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Thermal studies of *N*,*N*′-diethylethane-1,2-diamine complexes of nickel(II) in the solid state

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Abstract

$NiL_2X_2 \cdot nH_2O$ (where L = *N*,*N*′-diethylethane-1,2-diamine; $n = 2$ when X is Cl^-, Br^-, I^-, NO_3^-, $0.5SO_4^{2-}$, $0.5SeO_4^{2-}$ or $CF_3SO_3^-$; $n = 0$ when X is $CF_3CO_2^-$ or $CCl_3CO_2^-$) have been synthesised from solution and investigated by TG–DTA and DSC in the solid state. All the hydrated complexes have *trans* octahedral geometry and on heating undergo dehydration–anation reactions. The dehydrated complexes are also *trans* octahedral, except NiL_2X_2 (X is NO_3^-, $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) for which *cis* octahedral geometry is proposed. $[NiL_2(H_2O)_2]X_2$ (X is Br^- or $CF_3SO_3^-$) shows thermochromism (blue → green) upon dehydration. NiL_2X_2 (X is Cl^-, Br^-, $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) yield mono-diamine species in the solid state on heating. NiL_2SO_4 undergoes a reversible phase transition (heating cycle, 178–193°C, $\Delta H = -4.0\ \mathrm{kJ\ mol^{-1}}$; cooling cycle, 186–172°C; $\Delta H = 4.0\ \mathrm{kJ\ mol^{-1}}$) without a visual colour change.

Keywords: DSC; DTA; Nickel diamine complex; Phase transition; Thermochromism; TG

1. Introduction

A dehydration–anation reaction of $[Ni(N\text{–}N)_2(H_2O)_2]X_2$ (where N–N is *N*,*N*-dimethylethane-1,2-diamine (NNdmen); *N*,*N*′-dimethylethane-1,2-diamine (NN′dmen); *N*,*N*-diethylethane-1,2-diamine (NNdeen) or *N*,*N*′-diethylethane-1,2-diamine (NN′deen) and X is Cl^-, Br^-, I^-, NO_3^- or ClO_4^-) in the solid phase has been reported by Ihara et al. [1,2] and by our laboratory [3–5]. The aim of Ihara et al. [1,2] was to

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investigate the geometrical isomerism on dehydration. All the dihydrate species reported by them are found to possess *trans*-octahedral geometry except for *cis*-$[Ni(H_2O)_2(NNdmen)_2]I_2$ and on dehydration–anation the original *trans* configuration is retained in the symmetric diamines (NN'dmen and NN'deen)$_2$]I_2, whereas in the complexes with asymmetric diamines (NNdmen and NNdeen) *trans* → *cis* configurational change takes place. A notable exception to this general conclusion is the complex containing nitrate ions, which may either be *trans*-dinitrato or *cis*-mononitrato depending on the diamines. However, the studies of Ihara et al. were performed with a limited number of anions (halides, nitrate and perchlorate) and the thermal reactions were studied within the temperature range room temperature to 200°C. In previous communications [3–5] we noticed that the complexes of nickel(II)-diamine can show several interesting thermal reactions at higher temperatures (above 200°C) and also with other anions. The decomposition patterns of the complexes are sometimes very useful as they may provide an easy way to synthesise ligand-deficient compounds which are otherwise very difficult, if not impossible, to synthesise.

The present paper reports a thermal study of *N,N'*-diethylethane-1,2-diamine (L) complexes of nickel(II) except $[NiL_2](ClO_4)_2$ owing to its explosive nature, together with some new complexes having $SO_4{}^{2-}$, $SeO_4{}^{2-}$, $CF_3SO_3{}^-$, $CF_3CO_2{}^-$ and $CCl_3CO_2{}^-$ as counter anions.

2. Experimental

High purity *N,N'*-diethylethane-1,2-diamine (L) was obtained from Aldrich Chemical Company Inc. and used as received. All other chemicals were AR grade. The equipment employed to record electronic spectra, elemental analyses and thermal measurements (TG–DTA) have been described [6]. The enthalpy changes for phase transformation and dehydration were measured with a Perkin–Elmer DSC-7 differential scanning calorimeter using indium metal as calibrant (rate of heating/cooling 10°C min^{-1}). Elemental analyses and thermal data are listed in Tables 1 and 2, respectively.

2.1. Preparation of the complexes

$[NiL_2(H_2O)_2]X_2$ (X is Cl^-, Br^-, I^- or $NO_3{}^-$) were prepared following the methods described in the literature [7]. $[NiL_2(H_2O)_2](CF_3SO_3)_2$ and $[NiL_2X_2]$ (X is $CF_3CO_2{}^-$ or $CCl_3CO_2{}^-$) were prepared similarly.

$[NiL_2(H_2O)_2]AO_4$ (A is S or Se) were prepared by adding diamine (2 mmol) slowly to the corresponding metal salt (1 mmol) dissolved in water–ethanol (1:3) mixture (10 cm^3). On keeping the resulting solution in a desiccator for several days, fine crystals separated out. These were filtered, washed with ethanol and stored in a desiccator.

$[NiL_2Cl_2]$ (**1a**), $NiLCl_2$ (**1b**), $[NiL_2Br_2]$ (**2a**), $NiLBr_2$ (**2b**), $[NiL_2I_2]$ (**3a**), $[NiL_2(NO_3)]NO_3$ (**4a**), $[NiL_2SO_4]$ (**5a**), $NiLSO_4$ (**5b**), $[NiL_2SeO_4]$ (**6a**), and $[NiL_2(CF_3SO_3)_2]$ (**7a**) were isolated in the solid state pyrolytically at 102, 190, 115, 230, 124, 108, 104, 193, 100 and 150°C, respectively, from the corresponding parent bis-diamine complexes (Table 2).

3. Results and discussion

3.1. Characterisation of the complexes

The synthesis and characterisation of the complexes $[NiL_2(H_2O)_2]X_2$ (X is Cl^-, Br^-, I^-, NO_3^- or ClO_4^-) and their corresponding anhydrous species have been reported by Ihara et al. [1, 2]. In addition to these complexes, we synthesised additional hydrated complexes, $[NiL_2(H_2O)_2]X_2$ (X is $CF_3CO_2^-$, $CCl_3CO_2^-$, $CF_3SO_3^-$, $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$). The electronic spectra and magnetic moments of all the complexes (Table 1) are typical of octahedral geometry. Moreover, the electronic spectra of the complexes $[NiL_2X_2]$ (X is $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) in the near infrared (NIR) region do not show any splitting, indicating *cis* geometry, whereas the appearance of two bands (Table 1) in the NIR region of all the other complexes suggests *trans* octahedral geometry [4, 8, 9]. It is noted that Ihara et al. [1, 2] identified the *cis* and

Table 1
Elemental analyses, magnetic and electronic (mull) spectral data of *N*,*N*′-diethylethane-1,2-diamine (L) complexes of nickel(II)

Complex	No.	Colour	Elemental analyses/%[a]			$\mu_{eff.}$/BM	λ_{max}/nm
			C	H	N		
$[NiL_2(H_2O)_2]Cl_2$	1	Blue	33.2(33.1)	9.2(9.0)	14.1(14.1)	3.0	360, 575
$[NiL_2Cl_2]$	1a	Blue	39.9(39.8)	8.6(8.8)	15.4(15.5)	2.9	365, 582
$NiLCl_2$	1b	Green	29.4(29.3)	6.7(6.5)	11.5(11.4)	3.2	412, 542
$[NiL_2(H_2O)_2]Br_2$	2	Blue	29.7(29.6)	7.6(7.4)	11.4(11.5)	3.0	362, 570
$[NiL_2Br_2]$	2a	green	32.0(31.9)	7.0(7.1)	12.3(12.4)	3.0	369, 592
$NiLBr_2$	2b	Yellowish-green	21.4(21.5)	4.7(4.8)	8.3(8.4)	3.3	423, 542
$[NiL_2(H_2O)_2]I_2$	3	Blue	24.6(24.8)	6.1(6.2)	9.4(9.6)	3.0	354, 580
$[NiL_2I_2]$	3a	Blue	26.5(26.4)	5.7(5.9)	10.4(10.3)	2.9	360, 586
$[NiL_2(H_2O)_2](NO_3)_2$	4	Blue	31.6(31.9)	7.9(8.0)	18.6(18.6)	2.9	360, 580
$[NiL_2(NO_3)]NO_3$	4a	Blue	35.0(34.7)	7.9(7.7)	20.5(20.7)	2.9	382, 588
$[NiL_2(H_2O)_2]SO_4$	5	Blue	34.1(34.0)	8.4(8.5)	13.2(13.2)	3.0	375, 612
$[NiL_2SO_4]$	5a	Blue	37.1(37.2)	8.4(8.3)	14.4(14.5)	3.0	387,625
$NiLSO_4$	5b	Green	26.8(26.6)	6.3(5.9)	10.4(10.3)	3.1	392,638
$[NiL_2(H_2O)_2]SeO_4$	6	Blue	30.6(30.6)	7.6(7.7)	12.0(11.9)	3.0	365, 590
$[NiL_2SeO_4]$	6a	Blue	33.0(33.2)	7.6(7.4)	13.0(12.9)	3.1	372, 605
$[NiL_2(H_2O)_2](CF_3SO_3)_2$	7	Blue	26.7(26.9)	5.9(5.8)	8.9(9.0)	2.9	370, 585
$[NiL_2(CF_3SO_3)_2]$	7a	Green	28.4(28.5)	5.3(5.5)	9.3(9.5)	3.0	372, 593
$[NiL_2(CF_3CO_2)_2]$	8	Blue	37.3(37.1)	6.4(6.2)	10.7(10.8)	2.9	365,560
$[NiL_2(CCl_3CO_2)_2]$	9	Blue	31.0(31.2)	5.3(5.2)	9.0(9.1)	2.9	367, 571

[a] Percentages in parentheses are theoretically calculated values.

trans geometry using the same method and found that, except for *cis*-$[NiL_2(NO_3)](NO_3)$, all complexes possess *trans* octahedral geometry.

$NiLX_2$ (X is Cl^- or Br^-) is stable and can be stored in a desiccator for a few days. They are not hygroscopic and even on crystallisation from water do not yield hydrated species. We could not produce single crystals of these complexes. The structures of these complexes are tentatively assigned as octahedral geometry, on evidence from their electronic spectra and magnetic moment values (Table 1). Conversely, $NiLX_2$ (X is $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) are hygroscopic and absorb moisture readily in a humid atmosphere. Their electronic spectra (Nujol) and magnetic moment data also suggest octahedral geometry.

3.2. *Thermal analysis*

All the aquated complexes on heating lose two molecules of water in a single step, except $[NiL_2(H_2O)_2]X_2$ (X is Br^- or $0.5SO_4^{2-}$) for which the elimination of water molecules takes place in two overlapping steps as is evident from their DTA curves (Figs. 1 and 2) . The enthalpy changes for dehydration–anation reactions are around 100 kJ mol^{-1}. The interesting observation is that even on *trans* → *cis* transformation in

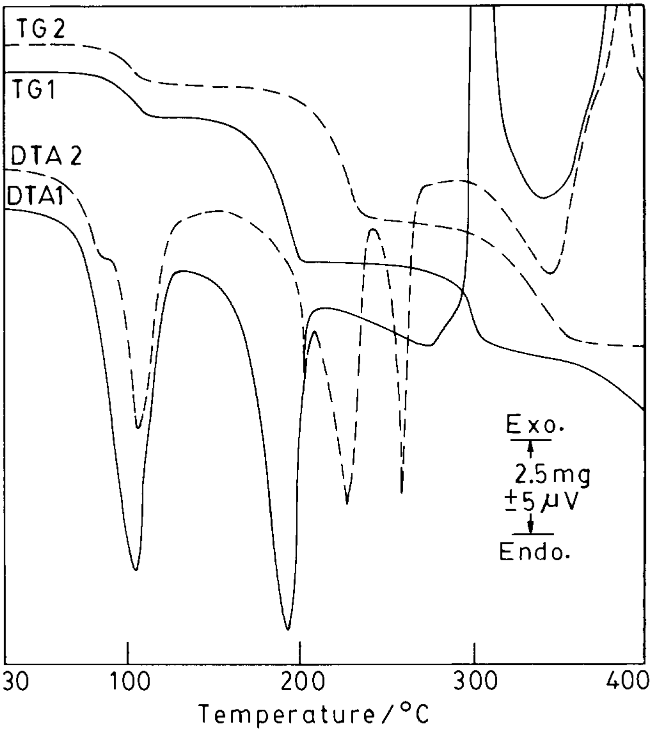

Fig. 1. TG–DTA curves: ——, $[NiL_2(H_2O)_2]Cl_2$ (1) (sample mass, 13.19 mg); and – – –, $[NiL_2(H_2O)_2]Br_2$ (2) (sample mass, 13.46 mg).

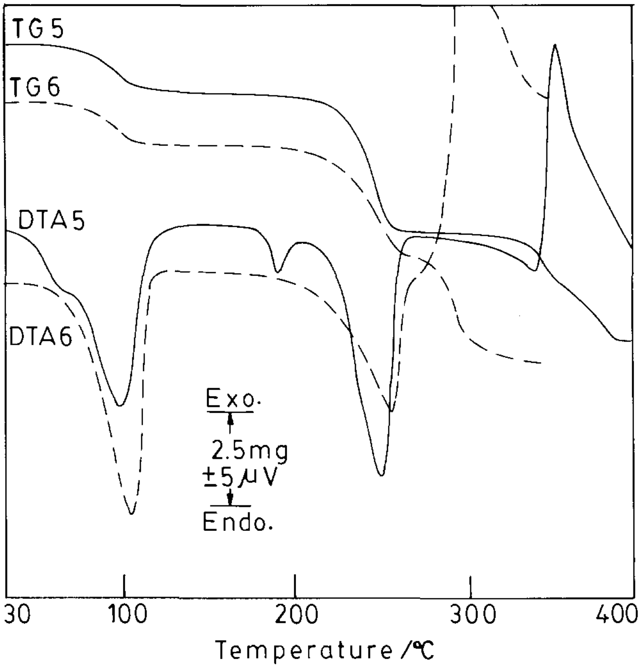

Fig. 2. TG–DTA curves: —— $[NiL_2(H_2O)_2]SO_4$(5) (sample mass, 13.45 mg); and - - -, $[NiL_2(H_2O)_2]SeO_4$(6) (sample mass, 11.83 mg).

the case of nitrate, sulphate and selenate upon dehydration, the enthalpy change appears to be the same with *trans* → *trans* transformation although earlier studies show that the geometrical isomerism is usually associated with a considerable amount of enthalpy change. However as the enthalpy of dehydration is dependent on several factors, e.g. strength of hydrogen bond, coordination mode, etc., no conclusion can be drawn from this ΔH value. There is blue → green thermochromism in $[NiL_2(H_2O)_2]X_2$ (X is Br^- or $CF_3SO_3^-$) on losing two molecules of water. This colour can be attributed to the change of ligand field strength, and arises due to the replacement of water molecules by the anions Br^- and $CF_3CO_2^-$ in the coordination sphere. This is also corroborated by the shift of band maxima in the electronic spectra.

$[NiL_2Cl_2]$ starts to decompose at ~ 135°C and transforms to $NiLCl_2$ at 190°C in a single step (Fig. 1). The mono-diamine species upon further heating decomposes to $NiCl_2$ via the formation of an intermediate $NiL_{0.5}Cl_2$, as is evident from the corresponding TG curve. $[NiL_2Br_2]$ on heating decomposes at 152°C and transforms to $NiLBr_2$ at 230°C in two overlapping steps as is evident from its DTA curves. This on further heating first melts at ~ 250°C and then decomposes to $NiBr_2$ in a single step (Fig. 1).

NiL_2SO_4 undergoes a reversible endothermic phase transition (heating cycle, 178–193°C; $\Delta H = -4.0\,kJ\,mol^{-1}$; cooling cycle, 186–172°C, $\Delta H = 4.0\,kJ\,mol^{-1}$; Fig. 3)

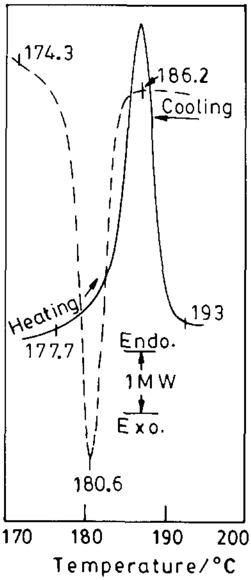

Fig. 3. DSC curves of $[NiL_2SO_4]$ (5a) (sample mass, 13.10 mg): ——, heating; – – –, cooling.

with no visual colour change. The study of the high-temperature phase species is extremely difficult as the decomposition starts immediately after the transitions. The high-temperature phase species, NiL_2SO_4 on further heating transforms to $NiSO_4$ via the formation of $NiLSO_4$ as intermediate (Fig. 2) whereas NiL_2SeO_4 does not show any such phase transition. It decomposes upon heating via the formation of $NiLSeO_4$ as intermediate, as for the corresponding sulphato complex. It is interesting to note that there is a prominent colour change, blue → green, when the bis-diamine complex on heating yields the mono-diamine species. This may be due to a chromophoric change around nickel(II).

$[NiL_2X_2]$ (X is $CF_3SO_3^-$ or $CF_3CO_2^-$) on heating melt at about 240 and 190°C, respectively, and then decompose. The nature of the decomposition is complicated. The other bis-diamine complexes $[NiL_2X_2]$ (X is I^-, NO_3^- or $CCl_3CO_2^-$) do not melt before decomposition and decompose to metal oxide without an identifiable intermediate.

The thermal stability of $[NiL_2X_2]$ (X is Cl^-, Br^-, I^-, NO_3^-, $0.5SO_4^{2-}$, $0.5SeO_4^{2-}$, $CF_3SO_3^-$, $CF_3CO_2^-$ or $CCl_3CO_2^-$) with respect to T_i (initial temperature of decomposition, Table 2) follows the sequence:

$$SO_4^{2-} \geq CF_3SO_3^- > CF_3CO_2^- \geq NO_3^- > I^-$$
$$\geq SeO_4^{2-} > Br^- > Cl^- > CCl_3CO_2^-.$$

The anions $CF_3SO_3^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$ and NO_3^- start to decompose at the initial temperature of decomposition (T_i). Therefore, the T_i values of these complexes

Table 2
Thermal data for the *N*,*N'*-diethylethane-1,2-diamine (L) complexes of nickel(II)

Thermally induced reactions	Temperature range/°C	DTA peak temperature/°C	
		Endo.	Exo.
$[NiL_2(H_2O)_2]Cl_2$ (1) → $[NiL_2Cl_2]$ (1a)	56–102	93	–
$[NiL_2Cl_2]$ (1a) → $NiLCl_2$ (1b)	135–190	184	–
$NiLCl_2$ (1b) → $NiL_{0.5}Cl_2$ (1c)	253–310	–	298
$NiL_{0.5}Cl_2$ (1c) → $NiCl_2$	310–420	–	405
$[NiL_2(H_2O)_2]Br_2$ (2) → $[NiL_2Br_2]$ (2a)	60–115	86	–
$[NiL_2Br_2]$ (2a) → $NiLBr_2$ (2b)	152–230	189, 217	–
$NiLBr_2$ (2b) → $NiBr_2$	240–340	250, 322	–
$[NiL_2(H_2O)_2]I_2$ (3) → $[NiL_2I_2]$ (3a)	82–124	114	–
$[NiL_2I_2]$ (3a) → $NiLI_2$ (3b)	178–277	212	–
$NiLI_2$ (3b) → $NiL_{0.5}I_2$ (3c)	277–319	282	–
$NiL_{0.5}I_2$ (3c) → [b]	319–380	–	343
$[NiL_2(H_2O)_2](NO_3)_2$ (4) → $[NiL_2(NO)_3]NO_3$ (4a)	80–108	98	–
$[NiL_2(NO_3)](NO_3)$ (4a) → [b]	180–310	208	269, 298
$[NiL_2(H_2O)_2]SO_4$ (5) → NiL_2SO_4 (5a)	50–104	67, 85	–
$[NiL_2SO_4]$ (5a) → $[NiL_2SO_4]$ (5b)	178–193	187	–
$[NiL_2SO_4]$ (5b) → $NiLSO_4$ (5c)	208–242	228	–
$NiLSO_4$ (5c) → $NiSO_4$	306–410	–	332
$[NiL_2(H_2O)_2]SeO_4$ (6) → $[NiL_2SeO_4]$ (6a)	52–100	88	–
$[NiL_2SeO_4]$ (6a) → $NiLSeO_4$ (6b)	172–248	237	–
$NiLSeO_4$ (6b) → $NiSeO_4$	260–282	–	278
$[NiL_2(H_2O)_2](CF_3SO_3)_2$ (7) → $[NiL_2(CF_3SO_3)_2]$ (7a)	88–150	126	–
$NiL_2(CF_3SO_3)_2]$ (7a) → [b]	208–400	240[a], 405	–
$[NiL_2(CF_3CO_2)_2]$ (8) → [b]	180–260	190[a]	–
$[NiL_2(CCl_3CO_2)_2]$ (9) → [b]	110–300	152	112, 280

[a] Peak due to melting.
[b] Decompositions are complicated.

are more or less independent of the diamines. The halides and sulphate ions are thermally stable in the temperature range where the bis-diamine complex starts to lose diamine. Thus, the effect of anion as well as diamine variation can be studied only with these complexes. In general, it has been found that the alkyl substituents on the N– of the diamines reduce the thermal stability of the complex; the larger the number and size of the substituents, the lower is the decomposition temperature (Table 3). It is also of interest to note that the chloride complexes of the bis-diamine compounds are almost invariably less thermally stable than the corresponding bromide or iodide complexes; the greater coordination ability of Cl^- to the metal is probably responsible for this.

Table 3
Initial decomposition temperatures, T_i (°C) of $Ni(diamine)_2X_2$ [3, 10–20]

Diamine[a]	X				
	Cl^-	Br^-	I^-	SO_4^{2-}	SeO_4^{2-}
en	279	280	325	[b]	[b]
Nmen	232	248	260	285	270
Neen	222	255	250	248	258
Npen	210	270	280	250	240
NNdmen	174	212	[b]	220	202
NN'dmen	225	255	[b]	255	250
pn	242	225	[b]	225	265
ibn	208	237	275	300	305
npda	210	230	225	260	240
NN'deen	135	152	178	208	172

[a] en, ethane-1,2-diamine; Nmen, *N*-methylethane-1,2-diamine; Neen, *N*-ethylethane-1,2-diamine; Npen, *N*-propylethane-1,2-diamine; NNdmen, *N,N*-dimethylethane-1,2-diamine; NN'dmen, *N,N'*-dimethyl ethane-1,2-diamine; pn, propane-1,2-diamine; ibn, 2-methylpropane-1,2-diamine; npda, *N'*-isopropyl-2-methylpropane-1,2-diamine; NN'deen, *N,N'*-diethylethane-1,2-diamine.

[b] datum is not available.

4. Conclusions

Mono-diamine species, $NiLX_2$ (X is Cl^-, Br^-, $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) have been synthesised pyrolytically in the solid state from their respective parent diamine complexes. $NiLX_2$ (X is Cl^- or Br^-) is not hygroscopic, whereas $NiLX_2$ (X is $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) are hygroscopic. $[NiL_2(H_2O)_2](CF_3SO_3)_2$ and $[NiL_2(H_2O)_2]Br_2$ show thermochromism on dehydration. Dehydration–anation reactions in $[NiL_2(H_2O)_2]X_2$ (X is $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) result in *trans*→*cis* octahedral transformations unlike $[NiL_2(H_2O)_2]X_2$ (X = Cl^-, Br^-, I^-, $CF_3SO_3^-$, $CF_3CO_2^-$ or $CCl_3CO_2^-$) where a *trans*→*trans* transformation, takes place. Only NiL_2SO_4 shows an endothermic, reversible phase transition.

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