Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 895-902

THERMAL STUDIES OF N-PHENYLETHANE-1,2-DIAMINE COMPLEXES OF NICKEL(II) IN THE SOLID STATE

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(Received December 19, 1997; in revised form March 16, 1998)

Abstract

$[NiL_3]X_2$ (where L=N-phenylethane-1,2-diamine and X=I^- and ClO_4^-), $[NiL_2X_2]$ (X is Cl^-, Br^-, NCS^-, $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) and $[NiL_2(H_2O)_2](NO_3)_2$ have been synthesized from solution and their thermal study has been carried out in the solid phase. $[NiL_2Cl_2]$ upon heating undergoes irreversible endothermic phase transition (142–152°C, ΔH=0.35 kJ mol^{-1}) without showing any visual colour change. This phase transition is assumed to be due to conformation changes of the diamine chelate rings. $NiLCl_2$ and $NiL_{2.5}I_2$ have been prepared pyrolytically from $[NiL_2Cl_2]$ and $[NiL_3]I_2$ respectively in the solid state. $[NiL_2(H_2O)_2](NO_3)_2$ upon heating undergoes deaquation-anation reaction without showing any visual colour change. $[NiL_2X_2]$ (X is Cl^-, Br^-, NCS^-), $[NiL_2(H_2O)_2](NO_3)_2$ and $[NiL_2(NO_3)_2]$ possess *trans*-octahedral configuration, whereas, $[NiL_2X_2]$ (X is $0.5SO_4^{2-}$ or $0.5SeO_4^{2-}$) are having *cis*-octahedral configuration. Amongst the complexes, only $NiLCl_2$ shows unusually high (5.1 BM at 27°C) magnetic susceptibility value.

Keywords: nickel(II) diamine complexes, N-phenylethane-1,2-diamine, phase transition

Introduction

Solid state thermal studies of nickel(II) complexes of ethane-1,2-diamine and its N-alkyl substituted derivatives are well documented in the literature [1–10]. It is observed that inductive and steric effect of the alkyl groups influence the thermal properties of the complexes i.e., the thermally induced phase transitions and/or decomposition of the complexes in the solid state. Similar study with analogous complexes of N-phenyl substituted derivatives of ethane-1,2-diamine is not documented and the mesomeric effect of the phenyl group *vis-à-vis* the positive inductive effect of the alkyl group and high steric effect of phenyl group make such study relevant. Here we report the syntheses and characterization of

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

N-phenylethane-1,2-diamine complexes of Ni(II)X_2 (X=Cl^-, Br^-, I^-, NCS^-, NO_3^-, ClO_4^-, $0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$), their solid state thermal properties and comparison of their thermal stability with those of analogous complexes of N-alkyl substituted ethane-1,2-diamine in the solid state.

Experimental

High purity (98%) N-phenylethane-1,2-diamine(L) was purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals used were of AR grade. The equipments used for elemental analyses, IR (4000–250 cm^{-1}) and electronic spectra (mull) (1500–300 nm), magnetic susceptibility measurements and for thermal analyses (TG-DTA and DSC) were reported earlier [11].

Commercial anhydrous nickel(II) iodide was practically insoluble in ethanol. Therefore, an ethanolic solution of nickel(II) iodide was prepared by mixing nickel(II) nitrate hexahydrate and sodium iodide in ethanol in 1:2 molar ratio and removal of sodium nitrate by filtration as described by Goodgame and Venanzi [12].

Preparation of the complexes

$[NiL_3]X_2$ (X is I^- and ClO_4^-) were prepared by slow addition of an ethanolic solution (5 cm^3) of N-phenylethane-1,2-diamine (3 mmol) to the corresponding nickel(II) salts (1 mmol) dissolved in ethanol (10 cm^3). The complexes which separated immediately were filtered, washed with ethanol and dried in a $CaCl_2$-desiccator.

$[NiL_2X_2]$ (X is Cl^-, Br^-, NCS^-, $0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$) and $[NiL_2(H_2O)_2](NO_3)_2$ were synthesized by adopting the above procedure but by changing metal-diamine ratio to 1:2.

$NiLCl_2$ (**1a**), $[NiL_2(NO_3)_2]$ (**5a**) and $NiL_{2.5}I_2$ (**3a**) were prepared in the solid state pyrolytically at 300, 120 and 185°C respectively from the corresponding parents species.

Results and discussion

Characterization of the complexes

Elemental analyses (Table 1) reveal that nickel(II) iodide and nickel(II) perchlorate form tris-diamine species, whereas, the rest nickel(II) salts yield bis-diamine species with N-phenylethane-1,2-diamine (L) and all attempts to prepare bis-species with iodide and perchlorate and tris-species with other nickel(II) salts from solution failed. IR-spectral study suggests that the diamine is chelated in all the complexes [3, 5, 10].

As a result, the tris-species appear to possess N_6-chromophore around nickel(II) and their electronic and magnetic susceptibility data conform to octa-

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

Complex	No.	Colour	Elemental analyses/%[a]			μ_{eff}/BM	λ_{max}/nm
			C	H	N		
trans-$[NiL_2Cl_2]$	**1**	blue	47.8(47.8)	6.0(6.0)	13.9(13.9)	3.1	1290, 780, 570, 360
$NiLCl_2$	**1a**	green	36.0(36.1)	4.5(4.5)	10.4(10.5)	5.1	b
trans-$[NiL_2Br_2]$	**2**	blue	39.1(39.1)	4.8(4.9)	11.2(11.4)	3.1	1300, 770, 560, 350
$[NiL_3]I_2$	**3**	pink	39.9(40.0)	4.9(5.0)	11.6(11.6)	3.2	900, 555, 370
$NiL_{2.5}I_2$	**3a**	light blue	36.8(36.8)	4.5(4.6)	10.7(10.7)	3.2	b
trans-$[NiL_2(NCS)_2]$	**4**	blue	48.3(48.3)	5.4(5.4)	13.9(13.9)	3.1	1280, 785, 565, 375
trans-$[NiL_2(H_2O)_2](NO_3)_2$	**5**	blue	39.1(39.1)	5.7(5.7)	17.1(17.1)	3.1	1310, 790, 570, 380
trans-$[NiL_2(NO_3)_2]$	**5a**	blue	42.1(42.2)	5.2(5.3)	18.4(18.4)	3.2	1290, 765, 560, 385
$[NiL_3](ClO_4)_2$	**6**	pink	43.3(43.3)	5.6(5.5)	12.5(12.6)	3.1	895, 570, 365
cis-$[NiL_2SO_4]$	**7**	blue	45.1(45.0)	5.7(5.6)	13.2(13.1)	3.1	935, 595, 385
cis-$[NiL_2SeO_4]$	**8**	blue	40.6(40.5)	5.1(5.1)	11.8(11.8)	3.1	900, 565, 340

[a] Percentages in parentheses are theoretically calculated values. [b] No well resolved spectrum

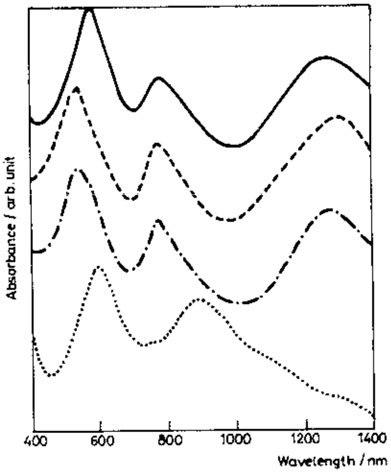

Fig. 1 Electronic spectra (mull) of *trans*-$[NiL_2Cl_2]$ (**1**) (—), *trans*-$[NiL_2Br_2]$ (**2**) (- - -); *trans*-$[NiL_2(NCS)_2]$ (**4**) (—-) and *cis*-$[NiL_2SO_4]$ (**7**) (····)

hedral geometry in them. The bis-species, $[NiL_2X_2]$, (X = Cl^-, Br^-, NCS^-, NO_3^-, $0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$), $NiL_2(NO_3)_2{\cdot}2H_2O$ and $[NiL_2(NO_3)_2]$ exhibit magnetic susceptibility value of ~3.1 BM and their electronic spectral band positions (Table 1) suggest that they should possess octahedral geometry. But these complexes may have *cis* or *trans* configuration and in order to know this configuration their electronic spectra in NIR-region have been studied. $[NiL_2X_2]$ (X= Cl^-, Br^-, NCS^- and NO_3^-) possess *trans*-octahedral configuration as they exhibit two d-d bands in NIR region [13, 14] (Fig. 1), whereas, $[NiL_2X_2]$ (X= $0.5SO_4^{2-}$ and $0.5SeO_4^{2-}$) appear to possess *cis*-configuration as they exhibit one d-d band in NIR-region [13, 14].

In order to attain *cis*-octahedral configuration, SO_4^{2-} and SeO_4^{2-} should act as bidentate chelating ligand. The actual mode of coordination of the nitrate ions in $NiL_2(NO_3)_2{\cdot}2H_2O$ and $NiL_2(NO_3)_2$ has been assigned by IR-spectral study in the region of 1700–1800 cm^{-1}, where the ν_1-symmetric stretching and the double degenerate in-plane bending mode of coordination of nitrate ion in metallic complexes have been assigned [13, 15]. The complex, $[NiL_2(H_2O)_2](NO_3)_2$ (**5**) shows only one relatively strong band at ~1750 cm^{-1} which suggests that the nitrate ions are not coordinated with the metal ion and thus indicating the coordination of two water molecules in the complex. On the other hand, $[NiL_2(NO_3)_2]$ (**5a**) exhibits two peaks at ~1755 and ~1743 cm^{-1} and the small separation (~12 cm^{-1}) between the two peaks indicates that the nitrate ions are acting as unidentate ligand in the complex. $[NiL_2(NCS)_2]$ (**4**) shows a single sharp $\nu_{(C-N)}$ band at ~2096 cm^{-1} which suggests that the thiocyanate groups are N-bonded [16].

The monodiamine species, $NiLCl_2$ (**1a**) obtained by pyrolysis of $[NiL_2Cl_2]$ (**1**) in the solid state possesses unusually high magnetic susceptibility value (5.1

BM at 27°C) considering the above formula. This may be due to the ferromagnetic behaviour which is possibly developed from the Cl^- bridging [17–19] and metal-metal interaction. The foregoing facts and the stoichiometry of the compound would require either pentacoordinated or tetracoordinated tetrahedral species [3]. IR and electronic spectra of (mull) of the species are not so well resolved. Therefore it is very difficult to comment on the structure of the complex. Another interesting species is $NiL_{2.5}I_2$ (**3a**) which is obtained by pyrolysis of $[NiL_3]I_2$ (**3**) in the solid state. Its magnetic susceptibility value (3.2 BM at 27°C) is typical of octahedral nickel(II) and its electronic spectra (Table 1) corroborates this geometry. X-ray single crystal structural analyses of these species are essential to understand the actual structure. But we could not synthesize single crystals of any of the complexes.

Thermal analysis

$[NiL_2Cl_2]$ (**1**) upon heating undergoes an endothermic phase transition (142–152°C, ΔH=1.35 kJ mol^{-1}) (Fig. 2) and gets transformed to $[NiL_2Cl_2]$ (**1a**) with no visual change in colour. The species (**1a**) on cooling to ambient temperature does not show any exotherm but on immediate reheating shows endothermic phase transition in the same temperature range with smaller peak area than that in the initial heating (Fig. 2). However, $[NiL_2Cl_2]$ (**1a**) on exposure to humid atmosphere (60% or above) for several h reverts to (**1**) as is evident from the ΔH value (Fig. 2). The above facts suggest that the reversibility of the transition is dependent on time. The species (**1a**) upon further heating decomposes and transforms to nickel(II) chloride through the formation of the intermediates, $NiLCl_2$ and $NiL_{0.5}Cl_2$ as is evident from the plateaus in the TG curve (Fig. 3). $NiLCl_2$ has

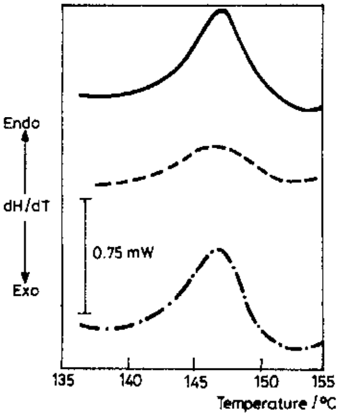

Fig. 2 DSC curves for *trans*-$[NiL_2Cl_2]$ (**1**) (wt. taken=8.1 mg); [(—) first heating curve; ΔH= 1.35 kJ mol^{-1}; (- - -) second heating curve (the sample was heated immediately after cooling to ambient temperature; ΔH=0.76 kJ mol^{-1} and (–·–), third heating curve (the sample was heated after a time gap 5 h cooling to ambient temperature), ΔH=1.33 kJ mol^{-1}]

Table 2 Initial decomposition temperatures, T_i (°C) of Ni(diamine)$_2$X$_2$[3, 8–10, 20]

Diamine[a]	*X*					
	Cl^-	Br^-	I^-	NCS^-	$0.5SO_4^{2-}$	$0.5SeO_4^{2-}$
en	279	280	325	b	b	b
Nmeen	232	248	260	222	285	270
Neten	222	255	250	224	248	258
Npren	210	270	280	b	250	240
Nipren	192	205	210	b	230	235
Nphen	200	240	b	195	270	250

[a] en, ethane-1,2-diamine; Nmeen, N-methylethane-1,2-diamine; Neten, N-ethylethane-1,2-diamine; Npren, N-prophylethane-1,2-diamine; Nipren, N-isoprophylethane-1,2-diamine; Nphen, N-phenylethane-1,2-diamine. [b] datum is not available

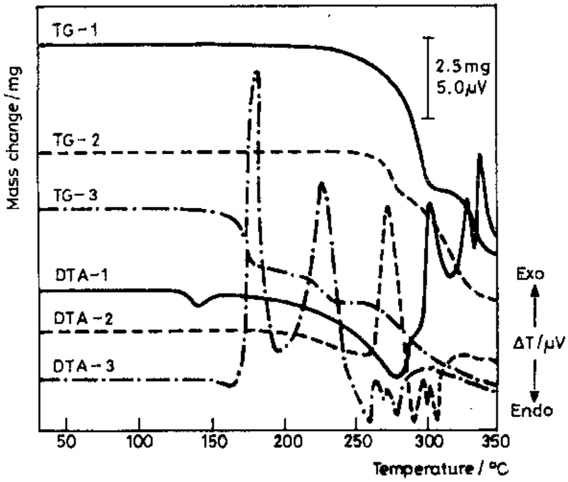

Fig. 3 TG-DTA curves for *trans*-[NiL_2Cl_2] (**1**) (—)(wt. taken= 13.30 mg); *trans*-[NiL_2Br_2] (**2**) (---)(wt. taken=12.95 mg); and [NiL_3]I_2 (**3**) (– –)(wt. taken=14.70 mg)

been synthesized pyrolytically in pure form in the solid state and characterized. But we could not prepare $NiL_{0.5}Cl_2$ in pure form [NiL_2Br_2] (2) on the other hand does not exhibit any phase transition and starts to decompose at 260°C. Its decompositions pattern is very much similar to that of (**1a**). But the plateaus corresponding to $NiLBr_2$ and $NiL_{0.5}Br_2$ are not so well resolved and all attempts to prepare them have failed. [NiL_3]I_2 (**3**) upon heating undergoes decomposition through the formation of intermediates, $NiL_{2.5}I_2$ and NiL_2I_2 as is evident from the plateaus in the TG curve. $NiL_{2.5}I_2$ may be synthesized in pure form in the solid state but synthesis of NiL_2I_2 is not feasible. [NiL_3]$(ClO_4)_2$ (**6**) as well as [$NiL_2(NCS)_2$] (**4**) upon heating do not show any phase transition before decomposition. The former decomposes at ~200°C whereas the latter at ~240°C. But in both cases there are no plateaus in the TG curves for the formation of any intermediate. [$NiL_2(H_2O)_2(NO_3)_2$ (**5**) upon heating undergoes deaquation-anation reaction without showing any visual colour change and transforms to [$NiL_2(NO_3)_2$] (**5a**) at 120°C retaining the geometry as well as chromophore (N_4O_2) around nickel(II). However [$NiL_2(NO_3)_2$] (**5a**) reverts to (**5**) on exposure to humid atmosphere (60% or above). [NiL_2SO_4] (**7**) and [NiL_2SeO_4] (**8**), on the other hand undergo decomposition without showing any plateau in the TG-curves.

Conclusions

Table 2 represents the T_i (initial temperature of decomposition) of $RNHCH_2CH_2NH_2$ (*R*=methyl/ethyl/*n*-propyl/isopropyl) and N-phenylethane-1,2-diamine complexes of nickel(II). It is observed that the sequence of T_i with respect to the counter anions for N-phenylethane-1,2-diamine complexes follows the same trend as observed with RNH–CH_2–CH_2–NH_2 i.e. SO_4^{2-}>SeO_4^{2-}> Br^->Cl^-. It is also to mention that thermal stability of with respect to Ti of N-phenylethane-1,2-diamine is very close to that of N-propylethane-1,2-diamine. Thus, mesomeric and steric effect of phenyl groups have little influence on the thermal stability/thermal properties of N-phenylethane-1,2-diamine complexes of nickel(II).

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We are grateful to Professor A. K. Pal, Department of Material Science, IACS for NIR spectra.

References

1 W. W. Wendlandt and J. P. Smith, The thermal properties of transition metal ammine complexes, Elsevier, 1967, p. 148.
2 D. R. Bloomquist and R. D. Willett, Coord. Chem. Rev., 47 (1982) 125.
3 G. De, P. K. Biswas and N. Ray Chaudhuri, Bull. Chem. Soc. Jpn., 56 (1983) 3145.
4 Y. Ihara and R. Tsuchiya, Bull. Chem. Soc. Jpn., 57 (1984) 2829.
5 G. De, P. K. Biswas and N. Ray Chaudhuri, J. Chem. Soc., Dalton Trans., (1984) 2591.
6 Y. Ihara, Y. Fukuda and K. Sone, Bull. Chem. Soc. Jpn., 59 (1986) 1825.
7 Y. Ihara, Y. Fukuda and K. Sone, Inorg. Chem., 26 (1987) 3745.
8 S. Roy, A. Ghosh and N. Ray Chaudhuri, Thermochim. Acta, 136 (1988) 191.
9 S. Roy, A. Ghosh and N. Ray Chaudhuri, Thermochim. Acta, 155 (1989) 297.
10 D. Das, A. Ghosh and N. Ray Chaudhuri, Thermochim. Acta, 2973 (1996) 1.
11 C. Pariya, A. Ghosh and N. Ray Chaudhuri, Thermochim. Acta, 268 (1995) 153.
12 D. M. L. Goodgame and L. M. Venanzi, J. Chem. Soc., (1963) 616.
13 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, Can. J. Chem., 49 (1971) 1957.
14 A. B. P. Lever, Inorganic electronic spectroscopy, 2nd edn., Elsevier, Amsterdam 1984, p. 507.
15 N. F. Curtis and Y. M. Curtis, Inorg. Chem., 4 (1965) 804.
16 K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, Wiley-Interscience, New York, 3rd edn., 1977, p. 270.
17 O. Kahn, P. Tola, J. Galy and H. Coudanne, J. Am. Chem. Soc., 100 (1978) 3931.
18 S. Foner, R. B. Frankel, H. Wong, W. M. Reiff and G. J. Long, J. Chem. Phys., 68 (1978) 4781.
19 S. O'Brien, R. M. Gaura, C. P. Landee and R. D. Willett, Solid State Commun., 39 (1981) 1333.