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THERMAL INVESTIGATION OF DIAMINE COMPLEXES OF NICKEL(II) IN THE SOLID PHASE

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ABSTRACT

Thermal investigations have been carried out on $[NiL_2X_2] \cdot n\ H_2O$, where L = *N,N*-diethylethylenediamine, $X = Cl^-$, SCN^- or CCl_3COO^- and $n = 2$ or 0, $[NiL_2(H_2O)_2]Br_2$ and $[NiLX_2(H_2O)_2]$, where $X = CH_3COO^-$. All the complexes are characterized by elemental analyses, magnetic and spectral [IR and electronic(mull)] data. All the complexes possess O_h symmetry. They generate several thermally isolable as well as non-isolable complex species as intermediates upon heating. Some of the intermediate species lose their original symmetry and attain either square planar or T_d symmetry. A unique feature is observed in the case of $[NiL_2(CCl_3COO)_2]$ which on heating first transforms to $[NiL_2CO_3]$ and then to $NiCO_3$ through the transformation of several non-isolable intermediate complex species. Thermal parameters have been evaluated for each step of the decomposition. The probable mechanistic paths of decomposition of these complexes have been proposed.

INTRODUCTION

Work on diamine and substituted diamine complexes is well-known. Some thermal studies of the diamine complexes have been made [1–4]. Recently, a thermal investigation of some Ni(II) diamine complexes in the solid phase was reported from this laboratory [5]. But thermal decompositions of alkyl substituted diamine complexes have not yet been carried out. Only a few workers [6–8] have investigated the thermochromism phenomenon with the Ni(II) and Cu(II) complexes of some substituted diamines. The aim of the present study is to investigate the thermal decomposition of the substituted ethylenediamine complexes of Ni(II) and to isolate the possible intermediate products formed during heating and characterize them by elemental analyses, magnetic moments and spectral and thermal data. This study also reports the evaluation of enthalpy change for each step of decomposition and the probable mechanistic path of decomposition of these diamine complexes.

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EXPERIMENTAL

All the chemicals used were of A.R. grade. Complexes $[NiL_2Cl_2]\cdot 2\ H_2O$, $[NiL_2(H_2O)_2]\ Br_2$, $[NiL_2(NCS)_2]$, $[NiL_2(CCl_3COO)_2]$ and $[NiL(CH_3COO)_2(H_2O)_2]$ were prepared by the methods reported earlier [3]. All these complexes were characterized by elemental analysis (Table 1) and spectral and magnetic data (Table 1).

Thermal measurements

Thermal analysis was carried out using a thermal analyzer Model DT-30 by Shimadzu, Japan. Measurements were made under a constant flow of nitrogen. Platinum crucibles were used and Al_2O_3 was used as standard. Enthalpy changes were calculated from the DTA peak area using zinc metal as standard. Thermal parameters for decomposition of complexes are shown in Table 2.

Spectral measurements

Infrared spectra were recorded in KBr pellets using a Beckman IR20A infrared spectrophotometer and electronic spectra in mull were recorded using a Pye-Unicam model SP8 UV/VIS spectrophotometer.

TABLE 1

Analytical data of *N,N*-diethylethylenediamine (L) complexes of nickel(II)

Compound	Color	Ni		N		$\mu_{eff.}$ (B.M.)
		Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	
$[NiL_2Cl_2]\cdot 2\ H_2O$	Blue	14.61	14.75	13.86	14.08	3.22
$[NiL_2(H_2O)_2]Br_2$	Blue	11.70	12.06	11.66	11.50	3.06
$[NiL_2(NCS)_2]$	Light violet	14.52	14.43	20.81	20.65	3.19
$[NiL(CH_3COO)_2(H_2O)_2]$	Bluish Green	17.61	17.85	8.60	8.52	3.01
$[NiL_2(CCl_3COO)_2]$	Blue	9.76	9.53	9.44	9.09	3.27
$[NiLCl_2]$	Yellow	24.01	23.89	11.42	11.39	3.52
$[NiL_2CO_3]$	Yellowish green	16.61	16.73	15.42	15.97	3.27

TABLE 2

Thermal parameters for decomposition of *N*,*N*-diethylethylenediamine (L) complexes of nickel(II)

Decomposition reaction			Temp. range (°C)	DTA peak temp. (°C)		ΔH (kJ mole^{-1})
				Endo	Exo	
I.	(a)	$[NiL_2Cl_2]\cdot 2\ H_2O \rightarrow [NiL_2Cl_2]$	83–120	110		150.3
	(b)	$[NiL_2Cl_2] \rightarrow [NiLCl_2]$	130–190	170		138.7
	(c)	$[NiLCl_2] \rightarrow [NiL_{0.66}Cl_2]$	205–248	252		74.1
	(d)	$[NiL_{0.66}Cl_2] \rightarrow [NiL_{0.33}Cl_2]$	248–303		291	81.3
	(e)	$[NiL_{0.33}Cl_2] \rightarrow NiCl_2$	303–518		393	351.9 [a]
II.	(a)	$[NiL_2(H_2O)_2]Br_2 \rightarrow [NiL_2]Br_2$	55–100	90		176.5
	(b)	$[NiL_2]Br_2 \rightarrow [NiL_{1.5}Br_2]$	150–200	190, 202		35.2
III.	(a)	$[NiL_2(SCN)_2] \rightarrow [NiL_{1.66}(SCN)_2]$	155–200	195		135.5 [a]
	(b)	$[NiL_{1.66}(SCN)_2] \rightarrow Ni(SCN)_2$	205–292			
IV.	(a)	$[NiL(CH_3COO)_2(H_2O)_2] \rightarrow [NiL(CH_3COO)_2]$	100–172	155		196.5
	(b)	$[NiL(CH_3COO)_2] \rightarrow Ni(CH_3COO)_2$	172–444		372	305.4
	(c)	$Ni(CH_3COO)_2 \rightarrow NiCO_3$	444–515		505, 520	
	(d)	$NiCO_3 \rightarrow NiO$	515–530		525, 535	
V.	(a)	$[NiL_2(CCl_3COO)_2] \rightarrow [NiL_2CO_3]$	88–125		120	132.7
VI.	(a)	$[NiL_2CO_3] \rightarrow [NiLCO_3]$	60–170		160	
	(b)	$[NiLCO_3] \rightarrow [NiL_{0.5}CO_3]$	170–240		180, 220	
	(c)	$[NiL_{0.5}CO_3] \rightarrow [NiL_{0.25}CO_3]$	240–340		320	
	(d)	$[NiL_{0.25}CO_3] \rightarrow NiCO_3$	340–510		400	
	(e)	$NiCO_3 \rightarrow NiO$	510–630		580	

[a] Overall enthalpy change.

Magnetic measurement

The effective magnetic moments were evaluated from magnetic susceptibility measurements with EG and G PAR vibrating sample magnetometer model 15S at room temperature.

RESULTS AND DISCUSSION

*Dichlorobis(*N,N*-diethylethylenediamine)nickel(II) dihydrate*

Earlier, Goodgame and Venanzi [9] reported the synthesis of this compound. Later, while exploring the thermochromism phenomenon in diamine complexes, Tsuchiya et al. [8] tried to prepare this compound following the method reported [9]. Identical elemental composition, color and magnetic values were found in all the cases. Tsuchiya et al. reported the anion outside the coordination sphere though physicochemical evidence of this complex species in our case supports the observation reported by Goodgame and Venanzi. This dihydrate complex species becomes anhydrous at 120°C in a single step (Fig. 1). The dehydrated species retains its O_h symmetry. On further heating, this transforms to $[NiLCl_2]$ at 190°C in a single step. The monodiamine complex is isolated by temperature arrest technique and appears to have T_d symmetry as indicated by its magnetic as well as electronic (mull) spectral data (Fig. 2). This monodiamine species undergoes decomposition on further heating to metal chloride with the formation of two intermediates, e.g. $[NiL_{0.66}Cl_2]$ and $[NiL_{0.33}Cl_2]$ as indicated by the TG curve. Attempts were made to isolate these two species but without success. The composition of the intermediate complex species produced while pyrolysing $[NiL_2Cl_2] \cdot 2\ H_2O$ suggests that the decomposition is very complex. The monospecies does not possess polymeric structure as is shown by the geometry and the shape of the ligand molecule. IR spectral data of this monodiamine species suggest that the diamine is chelated.

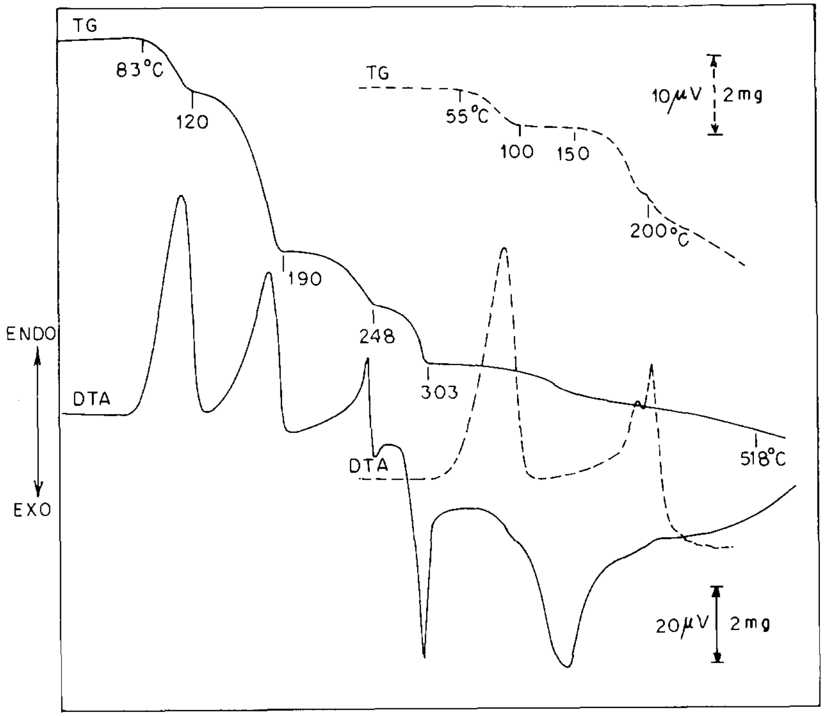

Fig. 1. Thermal curves of ————, $[NiL_2Cl_2] \cdot 2\ H_2O$, sample mass, 15.02 mg and - - - - - -, $[NiL_2(H_2O)_2]Br_2$, sample mass, 14.54 mg.

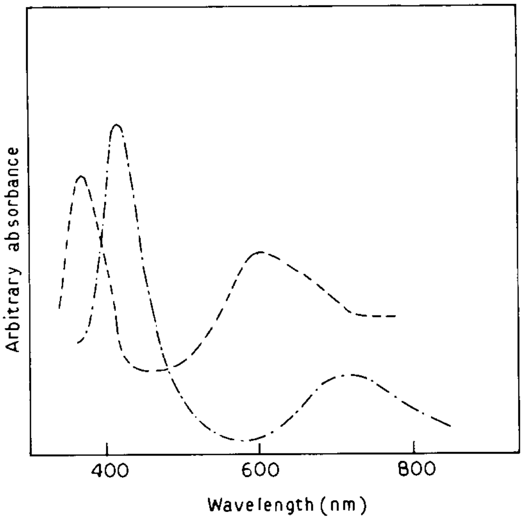

Fig. 2. Electronic spectra of - - - - - -, $[NiL_2Cl_2]\cdot 2\ H_2O$ and (· — · — ·) $[NiLCl_2]$.

*Diaquobis(*N,N*-diethylethylenediamine)nickel(II) bromide*

Attempts were made to isolate dibromobis(*N*,*N*-diethylethylenediamine) nickel(II) following the method reported earlier [9]. But diaquobis(*N*,*N*-diethylethylenediamine)Ni(II) bromide was isolated instead of the desired species. Tsuchiya et al. reported it as having one molecule of water outside the coordination sphere. This species shows O_h symmetry. On heating, it transforms to $[NiL_2]Br_2$ at 100°C (Fig. 1) which possesses square-planar geometry: this is corroborated by Tsuchiya et al. [8]. The attainment of square-planar geometry from octahedral geometry suggests that two coordinated water molecules exist in the complex. Moreover, this phenomenon also suggests that the anion has not taken part in coordination while deaquation proceeds. On further heating the anhydrous diamine species transforms to the non-isolable intermediate $[NiL_{1.5}Br_2]$ which then melts and decomposes instantaneously to nickel bromide: this is evident from its thermal curve (Fig. 1). However, we have very cautiously isolated the intermediate in an almost pure form. It has been shown to be paramagnetic. The parent diaquo as well as bisdiamine species are monomeric and the bis species decomposes through dimerization.

*Diisothiocyanatobis(*N,N*-diethylethylenediamine)nickel(II)*

This was prepared following the method reported earlier [9]. Color, magnetic moment and electronic and IR spectral data corroborated the observation made by Goodgame et al. [9]. This complex undergoes decomposition to $Ni(SCN)_2$ (Fig. 3) via a non-isolable intermediate $[NiL_{1.66}(SCN)_2]$. We tried to isolate this intermediate at a temperature where the TG curve shows the inflexion. The isolated intermediate (though its purity is questionable) shows paramagnetism as well as nitrogen linkage of the SCN group. The nature of the thermal profile shows the decomposition taking place in a complicated manner.

*Diacetatodiaquo(*N,N*-diethylethylenediamine)nickel(II)*

Attempts were made to isolate diacetatobis(*N*,*N*-diethylethylenediamine) nickel(II) following the method reported earlier [9]. But diacetatodiaquo(*N*,*N*-diethylethylenediamine)nickel(II) was synthesized instead of the desired species. The magnetic data and electronic spectra in mull suggest O_h symmetry. IR spectra suggest that the acetato group functions as a unidentate ligand [10] as is evident from the position of $\nu(C{=}O)$ (~ 1620 cm^{-1}) and $\nu(C–O)$ (1320 cm^{-1}) bands. On heating, this diaquo complex becomes $[NiLAc_2]$ (Fig. 3) but retains its octahedral geometry as is evident from its magnetic and electronic spectral data. The composition and geometry of this dehydrated species suggest bidentate character of the acetato

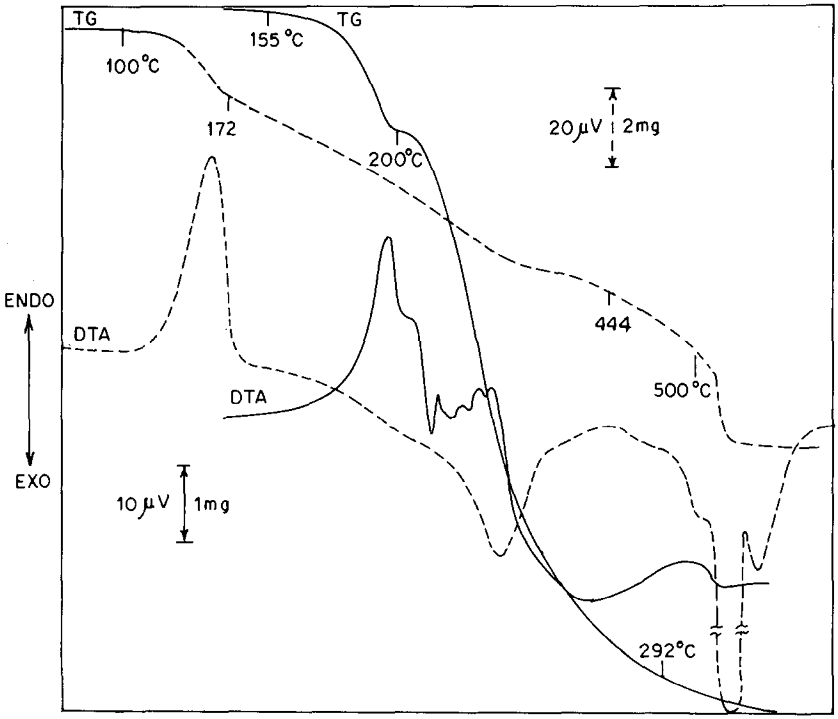

Fig. 3. Thermal curves of ———, $[NiL_2(NCS)_2]$, sample mass, 15.46 mg and - - - - -, $[NiL(CH_3COO)_2(H_2O)_2]$, sample mass, 14.83 mg.

group: this is supported by the shifting of ν(C=O) (1575 cm^{-1}) and ν(C–O) (1450 cm^{-1}) which has made these bands closer [10]. On further heating, the monodiamine species transforms to thermally unstable nickel acetate in a single step and then to nickel oxide through the formation of nickel carbonate. The existence of nickel acetate up to 444°C, as shown in the TG curve (Fig. 3), is very interesting as its decomposition starts at a much lower temperature [11,12]. This unusual phenomenon is probably due to complexation which might have changed the orientation of nickel acetate in the complex molecule in comparison to the free nickel acetate molecule.

*Ditrichloroacetatobis(*N,N*-diethylethylenediamine)nickel(II)*

The synthesis of this compound was also carried out by Goodgame and Venanzi [9]. The color, magnetic moment and electronic(mull) spectral data corroborate the observation made earlier and suggest O_h symmetry. On heating, this complex transforms to a novel yellowish green [NiL$_2$CO$_3$] at 125°C showing a sharp exotherm in the DTA curve (Fig. 4). The carbonatobisdiaminenickel(II) species is isolated and it also possesses O_h

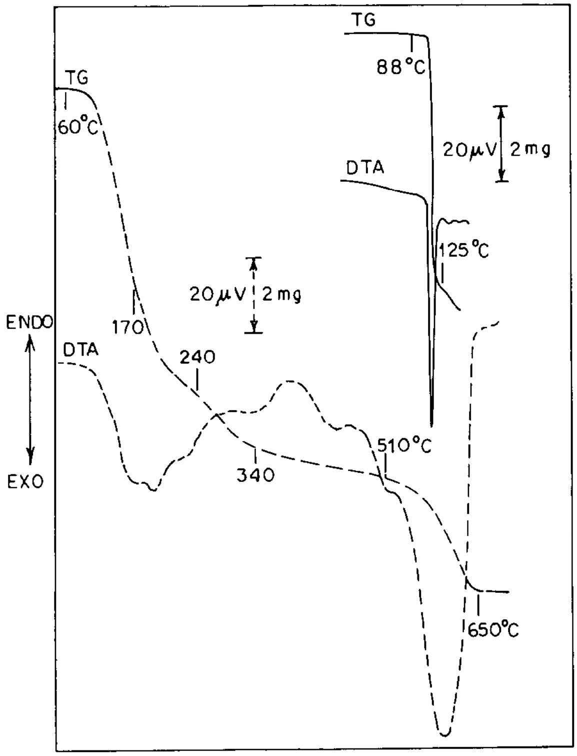

Fig. 4. Thermal curves of ———, [NiL$_2$(CCl$_3$COO)$_2$], sample mass, 14.21 mg and - - - - - -, [NiL$_2$CO$_3$], sample mass, 17.64 mg.

symmetry as is evident from its magnetic moment and electronic spectrum. Though IR spectra cannot clearly suggest the bidentate character of the carbonate group due to overlapping of the ligand band, the composition of the molecule indicates that the carbonate group acts here as a bidentate ligand. Further decomposition of this species shows a very complicated thermal profile from which it is very difficult to predict anything about its decomposition process. For a better thermal profile, the thermal decomposition of the carbonato complex was carried out. An appreciable amount of it is isolated from the parent. As a result decomposition of this carbonate complex has become very meaningful (Fig. 4). The TG curve shows the decomposition taking place as follows: $NiL_2CO_3 \rightarrow NiLCO_3 \rightarrow NiL_{0.5}CO_3 \rightarrow NiL_{0.25}CO_3 \rightarrow NiCO_3 \rightarrow NiO$. None of these intermediate complex species are isolable in the solid state. But it is clear from the very weakly resolved plateau that carbonato complex decomposition takes place through a polymeric structure.

One interesting phenomenon is that elimination of diamine for transformation of bisdiamine to monodiamine occurs in an endothermic process and for monodiamine to metal salt in an exothermic process: this was observed in the DTA curves. A similar type of observation was noticed in our laboratory dealing with ethylenediamine and 1,3-propanediamine complexes of nickel(II) [5]. In general, any process involving elimination of diamine or any amine from their complexes shows an endotherm in the DTA curve. This is probably due to the oxidation of the diamine occurring at elevated temperatures or liberation of more energy in Ni–N bond breaking or both [2].

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REFERENCES

1 T.D. George and W.W. Wendlandt, Tex. J. Sci., 14 (1962) 47.
2 T.D. George and W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 395.
3 W.W. Wendlandt, Anal. Chim. Acta, 27 (1962) 309.
4 F.Ya. Kul'ba, Yu.A. Makashev, D.M. Maskhaeva and A.V. Barsukov, Russ. J. Inorg. Chem., 16 (1971) 511.
5 G. De, P.K. Biswas and N. Ray Chaudhuri, Bull. Chem. Soc. Jpn., submitted for publication.
6 A.B.P. Lever, E. Mantovani and J.C. Donini, Inorg. Chem., 10 (1971) 2424.
7 B.P. Kennedy and A.B.P. Lever, J. Am. Chem. Soc., 95 (1973) 6907.

8 R. Tsuchiya, S. Joba, A. Uehara and E. Kyuno, Bull. Chem. Soc. Jpn., 46 (1973) 1454.
9 D.M.L. Goodgame and L.M. Venanzi, J. Chem. Soc., (1963) 616.
10 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 3rd edn., 1977, pp. 232, 243.
11 J.L. Doremieux, C.R. Acad. Sci., 261 (1965) 4426.
12 J. Leicester and M.J. Redmann, J. Appl. Chem., 12 (1962) 357.