table 1). The IR spectrum hints that the diamines are chelated. Upon heating, the complex starts to lose the water molecule at 68° C and generates $[Ni(eten)_2Cl_2]$ (**1a**) at 166° C (Table 2, Fig. 1).

The complex $[Ni(eten)_2Cl_2]$ (**1a**) appears to possess *cis*-octahedral geometry, and the diamines are chelated as in its corresponding en [4] and meen [9] analogues. This complex does not undergo any phase transition upon heating from the ambient temperature. On crystallization from ethanol–water or methanol–water (9.5 : 0.5) mixtures, the (**1a**) species yields the dihydrate, $[Ni(eten)_2Cl_2] \cdot 2H_2O$ (**1b**). Direct synthesis of the dihydrated species (**1b**) is

TABLE 1

Analytical, magnetic and electronic spectral (mull) data of nickel(II) eten and meen complexes

Compound	Number	Composition (%) Found (calc.)			μ_{eff} (B.M.)	λ_{max} (nm)
		Carbon	Nitrogen	Hydrogen		
$[Ni(eten)_3]Cl_2 \cdot H_2O$	(**1**)	34.7 (35.0)	20.0 (20.4)	9.4 (9.2)	3.0	555, 360
$[Ni(eten)_2Cl_2]$	(**1a**)	31.2 (31.4)	18.2 (18.3)	7.7 (7.8)	2.9	560, 362
$[Ni(eten)_2Cl_2] \cdot 2H_2O$	(**1b**)	27.8 (28.1)	16.2 (16.4)	8.1 (8.2)	3.1	562, 362
$[Ni(eten)_2Cl_2]$	(**1c**)	31.1 (31.4)	18.0 (18.3)	8.0 (7.8)	2.9	562, 362
$[Ni(eten)Cl_2]$	(**1e**)	22.1 (22.0)	12.8 (12.9)	5.4 (5.5)	3.2	660, 405
$Ni(eten)_{0.5}Cl_2$	(**1f**)	13.7 (13.8)	7.7 (8.0)	3.6 (3.4)	5.7	–
$[Ni(eten)_3]Br_2 \cdot H_2O$	(**2**)	28.5 (28.7)	16.6 (16.8)	7.6 (7.6)	3.1	550, 362
$[Ni(eten)_3]Br_2$	(**2a**)	29.6 (29.8)	17.1 (17.4)	7.5 (7.4)	3.1	551, 365
$[Ni(eten)_2Br_2]$	(**2c**)	24.1 (24.3)	14.2 (14.2)	6.0 (6.1)	3.0	552, 360
$[Ni(eten)_2Br_2] \cdot 2H_2O$	(**2d**)	22.2 (22.3)	12.8 (13.0)	6.5 (6.5)	3.1	550, 360
$[Ni(eten)_3](BF_4)_2$	(**3**)	28.7 (29.0)	16.8 (16.9)	7.0 (7.2)	3.1	560, 360
$[Ni(eten)_2(NCS)_2]$	(**4**)	34.2 (34.2)	23.8 (23.9)	6.7 (6.8)	2.9	547, 360
$[Ni(eten)_3](NO_3)_2$	(**5**)	32.1 (32.2)	25.0 (25.1)	7.7 (8.0)	3.0	540, 350
$[Ni(eten)_3]SO_4$	(**6**)	34.2 (34.4)	19.8 (20.1)	8.4 (8.6)	3.0	530, 340
$[Ni(eten)_2SO_4]$	(**6a**)	28.7 (29.0)	16.5 (16.9)	7.0 (7.2)	2.9	550, 350
$[Ni(eten)_3]SeO_4$	(**7**)	30.6 (30.9)	17.9 (18.0)	7.7 (7.7)	3.1	530, 338
$[Ni(eten)_2SeO_4]$	(**7a**)	25.3 (25.4)	14.7 (14.8)	6.1 (6.3)	2.9	550, 352
$[Ni(meen)_3]SO_4 \cdot 2H_2O$	(**8**)	26.3 (26.1)	20.4 (20.3)	8.0 (8.2)	3.1	558, 360
$[Ni(meen)_2SO_4]$	(**8a**)	23.6 (23.8)	18.4 (18.5)	6.4 (6.6)	3.0	555, 358
$[Ni(meen)_3]SeO_4 \cdot 2H_2O$	(**9**)	23.3 (23.5)	18.1 (18.3)	7.3 (7.4)	3.1	555, 360
$[Ni(meen)_3]SeO_4$	(**9a**)	25.4 (25.5)	19.7 (19.8)	7.0 (7.1)	3.1	550, 360
$[Ni(meen)_3]SeO_4$	(**9b**)	25.4 (25.5)	19.6 (19.8)	7.0 (7.1)	3.1	550, 360
$[Ni(meen)_2SeO_4]$	(**9c**)	20.5 (20.6)	16.1 (16.0)	5.6 (5.7)	3.0	555, 358

TABLE 2

Thermal reactions of eten and meen complexes of nickel(II)

Thermal reaction	Temperature range (° C)	DTA peak temperature (° C)	
		Endo	Exo
$[Ni(eten)_3]Cl_2 \cdot H_2O$ (**1**) → $[Ni(eten)_2Cl_2]$ (**1a**)	68–166	110, 152	–
$[Ni(eten)_2Cl_2]$ (**1a**) → $[Ni(eten)Cl_2]$ (**1e**)	222–297	287	–
$[Ni(eten)Cl_2]$ (**1e**) → $Ni(eten)_{0.5}Cl_2$ (**1f**)	305–354	–	348
$Ni(eten)_{0.5}Cl_2$ (**1f**) → $NiCl_2$	380–420	–	405
$[Ni(eten)_2Cl_2] \cdot 2H_2O$ (**1b**) → $[Ni(eten)_2Cl_2]$ (**1c**)	70–98	88	–
$[Ni(eten)_2Cl_2]$ (**1c**) → $[Ni(eten)_2Cl_2]$ (**1d**)	182–200	189	–
$[Ni(eten)_2Cl_2]$ (**1d**) → $[Ni(eten)Cl_2]$ (**1e**)	229–298	293	–
$[Ni(eten)Cl_2]$ (**1e**) → $Ni(eten)_{0.5}Cl_2$ (**1f**)	312–360	347	357
$Ni(eten)_{0.5}Cl_2$ (**1f**) → $NiCl_2$	372–420	–	400, 418
$[Ni(eten)_3]Br_2 \cdot H_2O$ (**2**) → $[Ni(eten)_3]Br_2$ (**2a**)	55–110	85	–
$[Ni(eten)_3]Br_2$ (**2a**) → $[Ni(eten)_2Br_2]$ (**2b**)	155–220	166, 207	–
$[Ni(eten)_2Br_2]$ (**2b**) → $[Ni(eten)_2Br_2]$ (**2c**)	49–35	41	–
$[Ni(eten)_2Br_2]$ (**2c**) → $[Ni(eten)_2Br_2]$ (**2b**)	50–76	61	–
$[Ni(eten)_2Br_2]$ (**2b**) → $NiBr_2$	255–380	305	377
$[Ni(eten)_2Br_2] \cdot 2H_2O$ (**2d**) → $[Ni(eten)_2Br_2]$ (**2b**)	80–142	120	–
$[Ni(eten)_3](BF_4)_2$ (**3**) → $[Ni(eten)_3](BF_4)_2$ (**3a**)	93–124	116	–
$[Ni(eten)_3](BF_4)_2$ (**3a**) [a]	190 [b]	–	–
$[Ni(eten)_2(NCS)_2]$ (**4**) [a]	224 [b]	–	–
$[Ni(eten)_3](NO_3)_2$ (**5**) → NiO	144–270	–	–
$[Ni(eten)_3]SO_4$ (**6**) → $[Ni(eten)_2SO_4]$ (**6a**)	161–214	193, 207	–
$[Ni(eten)_2SO_4]$ (**6a**) → $NiSO_4$	248–420	308, 325	339, 408
$[Ni(eten)_3]SeO_4$ (**7**) → $[Ni(eten)_2SeO_4]$ (**7a**)	170–215	205	–
$[Ni(eten)_2SeO_4]$ (**7a**) → $NiSeO_4$	258–325	–	315
$[Ni(meen)_3]SO_4 \cdot 2H_2O$ (**8**) → $[Ni(meen)_3]SO_4$	70–110	82, 95	–
$[Ni(meen)_3]SO_4$ → $[Ni(meen)_2SO_4]$ (**8a**)	162–223	210	–
$[Ni(meen)_2SO_4]$ (**8a**) → $NiSO_4$	285–430	–	416
$[Ni(meen)_3]SeO_4 \cdot 2H_2O$ (**9**) → $[Ni(meen)_3]SeO_4$ (**9a**)	75–140	100, 128	–
$[Ni(meen)_3]SeO_4$ (**9a**) → $[Ni(meen)_3]SeO_4$ (**9b**)	162–174	169	–
$[Ni(meen)_3]SeO_4$ (**9b**) → $[Ni(meen)_2SeO_4]$ (**9c**)	178–223	210	–
$[Ni(meen)_2SeO_4]$ (**9c**) → $NiSeO_4$	270–340	–	–

[a] Products not identified.

[b] Temperature at which decomposition began.

also possible by the reaction of $NiCl_2 \cdot 6H_2O$ (1 mmol) with eten (2 mmol) in ethanol (see Experimental). Upon heating, (**1b**) starts to lose the water molecule at 70 °C and becomes $[Ni(eten)_2Cl_2]$ (**1c**) at 98 °C (Table 2, Fig. 1). On further heating, this anhydrous species (**1c**) undergoes an endothermic phase transition (temperature range, 182–200 °C; $\Delta H = 2.9$ kJ mol^{-1})

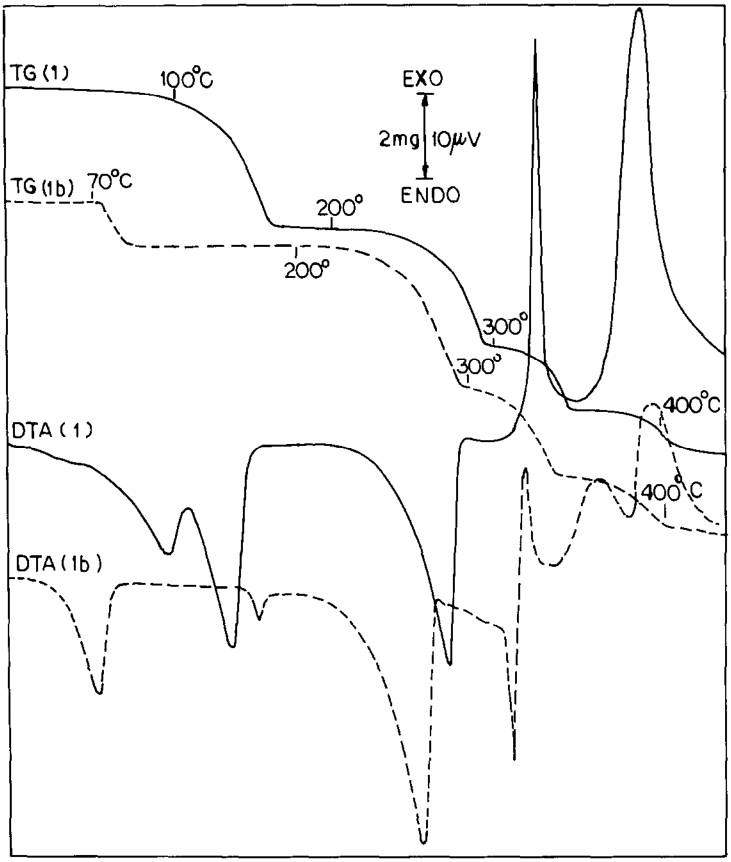
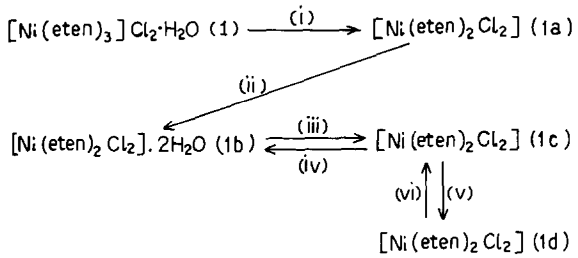


Fig. 1. TG–DTA curves of: ———, $[Ni(eten)_3]Cl_2 \cdot H_2O$ (**1**) (sample mass = 12.90 mg); and – – –, $[Ni(eten)_2Cl_2] \cdot 2H_2O$ (**1b**) (sample mass = 12.00 mg).

yielding its isomer (**1d**) (Table 1, Fig. 2). On immediate reheating, this species again shows the endothermic phase transition, though with a lower ΔH value (0.8 kJ mol^{-1}). However, if the post-phase species (**1d**) is kept at ambient temperature for ca. 30 min, it reverts completely to (**1c**), as is evident from the ΔH value. This transition can therefore be termed kinetically irreversible. It is interesting to note that on being kept in a humid atmosphere (relative humidity, 60–70%), the (**1c**) species transforms to (**1b**), whereas the (**1a**) species does not show any affinity for the water molecule under similar conditions (Scheme 1).

The (**1a**) and (**1c**) species generate similar electronic spectra (mull) and magnetic data (Table 1), suggesting the same configuration of the donor atoms around the nickel. However, the IR spectra of (**1a**), (**1c**) and (**1d**) recorded at ca. 30, 110 and 210 °C, respectively, differ slightly in the regions 3300–2800 and 1700–700 cm^{-1}, corresponding to $\nu_{(NH_2)}$, $\nu_{(CH_2)}$ and $\delta_{(NH_2)}$, $\delta_{(CH_2)}$, $\rho_{w(CH_2)}$, $[\tau_{(NH_2)} + \rho_{w(NH_2)} + \tau_{(CH_2)}]$ skeletal, $\rho_{r(CH_2)}$ vibrations respec-



Scheme 1. (i) 68–166 ° C; (ii) crystallization from aqueous methanol or ethanol; (iii) 70–98 ° C; (iv) ca. 3 h in humid atmosphere (relative humidity 60–70%) at ambient temperature; (v) 182–200 ° C; $\Delta H = 2.9$ kJ mol^{-1}; (vi) complete reversion takes place in ca. 30 min.

tively. This hints that these three species differ in the conformation of the diamine chelate rings [9,11]. The X-ray diffraction powder patterns of (**1a**) and (**1c**) were recorded. The only noticeable difference between the patterns is in the relative intensity of the peaks (Table 3). This observation, although

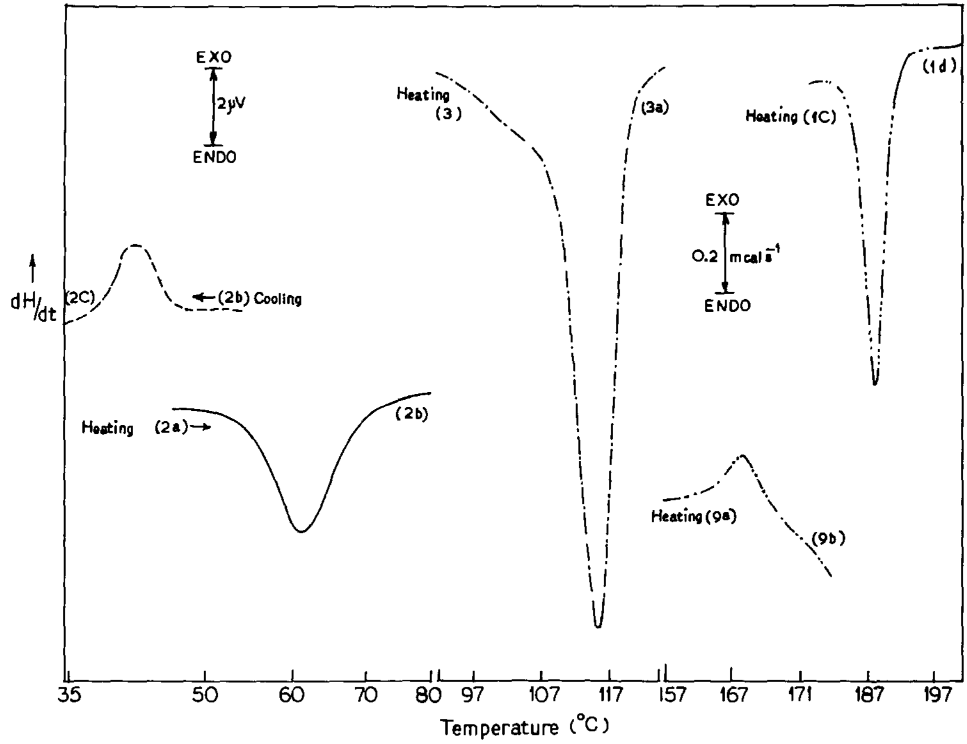


Fig. 2. DSC curves of: ·—·—·, [Ni(eten)$_3$](BF$_4$)$_2$ (**3**) (sample mass = 6.24 mg); — · · —, [Ni(eten)$_2$Cl$_2$] (**1c**) (sample mass = 11.02 mg); and — · · · —, [Ni(meen)$_3$]SeO$_4$ (**9a**) (sample mass = 5.60 mg). DTA curves of: ———, [Ni(eten)$_2$Br$_2$] (**2c**) (heating, sample mass = 13.36 mg); and — — —, [Ni(eten)$_2$Br$_2$] (**2b**) (cooling, sample mass = 13.36 mg).

TABLE 3

Prominent lines d (Å) [a,b] in the X-ray diffraction powder patterns of nickel(II) eten complexes

$[Ni(eten)_2Cl_2]$ **(1a)**		$[Ni(eten)_2Cl_2]$ **(1c)**	
7.61s	3.16vw	7.61s	3.18m
6.50s	3.12w	6.50m	3.12m
6.10s	2.97vw	6.10vs	2.97vw
5.97w	2.92w	5.97w	2.92w
5.33w	2.86vw	5.33m	2.86w
4.15w	2.81w	4.16w	2.81vw
3.99m	2.72w	3.99m	2.72vw
3.91m	2.68w	3.91vw	2.68w
3.86w	2.51w	3.86vw	2.51vw
3.76w		3.78m	2.42w
3.62w		3.65vw	2.40vw
3.60vw		3.60w	2.28w
3.52vw		3.52m	2.26vw
3.44m		3.44m	2.24vw
3.29m		3.29vs	2.20w
3.23vw		3.23vw	2.17w

[a] Intensities estimated visually.

[b] vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

inconclusive, is not inconsistent with the supposition that **(1a)** and **(1c)** are conformational isomers, between which a slight change in the unit cell and internal structures is to be expected. It was also noticed that both the **(1a)** and **(1c)** species generate $[Ni(eten)Cl_2]$ **(1e)** and $Ni(eten)_{0.5}Cl_2$ **(1f)** during their decomposition, with slight differences in the formation temperatures of **(1e)** and **(1f)** and the corresponding DTA profiles (Table 2, Fig. 1). This observation also supports the suggestion that the **(1a)** and **(1c)** species are not identical.

The electronic spectra and the magnetic moment of the complex $[Ni(eten)Cl_2]$ **(1e)** support an octahedral geometry. The IR spectrum of the complex hints that the diamine molecule is chelated. Considering the composition and the geometry, both the chloride ions should act here as bridging ligands, as in the corresponding meen analogue [9].

The complex $Ni(eten)_{0.5}Cl_2$ **(1f)** has an unusually high magnetic moment ($\mu_{eff} = 5.7$ B.M. at 26°C, for the formula $Ni(eten)_{0.5}Cl_2$). This unusual behaviour was also observed for the corresponding meen complex. The proposed interactions for this unusual magnetic behaviour are perhaps the same as reported for $Ni(meen)_{0.5}Cl_2$ [9].

Complexes of nickel(II) bromide

The magnetic moment and electronic spectral data of the complex $[Ni(eten)_3]Br_2 \cdot H_2O$ **(2)** indicate an octahedral geometry (Table 1). Upon

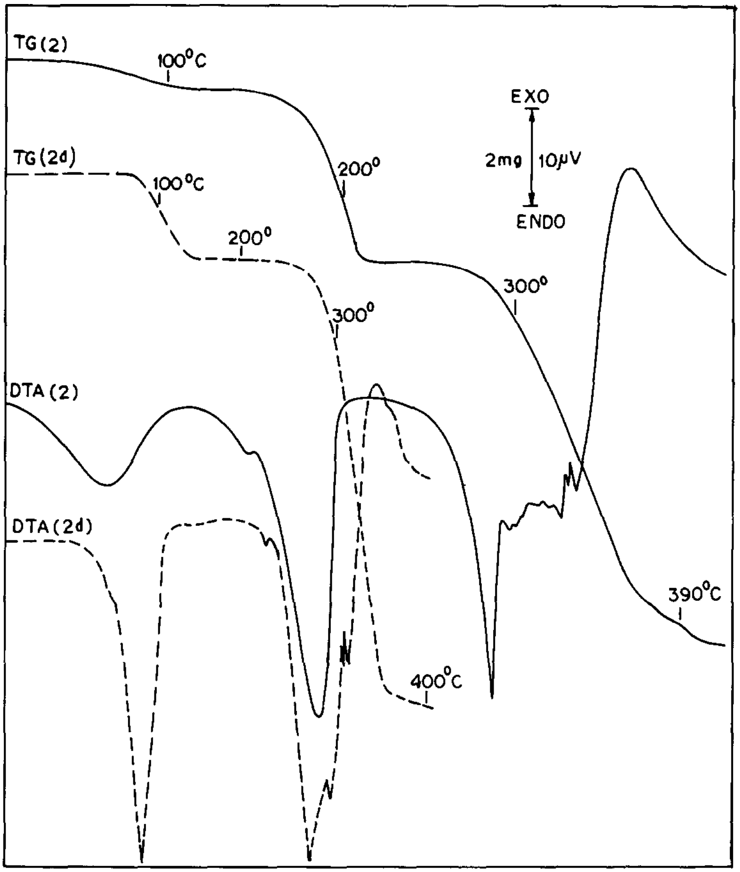
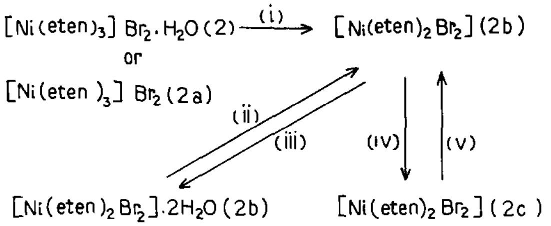


Fig. 3. TG–DTA curves of: ———, $[Ni(eten)_3]Br_2 \cdot H_2O$ (**2**) (sample mass = 21.20 mg); and — — —, $[Ni(eten)_2Br_2] \cdot 2H_2O$ (**2d**) (sample mass = 19.14 mg).

heating, this complex generates $[Ni(eten)_3]Br_2$ (**2a**) at 110 °C, $[Ni(eten)_2Br_2]$ at 220 °C, and finally decomposes to $NiBr_2$ at 380 °C (Table 2, Fig. 3). The decomposition pattern appears to be similar to that of the corresponding meen analogue [9].

The complex $[Ni(eten)_3]Br_2$ (**2a**) is also octahedral, given its magnetic and electronic spectral data (Table 1). This complex yields its hydrated form (**2**) on exposure to a humid atmosphere (Scheme 2).

The species $[Ni(eten)_2Br_2]$ (**2c**) has *cis*-octahedral geometry with chelated diamines, like its chloro analogue. Upon heating, (**2c**) undergoes an endothermic phase transition (temperature range, 50–76 °C; $\Delta H = 1.2$ kJ mol^{-1}) yielding its isomer (**2b**), which on cooling reverts to (**2c**) showing an exotherm (temperature range, 49–35 °C; $\Delta H = -0.8$ kJ mol^{-1}) (Table 2, Fig. 2). Recycling of the transition shows that all the heating and cooling curves are identical to the first. However, it should be noted that the ΔH value of the heating curve is greater than that of the cooling curve, which



Scheme 2. (i) 220 ° C; (ii) 80–142 ° C; (iii) ca. 3 h in humid atmosphere (relative humidity 60–70%) at ambient temperature; (iv) 50–76 ° C; $\Delta H = 1.2$ kJ mol^{-1}; (v) 49–85 ° C; $\Delta H = -0.8$ kJ mol^{-1}.

indicates that total reversion of (**2b**) to (**2c**) does not take place instantaneously on cooling, i.e. it is also time dependent like its chloro analogue, although the rate of reversion is much faster here.

The (**2c**) species yields the dihydrate $[Ni(eten)_2Br_2] \cdot 2H_2O$ (**2d**) both on being kept in a humid atmosphere and on crystallization from ethanol–water (9.5 : 0.5) mixture. Direct synthesis of this dihydrate is also possible by the reaction of $NiBr_2$ (1 mmol) with eten (2 mmol) in ethanolic medium (see Experimental). On heating, (**2d**) becomes anhydrous at 142 ° C (Table 2, Fig. 3). This anhydrous species shows identical thermal and spectral (IR and electronic) behaviour to that of (**2b**). Scheme 2 illustrates these transformations schematically. The IR spectrum of (**2b**) recorded at ca. 90 ° C differs from that of (**2c**) in the regions 3500–2800 and 1650–700 cm^{-1}, corresponding to $\nu_{(NH_2)}$, $\nu_{(CH_2)}$ and $\delta_{(NH_2)}$, $\delta_{(CH_2)}$, $\rho_{w(CH_2)}$, $[\tau_{(NH_2)} + \rho_{w(NH_2)} + \tau_{(CH_2)}]$ skeletal, $\rho_{r(CH_2)}$ vibrations, respectively. It was also observed that (**2b**) has a simpler spectrum than (**2c**). It can therefore be suggested that the (**2b**) and (**2c**) species are conformational isomers, with the chelate ring conformations of (**2b**) being more symmetrical than those of (**2c**) [11].

Complexes of nickel(II) tetrafluoroborate

The complex $[Ni(eten)_3](BF_4)_2$ (**3**) is octahedral with chelated diamines. Upon heating, it undergoes an endothermic phase transition (temperature range, 93–124 ° C; $\Delta H = 24.7$ kJ mol^{-1}) yielding its isomer (**3a**) without any visible colour change (Table 2, Fig. 2). The corresponding cooling curve does not show any exotherm. The species $[Ni(eten)_3](BF_4)_2$ (**3a**) cannot be isolated in pure form, as on cooling it reverts slowly to (**3**) and total reversion takes place in ca. 30 min. The IR spectrum of (**3a**) recorded at 130 ° C differs from that of (**3**) in the regions 3500–2800 and 1600–1200 cm^{-1}, corresponding to $\nu_{(NH_2)}$, $\nu_{(CH_2)}$ and $\delta_{(NH_2)}$, $\delta_{(CH_2)}$ vibrations, respectively. A similar type of phase transition has been observed in the corresponding meen analogue [9], in which the phase changes were reported to be due to opening of an H bond (between the anion and the diamine hydrogen) followed by conformational changes in the diamine chelate rings. In the present case, the temperature range, the enthalpy value, the nature of the transition and the differences in the IR spectra between the two phases are quite similar to those of $[Ni(meen)_3](BF_4)_2$ [9]. The reason for this transition from (**3**) to (**3a**) can therefore be expected to be the same as reported for the transformation of $[Ni(meen)_3](BF_4)_2$ [9].

Complexes of nickel(II) thiocyanate and nitrate

The IR spectrum of the complex $[Ni(eten)_2(NCS)_2]$ (**4**) shows $\nu_{(CN)}$ at 2096 cm^{-1} and $\nu_{(CS)}$ at 830 cm^{-1}, which is consistent with an *N*-bonded thiocyanate group in the *trans* position [13]. Magnetic moment and electronic spectral (mull) data (Table 1) suggest an octahedral geometry. Upon heating, this complex, like its meen analogue [9], does not undergo any phase transition and starts to decompose at 224 °C.

The complex $[Ni(eten)_3](NO_3)_2$ (**5**) has an octahedral geometry with chelated diamines. A single sharp and narrow band at 1761 cm^{-1} (a combination of ν_1 and ν_4) in the IR spectrum of this complex suggests non-coordination of the NO_3 group [14]. Upon heating, the complex starts to decompose at 144 °C and transforms to NiO at 270 °C without any characterizable intermediate (Table 2). In this context, it may be mentioned that the corresponding meen analogue [9] showed phase transition (temperature range, 141–167 °C) and then started to decompose at 169 °C. The non-existence of the phase transition in the present case may be assumed to be due to the lower decomposition temperature of complex (**5**).

Complexes of nickel(II) sulphate and selenate

The complexes $[Ni(eten)_3]SO_4$ (**6**) and $[Ni(eten)_3]SeO_4$ (**7**) both appear to have octahedral geometry, on the basis of magnetic and electronic spectral data (Table 1). The TG and DTA curves indicate that upon heating, both (**6**) and (**7**) yield the corresponding bis(diamine) complexes $[Ni(eten)_2SO_4]$ (**6a**) and $[Ni(eten)_2SeO_4]$ (**7a**) as intermediates (Tables 1 and 2).

The complexes $[Ni(meen)_3]SO_4 \cdot 2H_2O$ (**8**) and $[Ni(meen)_3]SeO_4 \cdot 2H_2O$ (**9**) are octahedral, with chelated diamines. Upon heating, (**8**) becomes anhydrous at 110 °C, showing two endotherms in the corresponding DTA profile (Table 2). On further heating, it starts to decompose at 162 °C and transforms to $NiSO_4$ at 430 °C via an isolable intermediate species, $[Ni(meen)_2SO_4]$ (**8a**), at 223 °C (Tables 1 and 2).

Upon heating, complex (**9**) starts to lose the water molecule at 75 °C, and transforms to $[Ni(meen)_3]SeO_4$ (**9a**) at 140 °C (Table 2). On further heating, the species (**9a**) undergoes an irreversible exothermic phase transition (temperature range, 162–174 °C; $\Delta H = -1.2$ kJ mol^{-1}), yielding its isomer (**9b**) (Table 2, Fig. 2). The complex (**9b**) starts decomposition at 178 °C and transforms to $NiSeO_4$ at 340 °C via an intermediate species, $[Ni(meen)_2SeO_4]$ (**9c**) (Tables 1 and 2).

The (**9a**) and (**9b**) species have identical electronic spectra (mull) and magnetic moments, but the intensity ratio of the IR active bands of the two species differ slightly in the region 1200–950 cm^{-1}. Conformational isomers of nickel(II) diamine systems showed similar differences in their IR spectra [7,9,11]. It can therefore be assumed that after dehydration the (**9a**) species is stabilized by 1.2 kJ mol^{-1} by rearrangement of the conformation of the diamine chelate rings. The stability of the post-phase species (**9b**) is corroborated by the fact that on exposure to open atmosphere, (**9a**) readily absorbs two molecules of water, yielding (**9**), while (**9b**) remains unaffected. However, on crystallization from methanol or ethanol (containing ca. 0.5% H_2O) (**9b**) transforms to (**9**).

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