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Thermal studies of bis(2-aminoethyl)methylamine complexes of nickel(II) in the solid state

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Abstract

$[NiL_2]X_2{\cdot}nH_2O$ (where L is bis(2-aminoethyl)methylamine, and $n=0$ when X is Cl^-, Br^-, SCN^- and CF_3COO^-, $n=3$ when X is $0.5SO_4{}^{2-}$ and $0.5SeO_4{}^{2-}$) and $NiLX_2{\cdot}nH_2O$ ($n=0$ when X is Cl^-, Br^-, $NO_3{}^-$, $n=1$ when X is CF_3COO^- and $n=3$ when X is $0.5SO_4{}^{2-}$ and $0.5SeO_4{}^{2-}$) have been synthesized and investigated thermally in the solid state. All the bis, as well as monotriamine complexes possess octahedral geometry. $[Nil_2](SCN)_2$ upon heating undergoes irreversible phase transition (155–180°C; $\Delta H = 5.6$ kJ mol^{-1}) yielding an isomeric species which on further heating shows reversible phase transition (182–205°C for heating, $\Delta H = 2.8$ kJ mol^{-1}; 170–200°C for cooling, $\Delta H = -2.8$ kJ mol^{-1}) and $[NiL_2]SO_3{\cdot}3H_2O$ undergoes an endothermic phase transition after deaquation 172–200°C; $\Delta H = 6.8$ kJ mol^{-1}). $Nil(NO_3)_2$ also shows a phase transition (195–220°C; $\Delta H = 8.9$ kJ mol^{-1}). The phase transitions are proposed to be due to the conformational change in the chelate rings of the triamine. $NiLAO_4{\cdot}3H_2O$ (A = S or Se) exhibit thermochromism, blue-to-greenish-blue for elimination of two molecules of water and greenish-blue-to-light-green for elimination of the residual water molecule. The effect of methyl substitution in N^2 – position of bis(2-aminoethyl)amine is not noticeable with respect to thermal stability of the complexes, but is pronounced in the case of thermally induced solid-state isomerization. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Bis(2-aminoethyl)methylamine; Nickel(II) complexes; Phase transition; Thermochromism; Thermal studies

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1. Introduction

Synthesis and characterization of unsubstituted triamine such as bis(3-aminopropyl)amine(dpt), (2-aminoethyl)(3-aminopropyl)amine(aepn) and bis(2-aminoethyl)amine(dien) complexes of transition and nontransition metals are well documented [1–7]. A systematic investigation of their thermal properties in the solid state has been reported [8,9] by this laboratory. The results are very encouraging and lead us to generalize that the thermal stability of the complexes decreases as the chain length of the triamine increases and the triamine, dien, is found to be more efficient in undergoing thermally induced isomerization in comparison to other triamines.

In the case of diamine complexes, it was observed that *N*-alkyl substitution played an important role in exhibiting conformational as well as configurational isomerism [10–12]. It is presumed that alkyl substitution in the N^2-position of DIEN ($NH_2{}^1$–CH_2–CH_2–$NH_2{}^2$–CH_2–CH_2–$NH_2{}^3$) may give rise to novel nickel(II) complexes showing thermally induced phase transition in the solid state. Searle et al. [13] and Fujita et al. [14] have reported cobalt(III) complexes with this alkyl substituted triamine. Recently, this

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Table 1
Elemental analyses, magnetic and electronic(mull) spectral data of bis(2-aminoethyl)methylamine(L) complexes of nickel(II)

Complex	No.	Colour	Elemental analysis/% [a] C	H	N	μ_{eff}/(B.M)	λ_{max}/nm
$[NiL_2]Cl_2$	**1**	pink	33.0(33.0)	8.4(8.2)	23.1(23.1)	3.0	527.0
$NiLCl_2$	**2**	light-blue	24.3(24.3)	5.8(6.0)	16.7(17.0)	3.0	632.5
$[NiL_2]Br_2$	**3**	pink	26.7(26.5)	6.3(6.6)	18.3(18.5)	3.0	530.5
$NiLBr_2$	**4**	green	17.8(17.9)	4.3(4.5)	12.2(12.5)	3.2	665.5
$[NiL_2]SO_4{\cdot}3H_2O$	**5**	pink	26.8(27.1)	7.9(8.1)	18.6(18.9)	3.1	530.5
$NiLSO_4{\cdot}3H_2O$	**6**	light-blue	18.4(18.4)	6.2(6.4)	12.6(12.9)	3.2	606.0
$[NiL_2]SeO_4{\cdot}3H_2O$	**7**	pink	24.5(24.5)	7.4(7.3)	17.0(17.1)	3.1	530.0
$NiLSeO_4{\cdot}3H_2O$	**8**	light-blue	16.0(16.1)	5.4(5.6)	11.1(11.3)	3.1	616.0
$[NiL_2](NCS)_2$	**9**	pink	35.0(35.2)	7.4(7.3)	27.3(27.4)	3.0	530.5
$NiL(NO_3)_2$	**10**	light-blue	20.2(20.0)	4.8(5.0)	23.1(23.3)	3.2	605.0
$[NiL_2](CF_3COO)_2$	**11**	pink	24.3(24.3)	5.1(5.0)	14.3(14.2)	3.0	565.0
$NiL(CF_3COO)_2{\cdot}H_2O$	**12**	light-blue	25.7(25.7)	4.0(4.0)	9.9(10.0)	3.2	597.4

[a] Percentages in parentheses are theoretically calculated values.

laboratory reported syntheses and single-crystal structures of $[NiL_2](NO_3)_2$ and $[NiL_2](CF_3COO)_2$ [15] which exist in the *s-fac* and *mer* forms, respectively. Here synthesis, characterization and thermal studies of bis(2-aminoethyl)methylamine(L) complexes of NiX_2 ($X = Cl^-$, Br^-, $0.5SO_4^{2-}$, $0.5SeO_4^{2-}$, NCS^-, NO_3^-, CF_3COO^-) have been reported.

2. Experimental

High-purity bis(2-aminoethyl)methylamine (medien) was purchased from Aldrich and used as received. All other chemicals were of AR grade. Thermal analysis (TG-DTA) was carried out using Shimadzu DT-30 thermal analyzer in a dynamic atmosphere of nitrogen (flow rate: 30 ml min^{-1}). The sample (particle size within 150–200 mesh) was heated in a platinum crucible at a rate of $10^\circ C\ min^{-1}$ with inert alumina as reference. The enthalpy changes of phase transitions were calculated by means of a Perkin–Elmer DSC-7 differential scanning calorimeter using indium metal as calibrant. Elemental analyses, IR spectra (at ambient temperature), electronic spectra (mull) (190–900 nm) and magnetic susceptibility were measured with a Perkin–Elmer 240C elemental analyzer, a Perkin–Elmer IR 783, a Shimadzu UV 2100, and EG and G PAR 155 vibrating sample magnetometer respectively. X-ray powder diffraction patterns were taken using a Seifert XRD-3000P, where the source of X-rays was Cu-radiation (30 KV/30 mA); the prime slits were 3 mm/Soller/2 mm and the secondary slits were Soller/0.2 mm. The high-temperature (up to 200°C) IR and far-IR spectra were recorded by homemade high-temperature sample holder with a Jasco IRA3 IR spectrophotometer and a Nicolet FTIR spectrometer.

2.1. Preparation of the complexes

$[NiL_2]Cl_2$(**1**), $[NiL_2]Br_2$(**3**), and $[NiL_2](SCN)_2$(**9**) $[NiL_2](CF_3COO)_2$(**11**) were prepared by adding triamine (2 m mol) dropwise with constant stirring to the corresponding metal salt (1 m mol) dissolved in methanol (10 ml). The resulting mixture was filtered and the filtrate was kept in a desiccator for a few days. The fine crystals were collected, washed with methanol and stored in a desiccator. The mono-triamine complexes (2, 4, 10, and 12) (Table 1) were obtained by mixing triamine to metal salt in a 1 : 1 ratio.

$[NiL_2]AO_4{\cdot}3H_2O$[A = S(**5**) or Se(**7**)] were prepared by adding triamine (2m mol) dropwise with constant stirring to the corresponding metal salt (1 mmol) dissolved in a minimum quantity of water (5 ml). The resulting solution, on treatment with isopropanol (5 ml), yielded pink crystals. They were separated, washed with isopropanol and stored in a desiccator. The mono-triamine analogues (**6** and **8**) (Table 1) were obtained by adding triamine to metal salts in 1 : 1 ratio.

3. Results and discussion

Bis complexes of bis(2-aminoethyl)amine(dien) may exist in three isomeric forms, namely *s-fac*, *u-fac* and *mer* [16–19]. The *mer* isomer is thermodynamically the most stable and this is the most common geometry of the bis triamine complexes reported so far. For the dien complexes, IR spectroscopy has been found to be a valuable method for the characterization of the different isomeric forms [17]. However, Searle et al. [13] and Fujita et al. [14] isolated only *s-fac* isomer of $[Co(medien)_2]^{3+}$ and showed that equilibrium geometric isomer distribution of $[Co(medien)_2]^{3+}$ is *s-fac* : *s-fac* : *mer* $=100:0:0$. Further, the single-crystal structure analyses of $[Ni(medien)_2](NO_3)_2$ and $[Ni(medien)_2](CF_3COO)_2$ reveal that they possess *s-fac* and *mer* octahedral geometries, respectively. The IR spectra of all the bis complexes have been compared with the above two structurally characterized complexes and found to be similar to the spectrum of $[Ni(medien)_2](NO_3)_2$, thereby suggesting that the bis complexes exist in the *s-fac* geometrical isomeric form.

All the mono complexes are octahedral, as is evident from their magnetic and electronic spectral data (Table 1). Recently, this laboratory reported single-crystal structures of $[\{Ni(medien)(NCS)\ (\mu SCN)\}_n]$, $[Ni_2(dien)_2(NCS)_4(H_2O)]$ and $[Ni(aepn)(NCS)_2]_n$ [7,20], where all of them possess octahedral geometries, thus corroborating the above statement. The far-IR spectrum of Ni LCl_2 shows bands at 163, 220 and 236 cm^{-1} for ν(Ni–Cl); the band appearing at 163 cm^{-1} is interpreted as ν_b(Ni–Cl) whilst the bands at 220 and 236 cm^{-1} are interpreted as ν_t(Ni–Cl) [21]. In the case of $NiLBr_2$, these bands shift to 145 cm^{-1}, 156 cm^{-1} for ν_b (Ni–Br) and 220, 236 cm^{-1} for ν_t(Ni–Br) [22]. It may therefore be presumed that both $NiLX_2$[X = Cl(**2**) and Br(**4**)] possess dimeric octahedral structure having two bridgings and two terminal X-atoms. The complexes, $NiLAO_4{\cdot}3H_2O$ [A = S(**6**) or Se(**8**)] are also octahedral, as is evident from their electronic spectral and magnetic data (Table 1). It is difficult to predict coordination of $SO_4{}^{2-}/SeO_4{}^{2-}$ as well as water molecule to nickel(II) from IR spectra. But, TG-DTA analyses (vide infra) reveal that at least one molecule of water is coordinated to nickel(II). Thus, the tentative structures stand at either $[NiL\text{-}\ (H_2O)_3]AO_4$ or $[NiL(H_2O)AO_4]{\cdot}2H_2O$ (A = S or Se). There is report on the synthesis of single crystal of $Ni(dpt)SO_4{\cdot}3H_2O$ only amongst the above analogous species which exists as $[Ni(dpt)(H_2O)_2SO_4]{\cdot}H_2O$[**8c**]. Repeated attempts at synthesising single crystals of (**6**) and (**8**) were not successful. In case of $NiL(NO_3)_2$, to ascertain the coordination mode of nitrate, the IR spectrum in Nujol in the 1700–1800 cm^{-1} range was taken. Three bands, 1710(br), 1730 and 1760 cm^{-1} were observed in the 1700–1800 cm^{-1} region. In general, mixed monodentate-bidentate-nitrato complex shows four combination bands in the 1700–1800 cm^{-1} region because a pair of frequencies is generated from each coordination mode [23], although occasionally two may overlap. There is no simple way of identifying which modes belong to which coordination mode. The foregoing facts hint that the complex possesses one nitrate as bidentate ($\Delta = 50\ cm^{-1}$). And to satisfy the octahedral geometry around nickel(II), the remaining nitrate group should act as a monodentate species. Molar conductance in methanol ($\Lambda m = 108\ ohm^{-1}$ $cm^2\ mol^{-1}$) is compatible with 1 : 1 electrolyte. The conductance value has probably arisen due to solvation of the monodentate nitrate group.

Complex $NiL(CF_3COO)_2H_2O$(**12**) is assumed to be octahedral, as seen from its electronic spectrum and magnetic susceptibility value (Table 1). The conductance datum in methanol ($\wedge m = 72.2\ \Omega^{-1}\ cm^2\ mol^{-1}$) suggests that it is a nonelectrolyte but the IR spectrum suggests that the water molecule is coordinated to nickel(II), a fact corroborated by its TG curve where dehydration is completed at ~180°C (vide infra). The above facts as well as the composition indicate that nickel(II) is coordinated by tridentate amine, two moieties of CF_3COO^- anion and a water molecule making a chromophore, N_3O_3, around it.

The complex $[NiL_2](NCS)_2$ (**9**) undergoes isomerization, upon heating, in the 155–180°C range ($\Delta H =$ 5.65 kJ mol^{-1}), thus yielding an isomeric species $[NiL_2](NCS)_2$ (**9a**) (Figs. 1 and 2). Electronic spectra and magnetic susceptibility studies of the isomeric pairs (**9**) and (**9a**) do not show any noticeable difference, excluding the possibility of configurational isomerism. However, IR active bands of triamine ligand $[\rho_w(CH_2),\tau(NH_2) + \rho_\omega(NH_2) + \nu(C\text{–}N) +$ $\nu(C\text{–}C)$ stretching vibration of skeleton $+ \rho_r(CH_2)]$ in each pair differ appreciably in the 400–1400 and 750–1150 cm^{-1} regions (Fig. 3). In our earlier study

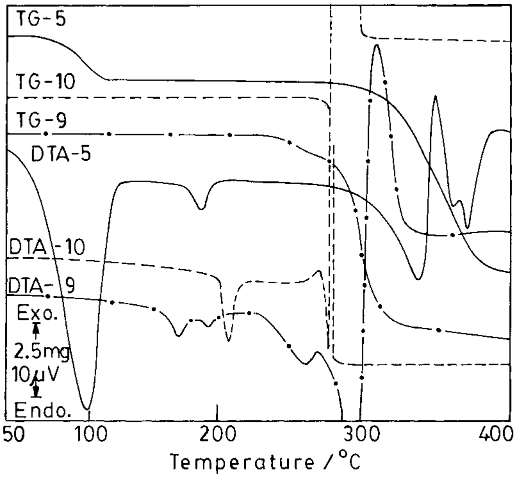

Fig. 1. TG-DTA curves: $[NiL_2]SO_4{\cdot}3H_2O$(**5**) (sample mass, 12.17 mg) (———), $NiL(NO_3)_2$(**10**) (sample mass 12.76 mg (— — —) and $[NiL_2](NCS)_2$(**9**) (sample mass, 11.15 mg) (– · – · –).

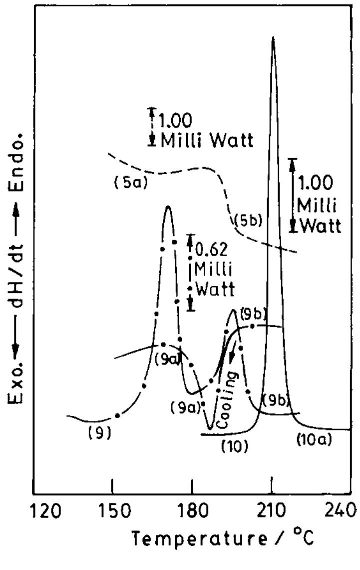

Fig. 2. DSC curves: $NiL(NO_3)_2$(**10**) (sample mass, 5.49 mg) (———) (heating curve **10**→**10a**); $[NiL_2]SO_4$ (sample mass, 6.73 mg) (— — —) (heating curve **5a**→**5b**) and $[NiL_2](NCS)_2$ (sample mass, 5.85 mg) (– · – · –) (heating curves **9**→**9a** and **9a**→**9b**; cooling curve **9b**→**9a**).

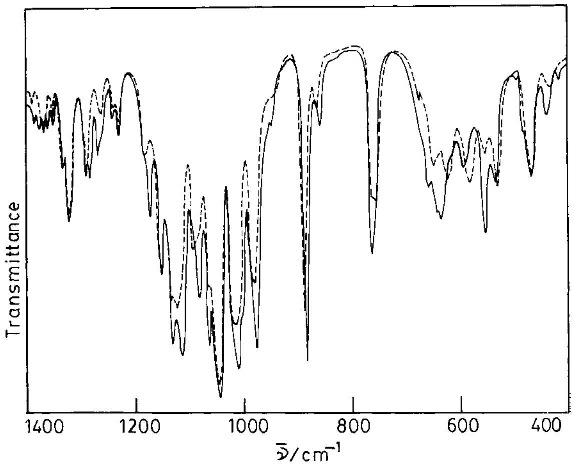

Fig. 3. IR spectra of $[NiL_2](NCS)_2$(**9**) (———) and $[NiL_2]$-$(NCS)_2$(**9a**) (— — —).

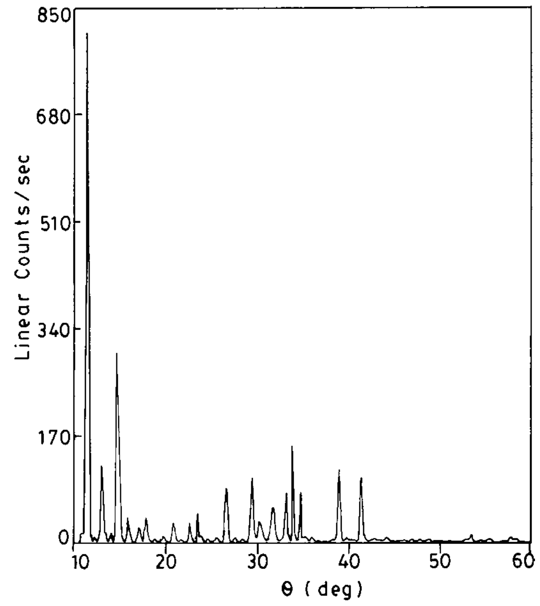

Fig. 4. XRD-powder patterns of $[NiL_2](NCS)_2$(**9**).

[24], two conformational isomers of $[NiL_2](NCS)_2$ (L = *NN′*-dimethylethane-1,2diamine) which were characterized by X-ray single-crystal analysis, showed a similar difference in their spectra. X-ray powder diagrams of (**9**) and (**9a**) are shown (Figs. 4 and 5) and indexing of peaks has been done. The initial cell parameters have been determined from powder diffraction data using the programme TREOR [25] and lattice parameters were obtained by least-squares refinement. The results are summarized in Tables 2 and 3, revealing the difference between the pairs (**9**) and (**9a**). Similar differences have been found in our

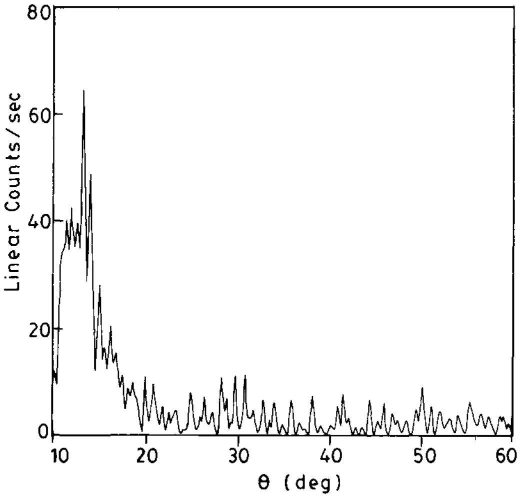

Fig. 5. XRD-powder patterns of [NiL$_2$](NCS)$_2$(**9a**).

Table 2
X-ray powder diffraction data of [NiL$_2$](NCS)$_2$(**9**). Crystal system = monoclinic; $\lambda = 1.540598$ Å; $a = 15.97(2)$ Å; $b = 15.04(1)$ Å; $c = 7.89(1)$ Å; $\beta = 98.56(2)^\circ$, and $V = 1873.9$Å^3

h	k	l	$2\theta_{\mathrm{obs}}$	$2\theta_{\mathrm{calc}}$
0	0	1	11.307	11.333
1	2	0	13.061	13.031
−2	0	1	14.742	14.712
−2	1	1	15.858	15.853
2	0	1	17.067	17.109
1	2	1	17.865	17.846
2	2	1	20.825	20.813
−1	0	2	22.589	22.633
0	1	2	23.523	23.543
−2	2	2	26.619	26.689
−5	1	1	29.465	29.459
1	5	0	30.241	30.230
2	5	0	31.785	31.816
0	4	2	33.102	33.069
−5	0	2	33.771	33.716-0
0	1	3	34.995	34.989
0	3	3	38.976	38.989
5	5	0	41.424	41.420

Table 3
X-ray powder diffraction data of [NiL$_2$](NCS)$_2$(**9a**). Crystal system = monoclinic; $\lambda = 1.540598$ Å; $a = 16.59(1)$ Å; $b = 11.92(2)$ Å; $c = 8.73(1)$ Å; $\beta = 93.54(1)$ Å $V = 1724.1$ Å^3

h	k	l	$2\theta_{\mathrm{obs}}$	$2\theta_{\mathrm{calc}}$
−1	0	1	11.224	11.168
1	0	1	11.754	11.754
2	1	0	13.013	13.007
1	1	1	13.850	13.907
0	2	0	14.867	14.846
3	0	0	16.040	16.044
−3	0	1	18.489	18.473
−3	1	1	19.923	19.927
−1	0	2	20.776	20.739
2	3	0	24.829	24.828
−3	1	2	26.323	26.324
−5	0	1	28.209	28.205
−4	1	2	29.767	29.769
3	2	2	30.818	30.787
5	2	2	38.168	38.208
−5	4	1	41.564	41.606
−2	4	3	44.416	44.387
1	6	0	45.936	45.955
3	6	1	50.078	50.065
−5	2	4	51.038	51.043
4	5	3	55.295	55.299

earlier studies [26,27] in X-ray powder diffraction patterns of the isomers which did not differ in their coordination geometries. Therefore, the X-ray powder diffraction patterns of the pair (**9**,**9a**) are not inconsistent with the conclusion that they are conformational isomers, that is to say they differ in the spatial orientation of five-membered chelate rings. In view of the decrease of cell volume, the high-temperature molecular framework becomes more compact, making the transition irreversible. The prediction of an exact three-dimensional structure of these two isomers is difficult unless X-ray single-crystal structures are determined. An attempt was made to synthesize single crystals of both the isomers, but unfortunately this did not materialize. The species (**9a**), upon further heating, also undergoes isomerization to the isomer (**9b**), which reverts to (**9a**) on cooling. Characterization of the high-temperature species (**9b**) could not be done, but it is fact that (**9b**) is also isomeric to (**9**).

NiL$_2$SO$_4$·3H$_2$O (**5**) starts dehydration at ~65°C and becomes anhydrous (**5a**) at ~125°C. The dehydrated species (**5a**), on further heating, undergoes a phase transition (172–200°C, $\Delta H = 6.8$kJ mol^{-1}) [Figs. 1 and 2] yielding NiL$_2$SO$_4$ (**5b**). The species (**5b**) cannot be stored and it reverts on storing it in a humid atmosphere for a few minutes after cooling to ambient temperature. The IR spectra of (**5**), (**5a**) and (**5b**) were recorded but band positions responsible for the occurrence of conformational changes in the chelate ring remained unaltered. Besides, the probability of configurational isomerism is ignored as two tridentate amines remain ligated to nickel(II). As a result, it is likely to presume that the phase transition is due to conformational change in the chelate ring.

$NiL(NO_3)_2$ (**10**) also shows a phase transition (195–220°C, $\Delta H = 8.9 kJ mol^{-1}$) [Figs. 1 and 2] yielding its isomeric species $NiL(NO_3)_2$ (**10a**). The species (**10a**) reverts in the same manner as (**5b**). The IR spectra of (**10**) and (**10a**) also do not provide information like (**5a**) and (**5b**). Here, the species (**10**) may undergo configurational isomerism. As the accommodation of one of the nitrates as a bidentate, and the other as a monodentate, may destabilize the octahedral geometry upon heating, and thus forming a transient penta-coordinated species (**10a**).

The complex, $NiLSO_4{\cdot}3H_2O$ (**6**) (blue), upon heating, becomes $NiLSO_4{\cdot}H_2O$(**6a**) (greenish-blue) at ~130°C whereas the monohydrate species (**6a**), upon further heating, transforms to the dehydrated species, $NiLSO_4$ (**6b**) (light-green) at ~212°C. This is evident from its TG-DTA curves (Fig. 6) which differ from the analogous Ni (N–N–N) $AO_4{\cdot}nH_2O$ complexes (A = S or Se; N–N–N = dien or dpt, when $n = 3$, and N–N–N = aepn, when $n = 4$); here, dehydration takes place in a single step. The monohydrate (**6a**), as well as dehydrated species (**6b**), revert on exposure to a humid atmosphere (RH above ~60%). However, the species (**6b**) may be stabilized in Nujol mull for a few minutes. The foregoing facts suggest that the colour changes, blue to greenish-blue and greenish-blue to light-green are proposed to be due to the change in the coordination environment around nickel(II). The electronic spectrum (Nujol mull) of (**6b**) reveals that there is a red shift (606–647 nm and 360–396 nm) in (**6b**) with respect to its trihydrate species (**6**). An attempt has been made to measure the magnetic susceptibility of (**6b**) and the value is slightly higher than its trihydrate species.[1] The IR spectra at 30°, 130° and 212°C, respectively, are recorded. It is observed that there is no visible change in the spectral pattern amongst (**6**), (**6a**) and (**6b**).

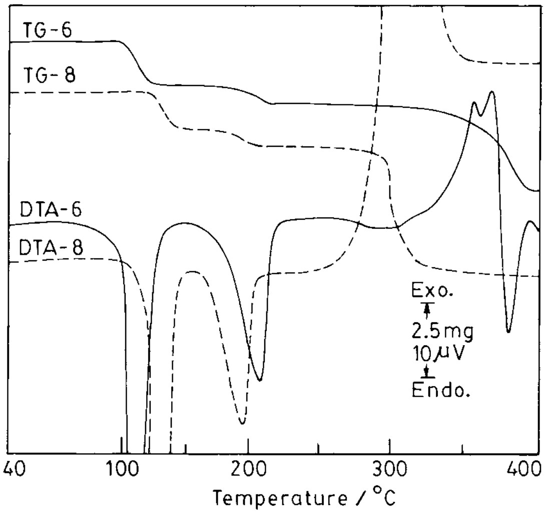

Fig. 6. TG-DTA curves: $NiLSO_4{\cdot}3H_2O$(**6**) (sample mass, 11.00 mg) (———), $NiLSeO_4{\cdot}3H_2O$(**8**) (sample mass 11.86 mg) (— — —).

Upon heating the complex, $NiLSeO_4{\cdot}3H_2O$(**8**) also loses water molecules accompanied by colour change, like its sulphate analogue (Fig. 6). Electronic spectral bands of (**8b**) shift to longer wavelengths with respect to its trihydrate (**8**). Magnetic susceptibility value of (**8b**) is slightly high in comparison to (**8**).[2] High-temperature IR spectra of $NiLSeO_4{\cdot}H_2O$ (**8a**) and $NiLSeO_4$ (**8b**) show some noticeable difference in the 500–1750 and 2750–3500 cm^{-1} regions [Fig. 7]. The colour changes associated with dehydration are expected to be due to similar causes reported for its sulphate analogue (vide supra).

$[NaL_2]AO_4{\cdot}3H_2O$ [A = S (**5**) or Se (**7**)] starts dehydration at 65° and 60°C, respectively, in a single step. Both, the dehydrated species and $[NiL_2]X_2$ (where $X = Cl^-, Br^-, SCN^-, NO_3, CF_3COO^-$) decompose at 310°, 292°, 230°, 265° and 225°C, respectively, without showing any intermediate complex species [Figs. 1 and 8]. $NiL(CF_3COO)_2{\cdot}H_2O$ (**12**) loses its water molecule in the 145–180°C range, [Fig. 8]. The dehydrated species becomes hydrated in a humid atmosphere (RH above ~60%). The monotriamine complex species, $NiLX_2$ ($X = Cl^-, Br^-, 0.5SO_4{}^{2-}, 0.5SeO_4{}^{2-}, NO_3{}^-, CF_3COO^-$) decompose at 270°, 285°, 310°, 265° and 210°C, respectively [Fig. 8].

In general, bis complexes of dien, upon heating, show decomposition through the formation of monotriamine complex as an intermediate in the solid state [1]. But on methyl substitution in the N^2-position, the

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[1] Partial hydration takes place even on cautions experimentation, resulting in a small deviation in magnetic susceptibility values.

[2] See Footnote 1.

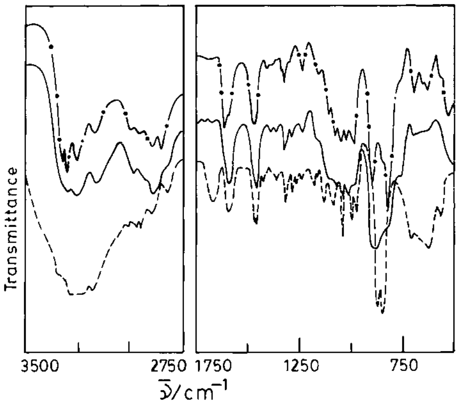

Fig. 7. IR spectra of $NiLSeO_4{\cdot}3H_2O$(**8**) at 27°C (— — —), 140°C (———) and 205°C (– · – · –).

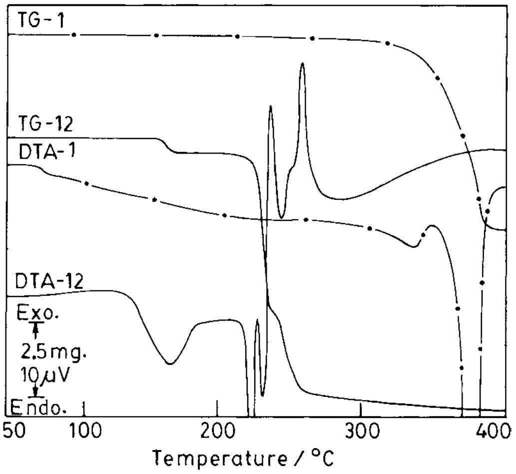

Fig. 8. TG-DTA curves: $NiL(CF_3COO)_2{\cdot}H_2O$(**12**) (sample mass, 12.43 mg) (———), and $[NiL_2]Cl_2$(**1**) (sample mass, 9.52 mg) (— — —).

thermal profile shows no such intermediate. Although the variation in initial temperature of decomposition amongst the bis as well as monotriamine complexes of bis(2-aminoethyl)amine and bis(2-aminoethyl)methylamine are not so noticeable (Table 4), it is noteworthy that $Ni(dien)_2X_2$ ($X = Cl^-$, Br^-, CF_3COO^-, $CF_3SO_3^-$, BF_4^-, ClO_4^-, SCN^-) show thermally induced phase transitions, whereas the present ligand exhibits phase transition in NiL_2X_2 ($X = SCN^-$, $0.5SO_4^{2-}$) and $NiL(NO)_3)_2$ only.

Table 4
Comparable chart for the initial temperature (T_i) of decomposition of bis(2-aminoethyl)amine(dien) and bis(2-aminoethyl)methylamine(medien)medien complexes of nickel(II)

Complex	L	
	dien	medien
$[NiL_2]Cl_2$	284	310
$NiLCl_2$	285	270
$[NiL_2]Br_2$	302	292
$NiLBr_2$	312	285
$[NiL_2]SO_4$	290	280
$NiLSO_4$	331	310
$[NiL_2]SeO_4$	260	265
$NiLSeO_4$	290	265
$[NiL_2](CF_3COO)_2$	218	225

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