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THERMAL OCTAHEDRAL ⇄ SQUARE-PLANAR TRANSFORMATION OF DIAMINE COMPLEXES OF NICKEL(II) TRIFLUOROMETHANESULPHONATE IN THE SOLID PHASE

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ABSTRACT

Complexes of the form $Ni(CF_3SO_3)_2 \cdot 2(diamine) \cdot 2H_2O$ were synthesized and investigated thermally in the solid phase, where the diamine was 1,2-ethanediamine, *N*-methyl-1,2-ethanediamine, *N,N'*-dimethyl-1,2-ethanediamine, *N,N*-dimethyl-1,2-ethanediamine, *N*-ethyl-1,2-ethanediamine, *N*-propyl-1,2-ethanediamine, *N*-isopropyl-1,2-ethanediamine or 1,3-propanediamine. The complexes with 1,2-ethanediamine, *N,N*-dimethyl-1,2-ethanediamine and *N*-isopropyl-1,2-ethanediamine show octahedral to square planar transformation upon deaquation, whereas the other complexes retain their octahedral geometry after deaquation. The deaquated complex of 1,3-propanediamine is octahedral at ca. 180 °C but transforms to a square-planar species on cooling to room temperature. However, $[NiL_2(CF_3SO_3)_2]$ (L = *N*-methyl-1,2-ethanediamine or *N*-ethyl-1,2-ethanediamine) transform to square-planar species simultaneously on melting. The octahedral to square planar transformations of complexes are explained in terms of ligand-field strength and steric hindrance of the diamines.

INTRODUCTION

The octahedral ⇄ square planar transformation of nickel(II) bis-(diamine) complexes is well documented in the literature [1–3]. The following factors are significant in a complex acquiring a particular configuration (i.e. octahedral or square planar): (i) the coordinating ability of anions; (ii) the steric hindrance resulting from substitution at the N or C atoms of the diamines; and (iii) the inductive effect of the substituents, i.e. the basicity of the diamines [1]. Among the *N*-substituted bis-(diamine) complexes the octahedral to square-planar transformations occur mainly due to the loss of a part of the ligand (e.g. water) on heating. Therefore, these complexes are not isomeric. However, it has been shown that a number of C substituted

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bis-(diamine) demonstrated square planar ⇄ octahedral transformations without any loss of ligands on heating. This difference in thermal behaviour arises due to the highly selective steric and inductive influences of the substituents which are bound to the donor N atom(s) of the diamines [2]. However, such effects are not so selective in the case of *C*-substituted diamines [2,3].

There is no systematic knowledge as to the factors that decide the preference of a certain configuration containing different diamines with a particular anion. The trifluoromethanesulphonate was selected as the anion in the present study because of its moderate coordinating ability [4], its bulkiness (which increase the probability that a complex will undergo an octahedral to square-planar transformation) and its nonexplosive nature. In the present paper we also describe the syntheses of some di(trifluoromethanesulphonate) complexes of nickel(II) which are not well documented in the literature [5].

EXPERIMENTAL

All chemicals used were of AR grade and the 1,2-ethanediamine (en), *N*-methyl-1,2-ethanediamine (*N*meen), *N*-ethyl-1,2-ethanediamine (*N*eten),

TABLE 1

Elemental analyses of the bis-(diamine) complexes of nickel(II) trifluoromethanesulphonate

Complex	Found (calc.) (%)			
	Nickel	Carbon	Hydrogen	Nitrogen
1 $[Ni(en)_2(H_2O)_2](CF_3SO_3)_2$	11.3(11.4)	13.8(14.0)	4.3(3.9)	11.0(10.9)
1a $[Ni(en)_2](CF_3SO_3)_2$	12.1(12.3)	15.2(15.1)	3.5(3.4)	11.6(11.7)
2 $[Ni(N\text{meen})_2(H_2O)_2](CF_3SO_3)_2$	11.1(10.8)	18.0(17.7)	4.4(4.4)	10.1(10.3)
2a $[Ni(N\text{meen})_2(CF_3SO_3)_2]$	11.5(11.6)	18.8(19.0)	3.9(4.0)	11.2(11.1)
3 $[Ni(NN'\text{dmen})_2(H_2O)_2](CF_3SO_3)_2$	10.2(10.3)	20.9(21.1)	4.5(4.9)	10.1 (9.8)
3a $[Ni(NN'\text{dmen})_2(CF_3SO_3)_2]$	10.8(11.0)	22.7(22.5)	4.4(4.5)	10.4(10.5)
4 $[Ni(NN\text{dmen})_2(H_2O)_2](CF_3SO_3)_2$	10.1(10.3)	21.2(21.1)	5.1(4.9)	10.1 (9.8)
4a $[Ni(NN\text{dmen})_2](CF_3SO_3)_2$	10.8(11.0)	22.7(22.5)	4.7(4.5)	10.8(10.5)
5 $[Ni(N\text{eten})_2(H_2O)_2](CF_3SO_3)_2$	10.1(10.3)	20.9(21.1)	5.1(4.9)	9.8 (9.8)
5a $[Ni(N\text{eten})_2(CF_3SO_3)_2]$	10.8(11.0)	22.4(22.5)	4.6(4.5)	10.7(10.5)
6 $[Ni(N\text{pren})_2(H_2O)_2](CF_3SO_3)_2$	10.1 (9.8)	23.8(24.1)	5.5(5.4)	9.6 (9.4)
6a $[Ni(N\text{pren})_2(CF_3SO_3)_2]$	10.5(10.5)	26.0(25.7)	4.8(5.0)	10.1 (9.9)
7 $[Ni(N\text{ipren})_2(H_2O)_2](CF_3SO_3)_2$	9.6 (9.8)	23.8(24.1)	5.3(5.4)	9.4 (9.4)
7a $[Ni(N\text{ipren})_2](CF_3SO_3)_2$	10.4(10.5)	25.6(25.7)	5.1(5.0)	10.2 (9.9)
8 $[Ni(tn)_2(H_2O)_2](CF_3SO_3)_2$	11.0(10.8)	17.8(17.7)	4.3(4.4)	10.2(10.3)
8b $[Ni(tn)_2](CF_3SO_3)_2$	11.7(11.6)	19.2(19.0)	3.9(4.0)	10.9(11.1)

TABLE 2

Thermal parameters of the bis-(diamine) complexes of nickel(II) trifluoromethanesulphonate

Thermally induced reaction	Temp. range (°C)	Configuration change [a]	ΔH (kJ mol^{-1})
1 → **1a**	52–115	$O_h \rightarrow S_p$	–
2 → **2a**	68–115	$O_h \rightarrow O'_h$	–
2a → **2b**	160–178 [b]	$O'_h \rightarrow S_p$	28.1
2b → **2a**	123– 94 [c]	$S_p \rightarrow O'_h$	25.4
3 → **3a**	75–125	$O_h \rightarrow O'_h$	–
4 → **4a**	80–140	$O_h \rightarrow S_p$	–
5 → **5a**	75–142	$O_h \rightarrow O'_h$	–
5a → **5b**	179–200 [b]	$O'_h \rightarrow S_p$	19.6
5b → **5a**	152–124 [c]	$S_p \rightarrow O'_h$	15.6
6 → **6a**	75–132	$O_h \rightarrow O'_h$	–
7 → **7a**	58–125	$O_h \rightarrow S_p$	–
8 → **8a**	85–195	$O_h \rightarrow O'_h$	–
8a → **8b**	76–117	$O'_h \rightarrow S_p$	4.3
8b → **8a**	85–114	$S_p \rightarrow O'_h$	4.4

[a] O_h (or O'_h) and S_p represent an octahedral di-aqua (or di-aniono) and a square-planar species, respectively.

[b] Transformations are associated with melting.

[c] Transformations are associated with solidification.

TABLE 3

Data on some selected electronic spectral bands and magnetic moments of bis-(diamine) complexes of nickel(II) trifluoromethanesulphonate

Complex	Electronic spectra (nm)	Magnetic moment (BM)
1	1201, 715, 548	3.1
1a	450	Diamagnetic
2	1195, 710, 540	3.1
2a	1187, 698, 536	3.2
3	1190, 798, 570	3.1
3a	1177, 790, 561	3.1
4	1200, 835, 585	3.2
4a	456	Diamagnetic
5	1082, 773, 565	3.2
5a	1075, 762, 558	3.2
6	1080, 770, 562	3.1
6a	1071, 762, 558	3.1
7	998, 610	3.2
7a	465	Diamagnetic
8	1205, 788, 561	3.1
8a	582, 380	3.2
8b	455	Diamagnetic

N-propyl-1,2-ethanediamine (*N*pren), *N*-isopropyl-1,2-ethanediamine (*N*ipren), (*N,N*-dimethyl-1,2-ethanediamine (*NN*dmen), *N,N'*-dimethyl-1,2-ethanediamine (*NN'*dmen) and 1,3-propanediamine (tn) were purchased from Fluka AG (Switzerland) and used as received. The equipment employed to record the infra-red (IR) electronic spectra (mull), to measure the magnetic susceptibility (ambient and above ambient temperature), and to make the thermal measurements (thermogravimetric (TG), differential thermogravimetric analysis (DTA) and differential scanning calorimetry (DSC)) and elemental analysis has been described previously [6–8]. The visual morphology and colour changes associated with the dehydration, phase transformation and melting were inspected by keeping the complexes at the desired temperature range in an air oven. The electronic spectra of **8a** was recorded at 120 °C on a Pye-Unicam SP 8-150 spectrophotometer equipped with a heating arrangement (up to 120 °C). Analytical, thermal and electronic spectral, data and magnetic data are given in Tables 1 to 3, respectively.

Syntheses of the complexes

All the complexes described here were prepared by mixing the diamines in a 1 : 2 ratio with $Ni(CF_3SO_3)_2 \cdot 6H_2O$ dissolved in ethanol. Upon slow evaporation of the resulting mixture violet or blue crystals separated out. The crystals were filtered off, washed with ethanol and dried.

RESULTS AND DISCUSSION

Structures of the original complexes

The analytical data and magnetic moments (Tables 1 and 3) show that all the complexes prepared have the composition, $Ni(CF_3SO_3)_2 \cdot 2(\text{diamine}) \cdot 2H_2O$, and are high spin. The number of observed bands and their modes of splitting clearly indicate that all the hydrated complexes except for $Ni(CF_3SO_3)_2 \cdot 2(N\text{ipren}) \cdot 2H_2O$ possess *trans* octahedral structure [3,9,10], whereas the complex $Ni(CF_3SO_3)_2 \cdot 2(N\text{ipren}) \cdot 2H_2O$ has *cis* octahedral structure. Representative electronic spectra of the *trans* and *cis* isomers are shown in Fig. 1. The spectra of the other diamine complexes are almost the same as that of the complex $Ni(CF_3SO_3)_2 \cdot 2(\text{en}) \cdot 2H_2O$, leading to the formulae of these complexes given in Table 1.

Thermal analyses and thermochromism

The results of the simultaneous TG-DTA measurements of the complexes are given in Table 2 and Fig. 2. The weight losses observed near 100 °C in

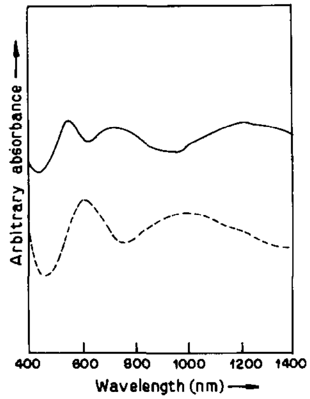


Fig. 1. Representative electronic spectra of *trans*- and *cis*-isomers near-IR–visible region): (———) *trans*-[Ni(en)$_2$(H$_2$O)](CF$_3$SO$_3$)$_2$ (**1**); (— — —) *cis*-[Ni(*N*ipren)$_2$(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ (**7**).

the TG curves and the corresponding endothermic DTA peaks are due to the liberation of two moles of coordinated water from the corresponding hydrated complexes: **1**, obs. 7.0, calc. 7.1; **2**, obs. 6.6, calc. 6.7; **3**, obs. 6.2, calc. 6.3; **4**, obs. 6.1, calc. 6.3; **5**, obs. 6.0, calc. 6.3; **6**, obs. 6.3, calc. 6.0; **7**, obs. 6.1, calc. 6.0; and **8**, obs. 6.6, calc. 6.7%.

On further heating after dehydration an endothermic peak appears at 175 and 180 °C in the DTA curves for complexes **2** and **5**, respectively, where their TG curves remain flat. Inspection of the visual morphology of these

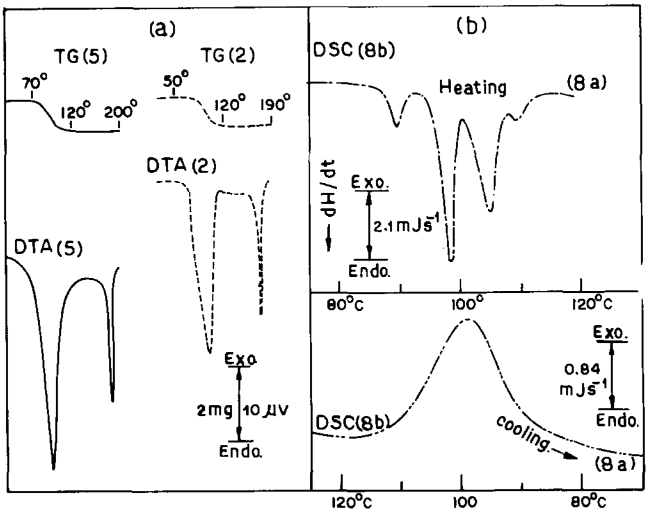
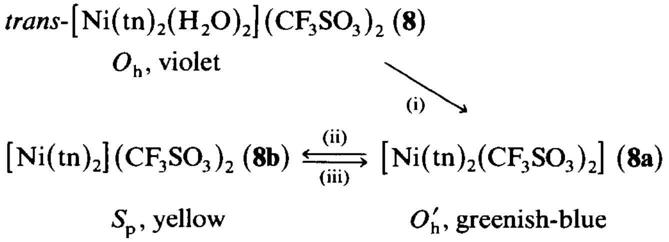


Fig. 2. (a) TG-DTA curves for *trans*-[Ni(*N*eten)$_2$(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ (**5**) (———) (sample mass = 15.45 mg) and *trans*-[*N*i(*N*meen)$_2$(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ (**2**) (— — —) (sample mass = 12.55 mg). (b) DSC curves of [Ni(tn)$_2$](CF$_3$SO$_3$)$_2$ (**8b**) (sample mass = 6.90 mg).



Scheme 1
(i) Dehydration, 85–195 °C; (ii) cooling, 76–117 °C; (iii) heating, 85–114 °C. O_h, O'_h and S_p have the same meaning as described in the footnote to Table 2.

complexes at these temperatures shows that these peaks are due to the melting (Fig. 2).

The dehydration of complexes **1**, **4** and **7** are highly thermochromic. In these cases the violet coloured hydrated complexes change to yellow or orange on dehydration. However, the colour changes shown by the remaining complexes are not so drastic. The colour change of **8** is particularly remarkable since on dehydration it shows a change from violet to greenish-blue at ca. 195 °C, but on cooling to room temperature the dehydrated species becomes yellow (Scheme 1) and this cooling corresponds to the appearance of an exothermic peak in the DSC curve (Fig. 2). However, a yellow to greenish-blue colour change (**8b** → **8a**) is observed on heating the room-temperature product (**8b**) (Table 2 and Scheme 1) which corresponds to four overlapping endotherms in the DSC profile (Fig. 2). The colour change and thermal behaviour of **8a** are reversible. A colour change from blue-violet to yellow was also observed in **2** and **5** after dehydration; the colour change is associated with melting and these colour changes are also reversible, i.e. the yellow complexes revert to the blue-violet species on solidification (Table 2). The enthalpy changes for the phase transformation of **8b** and for the melting of **2a** and **5a** were calculated using a differential scanning calorimeter and are given in Table 2.

Structures of the thermal reaction products

The dehydrated species **2a**, **3a**, **5a** and **6a** possess octahedral geometry as is evident from magnetic moment and electronic spectra (Table 3). The spectral patterns of these complexes remain virtually unchanged after dehydration, which indicates that the *trans* octahedral configuration is retained [9]. The IR spectral bands of coordinated CF_3SO_3 ions could not be distinguished due to the overlapping of diamine vibrations. However, the dehydrated species **1l**, **4a** and **7** are diamagnetic and show a broad and strong absorption band in the blue region of their electronic spectra, which is characteristic of a square-planar nickel(II) complex. Therefore, it is clear

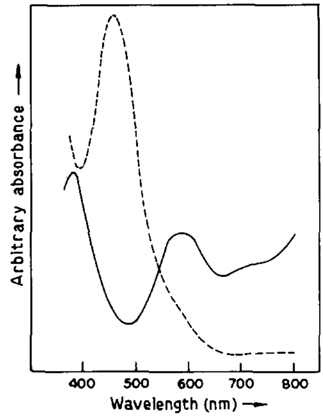


Fig. 3. Electronic spectra (ultraviolet–visible) of $[Ni(tn)_2(CF_3SO_3)_2]$ (**8a**) (———) at 120 °C and $[Ni(tn)_2](CF_3SO_3)_2$ (**8b**) (— — —) at room temperature.

that the dehydration of complexes **1**, **4** and **7** are accompanied by an octahedral to square planar structural transformation.

The dehydration of **8** deserves special mention, since its octahedral dehydrated species (**8a**), on cooling to room temperature, transforms to a square-planar species as is evident from its electronic spectra and magnetic moment (Table 3; Scheme 1). The electronic spectrum of **8a** (at ca. 120 °C) in the ultraviolet–visible region clearly shows that it possesses an octahedral configuration (Fig. 3). However, the spectrum of **8a** in the near-IR region at the elevated temperature could not be recorded due to a lack of facilities for measuring spectra above ambient temperature. Therefore, it is very difficult to comment on the geometry of the complex, i.e. whether it is *trans* or *cis*.

Similarly, the yellow melted products (**2b** and **5b**) could not be characterized due to a lack of proper spectral and magnetic measurement facilities, but it appears from their colour that they probably possess a square-planar configuration.

The yellow dehydrated species **1a**, **4a**, **7a** and **8a** revert to the corresponding dehydrated species on being kept in a humid atmosphere (relative humidity 70–80%).

Effect of diamines structure on thermal $O_h \rightarrow S_p$ transformations

The factors which cause a complex to possess a particular configuration (i.e. O_h or S_p) are described above. Pavkovic and Meek [11] synthesized several octahedral bis-(diamine) complexes of nickel(II) perchlorate by heating either a dihydrated octahedral or a dehydrated square-planar species in vacuum. They concluded that to obtain a dehydrated octahedral complex the steric requirement of the diamines should be such that it can trap the ClO_4 ions for coordination. These factors do not explain why on dehydration the complex with 1,2-ethanediamine acquires a square planar configuration whilst the complexes with *N*-methyl-, *N*-ethyl- or *NN*′-dimethyl-1,2-ethanediamine acquire an octahedral configuration, though the latter diamines are more sterically hindered than the former one. However, it is well known that the complex $[Ni(en)_2](ClO_4)_2$ acquires a square-planar configuration due to the strong ligand field strength of 1,2-ethanediamine [12].

Therefore, it is suggested that the two factors (ligand field strength and steric hindrance) should be considered simultaneously in order to explain why a deaquated species possesses a particular configuration in the present complexes. The spectrochemical series for a number of complexes of the type $[Ni(diamine)_3](ClO_4)_2$ is en > *N*meen > *N*eten > *N*pren > *NN*′dmen > *NN*dmen, etc., and it is also evident that the ligand field strength of the ligands which can form five-membered rings with the metal atom are stronger than those that can form six-membered rings [13]. So, one would expect a $O_h \rightleftarrows S_p$ transformation in a complex where the ligand field strength is not so strong and the ligand is less sterically hindered. It has been reported previously [14] that as the vibrations of the ligands increase on heating the lone pair of the nitrogen atom is less rigidly fixed in the optimal orientation for coordination and the ligand field strength decreases. Very probably due to the above stated reasons, the complex $[Ni(tn)_2](CF_3SO_3)_2$ (**8b**) undergoes $S_p \rightarrow O_h$ transformation on heating in the solid state. However, the overwhelming steric hindrance of the ligands *NN*dmen and *N*ipren cause the complexes $[Ni(NNdmen)_2](CF_3SO_3)_2$ (**4a**) and $[Ni(Nipren)_2](CF_3SO_3)_2$ (**7a**) to be square planar species.

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