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SOLID STATE THERMAL PHASE TRANSITIONS AND DECOMPOSITIONS OF NICKEL (II) DIAMINE COMPLEXES

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ABSTRACT

$[NiL_2X_2]$ and $[NiL_2Br_2].2H_2O$ complexes (L= N,N'-dimethyl 1,2-ethanediamine and X=Cl^-, SCN^-, CF_3COO^- and CCl_3COO^-) have been synthesised and their TG-DTA/DSC studies have been carried out. Thermally induced phase transition phenomena of $[NiL_2X_2]$ (X = SCN^-, CF_3COO^- and CCl_3COO^-) are noticed and their probable mechanisms explored. Solid state synthesis of $[NiLCl_2]$ and $[NiL_2Cl_2]$ is achieved through pyrolysis of $[NiL_2Cl_2]$ and $[NiL_2(OOCCCl_3)_2]$ respectively.

INTRODUCTION

The solid state thermal decomposition[1], thermochromism[2] and thermally induced phase changes phenomena[3] of metal diamine complexes have drawn attention to the coordination chemists. We have also published a few papers in this area[1,3]. We report here thermal decomposition and some unusual phase changes phenomena of N,N'-dimethyl 1,2-ethanediamine(L) complexes of nickel(II).

EXPERIMENTAL AND MEASURING METHODS

The complexes $[NiL_2Cl_2]$ (1), $[NiL_2Br_2].2H_2O$ (2), $[NiL_2(NCS)_2]$ (3), $[NiL_2(OOCCCl_3)_2]$ (4) and $[NiL_2(OOCCF_3)_2]$ (5) were prepared by stoichiometric addition of the ligand to the corresponding ethanolic solution of the metal salts.

$[NiLCl_2]$ (1A) was prepared by keeping (1) at ∿270°C for ∿15 min in dinitrogen atmosphere. $[NiL_2Cl_2]$ (4C) was synthesised by keeping (4) at ∿100°C for ∿ 60 min in air oven and subsequent washing with ethanol.

Elemental analyses of these compounds are in good conformity with their composition.

Phase transitions and thermal decompositions were investigated

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with a Perkin Elmer DSC-2 Differential Scanning Calorimeter and Shimadzu DT-30 thermal analyser. Indium metal was used as calibrant for the evaluation of enthalpy changes. Details of the measuring devices were reported earlier[1,3].

RESULTS AND DISCUSSION

$[NiL_2Cl_2]$ (1) shows O_h geometry evident from its magnetic datum and electronic spectrum (Table 1). I.r. spectrum analogous to trans-$[NiL_2(NCS)_2]$(vide infra) suggests chelating character of the diamines in trans form. It decomposes at 225°C and transforms to $NiCl_2$ at 395°C through the formation of intermediates $[NiLCl_2]$ (1A) (at 281°C) and $NiL_{0.5}Cl_2$ (at 320°C). Spectral and magnetic data[4] support the O_h configuration of $[NiLCl_2]$ (1A), where diamine is chelated and halogens are bridged.

$[NiL_2Br_2].2H_2O$ (2) starts deaquation at 145°C and becomes deaquated (2A) at 200°C through the formation of monohydrate. I.r. spectra of (2) and (2A) show splitting of ν(NH) band and the existence of more than three bands in 610-500 cm^{-1} are well confirmative to its cis geometry[5]. Again, ν(NH) bands of (2) get, more split and shift to longer wave length in addition to its usual bands. This suggests the existence of H-bonding between H_2O-oxygen and N-hydrogens of the diamine in (2). Elimination of water molecules at much higher temperature also support this. The complexes (2) and (2A) possess similar magnetic and electronic spectral data (Table 1) but they differ distinctly in their i.r. spectra specially in the region of τ (NH) and ν(C-N) suggesting deaquation causes some changes in the diamine chelate skeleton[3]. (2A) decomposes at 255°C and transforms to $NiBr_2$ at 420°C through nonisolable intermediates.

The thiocyanate groups in $[NiL_2(NCS)_2]$ (3) are N-bonded and in trans positions as indicated by ν(CN) (2095 cm^{-1}) and ν(CS) (701 cm^{-1}) bands[6]. The complex transforms to an isomer(3A) showing two overlapping endothermic irreversible phase transitions upon heating (Table 2). Geometrical/linkage isomerism is not taking place due to strong trans effect[7] of NCS group and the appearance of similar ν(CN) and ν(CS) bands in the i.r. spectra of these two isomers. The configuration (O_h) of the donor atoms around the metal ion is expected to be the same in both the cases,

TABLE 1. Magnetic and pertinent electronic spectral[a] data

Compound	μ_{eff}(B.M.)	λ_{max}(nm)
$[NiL_2Cl_2]$ (1)	3.1	595,380
$[NiLCl_2]$ (1A)	3.1	740sh,690,420
$[NiL_2Br_2].2H_2O$ (2)	3.2	575,370
$[NiL_2Br_2]$ (2A)	3.2	575,370
$[NiL_2(NCS)_2]$ (3)	3.2	545,345
$[NiL_2(NCS)_2]$ (3A)	3.2	560,355sh
$[NiL_2(OOCCCl_3)_2]$ (4)	3.2	557,358
$[NiL_2(OOCCF_3)]$ (5), (5A)	3.3	565,360

[a] spectra were taken in nujol mull.

TABLE 2. Phase transitions of Ni(II) diamine complexes

Transitions (°C)	Peak temperature (°C)	ΔH, $kJmol^{-1}$
(3) $\xrightarrow{182-206}$ (3A)	190sh,199	13.4
(4) $\xrightarrow{61-72\ (i)}$ (4A)	(i) 67	(i) 3.0
$\xleftarrow{56-65.5(ii)}$	(ii) 62.5	(ii) 2.2
(4A) $\xrightarrow{92-101(iii)}$ (4B)	(iii) 99	(iii) 4.3
$\xleftarrow{67.5-83(iv)}$	(iv) 74	iv) 4.1
(5) $\xrightarrow{168-189(i)}$ (5B)	(i) 175.5,182	(i) 9.5
$\xleftarrow{169-185(ii)}$	(ii) 179.5	(ii)5.2
(5A) $\xrightarrow{172-190(iii)}$ (5B)	(iii) 182	(iii)5.3
$\xleftarrow{169-185(iv)}$	(iv) 179.5	(iv)5.2

as is evident from their absorption bands and magnetic data (Table 1). As a consequence the phase changes are presumably responsible for the conformational changes[3] of the diamine chelate rings, which is also supported by their nonidentical ν(NH), $\rho_w(CH_2)$, τ(NH) and ν(C-N) i.r. data. (3A) melts at 220°C and then decomposes to $Ni(SCN)_2$ + NiS + C at ~360°C.

In $[NiL_2(OOCCCl_3)_2]$ (4) carboxylate groups are monodentate evident from the separation of ν_s(COO) and ν_{as}(COO) bands exhibited in i.r. spectra[8]. It appears trans alike $[NiL_2(NCS)_2]$ (3). Nonbonded oxygens of the carboxylate groups are presumed to be H-bonded with amine from the i.r. spectral bands of ν(NH) and ν(COO). It undergoes two reversible endothermic phase transitions (Table 2). The value of enthalpy changes obtained in the cooling curve of the two phases appear smaller than that of heating curve showing hysteresis in the system. The investigation relating to this phase transition becomes difficult due to its reversibility. This phenomenon is presumed to occur due to opening of H-bond which becomes necessary for its decomposition although the probability of the occurrence of the conformational changes of the chelate ring cannot be ignored. (4B) on further heating decomposes at 108°C and transforms to $[\mathrm{NiL_2Cl_2}]$ (4C) along with some organic fragments. This after purification is exactly similar in properties to the compound (1).

$[\mathrm{(NiL_2(OOCCF_3)_2}]$ (5) possesses similar structure like (4), evident from its magnetic and spectral data (Table 1). It also undergoes two endothermic phase transitions (Table 2). The first peak at 175.5°C is irreversible and the second peak is reversible. Species (5B) cannot be differentiated from (5A) (Table 2) by usual magnetic and spectral data (Table 1). The probable cause for these phase transitions are expected to be same as discussed in case of (4). Irreversibility of (5A) $\rightarrow$ (5) may be due to the attainment of stable form in (5A). Higher value of ΔH as well as transition at higher temperature supports the opening of H-bonding which is very likely to have more strength than that of (4).

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