ELSEVIER
Thermochimica Acta 268 (1995) 153–160
thermochimica acta

Thermal studies of N^1-isopropyl-2-methyl-1,2-propanediamine complexes of nickel(II)X_2 [$X = I^-, CF_3CO_2^-, 0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$] in the solid state

Chandi Pariya, Ashutosh Ghosh [1], Nirmalendu Ray Chaudhuri *

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received 11 September 1994; accepted 16 April 1995

Abstract

The complexes $NiL_2X_2 \cdot nH_2O$ ($L = N^1$-isopropyl-2-methyl-1,2-propanediamine; $X = 0.5SO_4^{2-}$ when $n = 0$; $X = I^-$ when $n = 2$; $X = CF_3CO_2^-$ when $n = 0$ or 2 and $X = 0.5SeO_4^{2-}$ when $n = 0$ or 3) have been synthesized and their thermal behaviour has been studied. All the hydrated complexes are yellow in colour and on heating lose water of hydration accompained by a yellow → light blue thermochromic transition, except in the case of the iodide complex, which retains the original yellow colour on dehydration. However, NiL_2I_2 undergoes an irreversible exothermic phase transition (166–193°C; $\Delta H = -7.5$ kJ mol^{-1}) with change in colour from yellow to reddish yellow. $NiL_2(CF_3CO_2)_2$ shows a reversible phase transition (heating cycle, 144–170°C; $\Delta H = 3.1$ kJ mol^{-1}; cooling cycle, 158–135°C; $\Delta H = -3.1$ kJ mol^{-1}) with no visual change in colour. All the yellow complexes possess square–planar geometry and the light blue complexes NiL_2X_2 ($X = CF_3CO_2^-, 0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$) are expected to be pentacoordinated. The phase transition occurring in NiL_2X_2 ($X = I^-$ and $CF_3CO_2^-$) is due to conformational changes of the diamine chelate rings.

Keywords: DSC; Nickel–N^1-isopropyl-2-methyl-1,2-propanediamine complexes; Phase transition; TG–DTA; Thermal decomposition; Thermochromism

---

1. Introduction

The ligand N^1-isopropyl-2-methyl-1,2-propanediamine (L) is an unsymmetrically substituted diamine having one isopropyl group on the amino group attached to C(1)

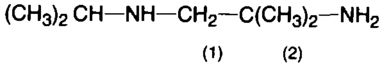
---

* Corresponding author.

[1] Present address: Department of Chemistry, Jhargram Raj College, Jhargram 721 507, West Bengal, India.

SSDI 0040-6031(95)02436-4

carbon and two methyl groups attached to the C(2) carbon of ethane-1,2-diamine.



$$(CH_3)_2CH{-}NH{-}\underset{(1)}{CH_2}{-}\underset{(2)}{C(CH_3)_2}{-}NH_2$$

(L)

The complexes of this ligand (L) with copper(II) and zinc(II) are well documented [1–7]. For the corresponding nickel(II) complex, only $[NiL_2](ClO_4)_2$ has been reported [8]. Recently, we have reported the synthesis and thermal studies of zinc(II) and cadmium(II) complexes of this ligand with various counteranions; some novel phase transition phenomena were noted [9]. Very recently, we reported [10, 11] thermal studies of NiL_2X_2 ($X = Cl^-$, Br^-, NCS^- and NO_3^-). In those studies we found that the hydrated bromide and nitrate complexes exist in square–planar geometry, whereas, dehydrated species possess either five-coordinate (chloride and bromide) or six-coordinate (nitrate and thiocyanate) octahedral geometry. The bromide and nitrate species show isomeric transformation in the solid state accompained by irreversible thermochromism. These results encouraged us to pursue further studies with other anions. The present paper reports the synthesis, characterization, thermochromism, phase transition and thermal decomposition of NiL_2X_2 ($X = I^-$, $CF_3CO_2^-$, $0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$) complexes.

2. Experimental

High purity (98%) N^1-isopropyl-2-methyl-1,2-propanediamine (L) was purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were AR grade. Thermal analysis (TG–DTA) were carried out using a Shimadzu DT-30 thermal analyser in a dynamic atmosphere of dinitrogen (flow rate: 30 $cm^3\,min^{-1}$). The sample (particle size within 150–200 mesh) was heated in a platinum crucible at a rate of 10°C min^{-1} with inert alumina as reference. The enthalpy changes of phase transitions were derived using a Perkin–Elmer DSC-7 differential scanning calorimeter and indium metal as calibrant (rate of heating/cooling 10°C min^{-1}).

Elemental analysis, IR spectra (4000–250 cm^{-1}), electronic spectra (mull) (1500–300 nm), magnetic susceptibility and conductance measurements were obtained using a Perkin–Elmer 240C elemental analyser, a Perkin–Elmer IR 783, an Hitachi U3410 UV–VIS–NIR spectrophotometer, an EG and G PAR 155 vibrating sample magnetometer and a Systronics 304 conductivity bridge, respectively.

Elemental analysis, magnetic and electronic (Nujol) spectral data are shown in Table 1.

2.1. Preparation of the complexes

$[NiL_2]I_2 \cdot 2H_2O$ (1), $[NiL_2](CF_3CO_2)_2 \cdot 2H_2O$ (2), $[NiL_2SO_4]$ (3) and $[NiL_2]SeO_4 \cdot 3H_2O$ (4) were prepared by slow addition of diamine (2 mmol) to the corresponding

Table 1
Elemental analysis, magnetic and electronic (Nujol) spectral data for N^1-isopropyl-2-methyl-1,2-propanediamine (L) complexes of nickel(II)

Complex	No.	Colour	Elemental analysis %[a]			$\mu_{eff.}$/B.M.	λmax/nm
			C	H	N		
$[NiL_2]I_2 \cdot 2H_2O$	1	Yellow	27.5(27.6)	6.7(6.6)	9.2(9.2)	Diamagnetic	450
$[NiL_2]I_2$	1a	Yellow	29.2(29.3)	6.4(6.3)	9.6(9.7)	Diamagnetic	450
$[NiL_2]I_2$	1b	Reddish yellow	29.2(29.3)	6.4(6.3)	9.6(9.7)	Diamagnetic	461
$[NiL_2](CF_3CO_2)_2 \cdot 2H_2O$	2	Yellow	37.5(37.2)	7.2(6.9)	9.4(9.6)	Diamagnetic	450
$[NiL_2(CF_3CO_2)](CF_3CO_2)$	2a	Light blue	39.8(39.6)	6.8(6.7)	10.4(10.3)	3.3	1145, 573, 354 $(\nu_2)(\nu_1)$
$[NiL_2SO_4]$	3	Light blue	39.9(40.2)	8.8(8.7)	13.1(13.4)	3.2	1181, 589, 362 $(\nu_2)(\nu_1)$
$[NiL_2]SeO_4 \cdot 3H_2O$	4	Yellow	32.3(32.5)	8.2(8.2)	10.5(10.8)	Diamagnetic	451
$[NiL_2SeO_4]$	4a	Light blue	36.3(36.3)	8.1(7.9)	12.3(12.1)	3.2	1195, 596, 366 $(\nu_2)(\nu_1)$

[a] Percentages in parentheses are theoretically calculated values.

metal salts (1 mmol) dissolved in water (10 cm^3) with constant stirring. Complexes 1 and 4 separated immediately whereas 2 and 3 were obtained on keeping the resulting yellow solution in a desiccator for a few days. They were filtered off, washed with ethanol and dried over P_4O_{10} in a desiccator.

$[NiL_2(CF_3CO_2)](CF_3CO_2)$ (2a) and $[NiL_2SeO_4]$ (4a) were prepared by the same procedure as for 1, using methanol–water (1:2) mixture as solvent.

Complexes $[NiL_2]I_2$ (1a), $[NiL_2]I_2$ (1b), $[NiL_2(CF_3CO_2)]$ (CF_3CO_2) (2a) and $[NiL_2SeO_4]$ (4a) were also prepared in the solid state pyrolytically at 125, 200, 92 and 88°C, respectively, from the corresponding parent bisdiamine complexes.

3. Results and discussion

3.1. Characterization of complexes

We have been able to synthesize only bis-diamine complexes of nickel(II) with N^1-isopropyl-2-methyl-1,2-propanediamine (L) and failed to isolate any corresponding tris-diamine complexes. Nickel(II) perchlorate yielded yellow, $[NiL_2](ClO_4)_2$ with excess diamine [8]. However in the case of cadmium(II) perchlorate, we recently reported [9] both bis-and tris-diamine complexes. The steric hindrance caused by the bulky isopropyl group on nitrogen (N^1) probably prevents the formation of the tris-diamine species in most cases.

Yellow complexes, $NiL_2I_2 \cdot 2H_2O$ (1), NiL_2I_2 (1a), $NiL_2(CF_3CO_2)_2 \cdot 2H_2O$ (2) and $NiL_2SeO_4 \cdot 3H_2O$ (4) show diamagnetic behaviour indicating square–planar geometry around nickel(II). This is corroborated by their electronic spectra which shows one relatively strong absorption band ($\lambda_{max} \sim 450$ nm) both in Nujol mull and in aqueous solution. The absorption coefficient in aqueous solution is found to be 64 $l\ mol^{-1}\ cm^{-1}$. Moreover, the conductance data of these complex species in water are ~ 110 $cm^2\ mol^{-1}\ \Omega^{-1}$, indicating non-involvement of the anion in the nickel(II) coordination sphere. Conversely, $NiL_2(CF_3CO_2)_2$ (2a), NiL_2SO_4 (3) and NiL_2SeO_4 (5a) are light blue in colour and their magnetic susceptibility values are in the order of 3.1 B.M. (Table 1). We could not isolate single crystals. However, the ν_2/ν_1 ratio in electronic spetra (ν_1 is assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and the second main peak, ν_2, ${}^3A_{2g} \rightarrow {}^3T_{1g}$) for the octahedral complex has been found to be ~ 1.74 [10, 12] and for the pentacoordinated species it is ~ 2 [11, 13]. The ν_2/ν_1 ratio of all the light blue complexes 2a, 3 and 4a reported here are found to be ~ 2, thus the pentacoordinated geometry is suggested for all of them. It is interesting to note that these pentacoordinated species become square–planar species in aqueous solution, as is evident from the appearance of a single absorption band in the electronic spectra ($\lambda_{max} = \sim 450$ nm), characteristic of square–planar nickel(II) and 1:2 electrolytic behaviour in water ($\Omega_m = \sim 110\ cm^2\ mol^{-1}\ \Omega^{-1}$).

3.2. Phase transition in $[NiL_2]I_2 \cdot 2H_2O$ (1)

The yellow complex $[NiL_2]I_2 \cdot 2H_2O$ (1) upon heating loses two molecules of water in two overlapping steps, as is evident from the TG–DTA curves (Fig. 1), without any

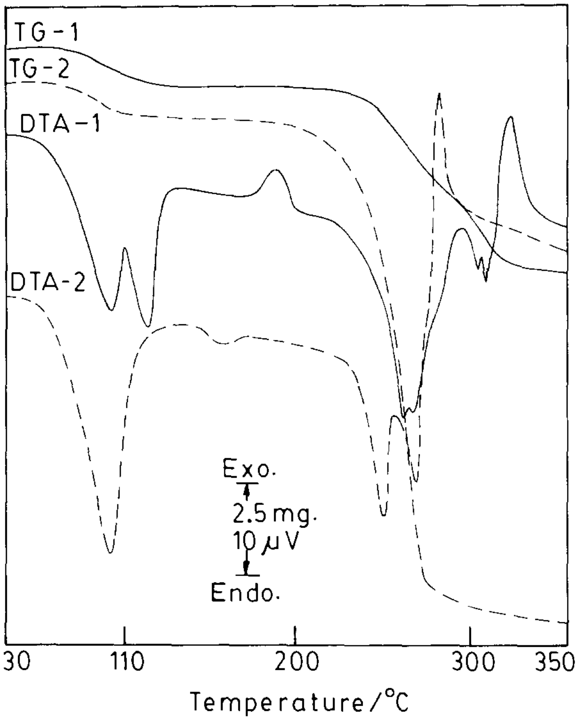


Fig. 1. TG–DTA curves : ——, $[NiL_2]I_2 \cdot 2H_2O$ (1) (sample mass, 12.58 mg); and – – –, $[NiL_2](CF_3CO_2)_2 \cdot 2H_2O$ (2) (sample mass, 16.10 mg).

visual colour change and is transformed to $[NiL_2]I_2$ (1a) at ca 125°C. This, on further heating, undergoes an irreversible exothermic phase transition (166–193°C; $\Delta H = -7.5$ kJ mol^{-1}; Fig. 2) being transformed into $[NiL_2]I_2$ (1b) accompained by yellow → reddish yellow thermochromism. Species 1a and 1b are both transformed to $[NiL_2]I_2 \cdot 2H_2O$ (1) on leaving in an open atmosphere for several days, but these can be stored in a desiccator over P_4O_{10}. Complex 1b does not revert to 1a directly without being hydrated $[NiL_2]I_2 \cdot 2H_2O$. It should be noted that although the species 1b is the thermodynamically favoured phase, the 1a → 1b transition does not occur at ambient temperature, indicating a large barrier to transition. Complex 1b is also diamagnetic. It shows an electronic spectral band at 461 nm in Nujol indicating that square–planar geometry is retained, although the band position is shifted (11 nm). The IR spectra of (1a) and (1b) differ appreciably in the regions 3300–3100, ~ 1600, 1400–1300 and 950–850 cm^{-1}, where major changes occur in the νNH_2, δNH_2, $\rho_w(CH_2)$ and skeletal vibration regions. A similar change in IR spectra was found in thermochromic $[ML'_2](ClO_4)_2$ (M = Cu 11 and Ni 11, L' = N,N-diethylethane-1,2-diamine) and in $[NiL_2](ClO_4)_2$ (L'' = N,N'-dimethyl-1,2-ethanediamine) [14, 15]. X-ray single crystal analysis of both the high and low- temperature phases of $[CuL'_2]ClO_4)_2$ reveals that the colour change is due to a sudden change of in-plane ligand field strength caused by

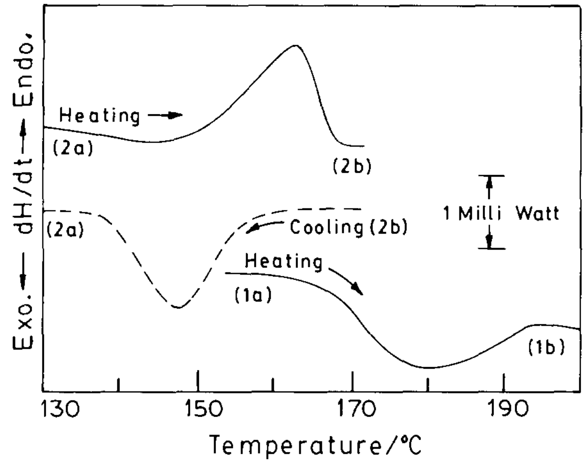


Fig. 2. DSC curves : ——, $[NiL_2]I_2$ (1a) (sample mass, 10.07 mg); and $[NiL_2CF_3CO_2](CF_3CO_2)$ (2a) (heating cycle, ——; cooling cycle, - - -) (sample mass, 8.48 mg).

Table 2

Comparative colour changes and spectral shifts for the thermochromic transition of *N,N*-diethyl-1,2-ethanediamine (L′), *N,N*′-dimethyl-1,2-ethanediamine (L″) complexes of nickel(II) perchlorate and N^1-isopropyl-2-methyl-1,2-propanediamine (L) complexes of nickel(II) iodide

Complexes	Colour change	Spectral shift/nm
$[NiL'_2](ClO_4)_2$ [a]	Orange → red	465 → 468
$[NiL''_2](ClO_4)_2$ [a]	Yellow → red	455 → 478
$[NiL_2]I_2$	Yellow → reddish yellow	450 → 461

[a] Data taken from Ref. [15].

the conformational changes of the diamine chelate rings [16]. The colour change and electronic spectral shift (Table 2) of $[NiL_2]I_2$ (1a) closely resemble those of $[NiL'_2](ClO_4)_2$ and $[NiL''_2](ClO_4)_2$. Therefore the same mechanism, i.e. conformational changes in the diamine chelate rings, is probably operative here.

3.3. *Thermochromism in* $[NiL_2](CF_3CO_2)_2\cdot 2H_2O$ (2) *and* $[NiL_2]SeO_4\cdot 3H_2O$ (4)

Yellow complexes $[NiL_2]X_2\cdot nH_2O$ ($n=2$ when $X=CF_3CO_2^-$; $n=3$ when $X=0.5SeO_4^{2-}$) upon heating lose water molecules (45–114°C; $\Delta H = 28.6$ kJ mol^{-1} and 50–98°C; $\Delta H = 18.8$ kJ mol^{-1} for 2 and 4, respectively, Figs. 1 and 3) and transform to light blue anhydrous species 2a and 4a, respectively. Dehydration occurs in each case in a single step, as is evident from the respective TG–DTA curves (Figs. 1 and 3). The yellow → light blue thermochromism is thought to be due to a square-planar (four-coordinated) to trigonal bipyramidal (five-coordinated) transformation

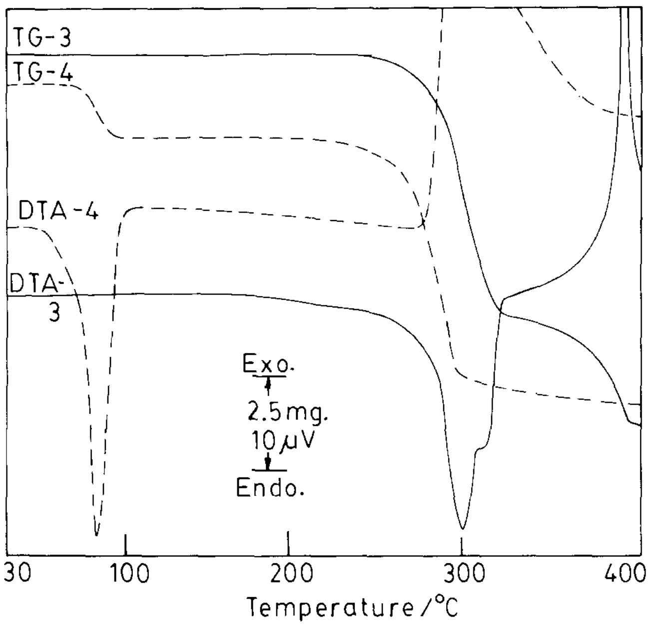


Fig. 3. TG–DTA curves : ——, $[NiL_2SO_4]$ (3) (sample mass, 14.59 mg); and - - -; $[NiL_2]SeO_4 \cdot 3H_2O$ (4) (sample mass, 12.90 mg).

around nickel(II). A similar transformation was reported in the corresponding hydrated square–planar nickel(II) bromide [10].

The anhydrous blue species 2a upon further heating undergoes a reversible phase transition (heating cycle, 144–170°C, $\Delta H = 3.1$ kJ mol^{-1}; cooling cycle, 158–135°C, $\Delta H = -3.1$ kJ mol^{-1}; Fig. 2) with no visual change in colour, whereas the species 4a does not show such a phenomenon.

3.4. Decomposition of the complexes

Dehydrated species (1b, 3 and 4a) upon heating transform to the corresponding metal salts (Figs. 1 and 3) whereas complex 2b decomposes to nickel(II) oxide in a single step. Only NiL_2SO_4 transforms to $NiSO_4$ via the hemidiamine species as an intermediate, as is evident from the plateau of the TG curve (Fig. 3). The initial temperature of decomposition (T_i) of the anhydrous complex species are 225, 210, 260 and 240°C for 1b, 2b, 3 and 4a, respectively (Figs. 1 and 3). The T_i of $[NiL_2Cl]Cl$, $[NiL_2Br]Br$ and $[NiL_2(NCS)_2]$ reported earlier [10] are 210, 230 and 210°C, respectively. Thus the role of anion on thermal stability does not appear to be very prominent.

4. Conclusion

$[NiL_2](CF_3CO_2)_2 \cdot 2H_2O$ (2) and $[NiL_2]SeO_4 \cdot 3H_2O$ (4) upon heating show irreversible yellow → light blue thermochromism. Conversely, the colour change (yellow → reddish yellow) in $[NiL_2]I_2$ (1a) is not very sharp like 2 and 4. Thermochromism occurring in 2 and 4 is due to the square–planar → trigonal bipyramidal transformation around nickel(II) and the latter is assumed to be due to a change of in-plane ligand field strength caused by the conformational changes of the diamine chelate rings. The large size of the iodide ion probably prevents its coordination in the dehydrated species unlike 2 and 4.

References

[1] J. Kansikas, Acta Chem. Scand. Ser. A:41 (1987) 533.
[2] M. Ahlgren, U. Turpeinen and R. Hamalainen, Acta Chem. Scand. Ser. A:38 (1984) 169.
[3] A. Pajunen and S. Pajunen, Cryst. Struct. Commun., 11 (1982) 539.
[4] J. Kansikas and A. Pajunen, Acta Crystallogr. Sect. B:38 (1980) 2423.
[5] A. Pajunen and S. Pajunen, Acta Crystallogr. Sect. B:35 (1979) 3058.
[6] J. Kansikas and R. Hamalainen, Finn. Chem. Lett., (1978) 118.
[7] M. Ahlgren, U. Turpeinen and R. Hamalainen, Acta Chem. Scand. Ser. A:36 (1982) 841.
[8] M. Ahlgren and P. Tilus, Acta Chem. Scand. Ser. A:37 (1983) 179.
[9] C. Pariya, A. Ghosh, S. Ganguli and N. Ray Chaudhuri, Thermochim. Acta, 242 (1994) 195.
[10] C. Pariya, S. Ghosh, A. Ghosh, M. Mukherjee, A.K. Mukherjee and N. Ray Chaudhuri, J. Chem. Soc. Dalton Trans., (1995) 337.
[11] C. Pariya, A. Ghosh and N. Ray Chudhuri, J. Chem. Res., (S), (1994) 428.
[12] M. Nonoyama, Inorg. Chim. Acta, 26 (1976) 53.
[13] W. Manch and W.C. Ferelius, J. Chem. Educ., 38 (1961) 192.
[14] R.J. Pylkii, R.D. Willett and H.W. Dodgen, Inorg. Chem., 23 (1984) 594.
[15] S. Koner, A. Ghosh and N. Ray Chaudhuri, Bull. Chem. Soc. Jpn., 63 (1990) 2387.
[16] I. Grenthe, P. Paoletti, M. Sandstrom and S. Glikberg, Inorg. Chem., 18 (1979) 2687.