Synthesis of *cis* and *trans* Isomers of *N,N'*-Dimethyl-1,2-ethanediamine Complexes of Nickel(II) Nitrate and Solid-phase Thermal *cis*-to-*trans* Isomeric Transformation

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The octahedral *cis* and *trans* isomers of $[NiL_2(NO_3)_2] \cdot nH_2O$ (L = *N,N'*-dimethyl-1,2-ethanediamine; n = 0, 2, or 4) have been synthesised. On heating in the solid state the deaquated *cis*-$[NiL_2(NO_3)]NO_3$ isomerises exothermically to *trans*-$[NiL_2(NO_3)_2]$ accompanied by an irreversible thermochromic colour change from deep blue to pink. This transformation can also be brought about at room temperature in the presence of a humid atmosphere (*ca.* 60%) as catalyst. The effect of humidity on the composition and geometry of the complexes has been investigated.

Solid-state geometrical isomerism of octahedral bis(diamine) complexes of Co^{III} and Cr^{III} is well documented in the literature,[1,2] but for Ni^{II}, although there are many examples of the solid-state thermal reaction (*i*) configurational changes,[3] *i.e.* octahedral $\rightleftharpoons$ square planar, and (*ii*) conformational changes of the individual diamine chelate rings,[4] examples of *cis*–*trans* isomerism are quite rare. Moreover, a few of these transformations with Ni^{II}, are associated with[5,6] the loss of some of the ligands (generally water). Therefore, they are not isomeric. It has also been found that the water molecules play an important role in the isomerisation of cobalt(III) complexes.[1,2,7] In contrast, most of the chromium(III) complexes isomerise in the anhydrous state without participation of any water molecule,[2b] whereas for several nickel(II) complexes the relative humidity has a marked effect on the stability of the thermally synthesised conformers.[4b,e]

In this paper we report the first ever example of a solid-state *cis*–*trans* isomeric transformation of octahedral Ni^{II} in the complex $[NiL_2(NO_3)_2]$ (L = *N,N'*-dimethyl-1,2-ethanediamine) and the effect of relative humidity on the composition and isomerisation of the complex.

Experimental

All the chemicals used were A.R. grade and high-purity *N,N'*-dimethyl-1,2-ethanediamine was purchased from Fluka AG and distilled before use. Infrared and electronic spectra (visible and near-i.r. regions) were recorded in Nujol mulls with Perkin-Elmer 783 i.r. and Hitachi U-3400 spectrophotometers, respectively. The instruments used for thermal investigation [thermal gravimetric analysis (t.g.a.), differential thermal analysis (d.t.a.), and differential scanning calorimetry (d.s.c.)], elemental analyses, and magnetic susceptibility measurements were as reported earlier.[4b,f] The controlled-humidity atmospheres were obtained by keeping constant-humidity solutions (saturated aqueous $ZnSO_4 \cdot 7H_2O$ and $NaBr \cdot 2H_2O$ solutions for 90 and 60% humidity, respectively) in a closed vessel.[8]

Synthesis of the Complexes.—*N,N'*-Dimethyl-1,2-ethanediamine (20 mmol) was added dropwise to a stirred solution of $Ni(NO_3)_2 \cdot 6H_2O$ (10 mmol) in ethanol (10 cm³). The resulting blue solution was evaporated slowly in a bath until the total volume was reduced to *ca.* 5 cm³. After cooling to room temperature (*ca.* 25 °C), propan-2-ol (10 cm³) was added slowly with stirring. The blue solid which separated after a few minutes was washed with propan-2-ol. This crude product on crystallisation from different solvents yields the following pure compounds.

cis-$[NiL_2(H_2O)_2][NO_3]_2$ (1). The crude product was dissolved in hot propan-2-ol. On cooling to room temperature needle-shaped bright blue crystals slowly separated. After standing for 1 h the product was filtered off, washed with propan-2-ol, and kept at a constant humidity of *ca.* 60%. The bright blue crystals were found to lose their lustre and were finally converted into *cis*-$[NiL_2(H_2O)_2][NO_3]_2$ (1) in *ca.* 1 h (Found: C, 24.2; H, 7.0; N, 21.0; Ni, 14.2. Calc. for $C_8H_{28}N_6NiO_8$: C, 24.3; H, 7.1; N, 21.3; Ni, 14.9%).

cis-$[NiL_2(NO_3)]NO_3$ (2). The crude product was dissolved in ethanol to make an almost saturated solution at room temperature. The desired product separated as rhombic bright blue crystals on keeping the solution at 0 °C over a period of 48 h (Found: C, 26.8; H, 6.9; N, 23.1; Ni, 16.0. Calc. for $C_8H_{24}N_6NiO_6$: C, 26.8; H, 6.7; N, 23.4; Ni, 16.4%).

trans-$[NiL_2(NO_3)_2]$ (3). A methanolic solution of the crude product, on slow evaporation at room temperature, yielded big rhombic pink crystals of *trans*-$[NiL_2(NO_3)_2]$ (3) within 48 h. This complex can also be prepared by heating (1) at 160 °C (Found: C, 26.7; H, 6.6; N, 23.3; Ni, 16.3. Calc. for $C_8H_{24}N_6NiO_6$: C, 26.8; H, 6.7; N, 23.4; Ni, 16.4%).

trans-$[NiL_2(H_2O)_2][NO_3]_2 \cdot 2H_2O$ (4). This complex was prepared by keeping any of the complexes (1)—(3) at *ca.* 90% relative humidity for 72 h (Found: C, 22.7; H, 7.5; N, 19.7; Ni, 13.8. Calc. for $C_8H_{32}N_6NiO_{10}$: C, 22.3; H, 7.4; N, 19.5; Ni, 13.6%).

Results and Discussion

Thermal Analyses.—The results of simultaneous t.g.a.–d.t.a. for complexes (1) and (4) are shown in Figure 1. The weight loss observed in the t.g.a. curves of (1) and (4) [Found: 9.0 and 16.5. Calc.: 9.1 and 16.7% for (1) and (4), respectively] corresponds to 2 and 4 mol of water, respectively. The d.t.a. curve shows that the dehydration proceeds endothermically; thereafter a small exothermic peak appears at 127 and 126 °C for (1) and (4), respectively whereas the corresponding t.g.a. curves remain flat. The deep blue complex obtained by dehydration of both complexes becomes pink after the exothermic peak. The t.g.a.–d.t.a. curves of complexes (2) and (3) showed neither the weight loss (as they do not contain any water) nor the exothermic peak. However, all the complexes showed a sharp endothermic peak at *ca.* 200 °C due to melting. It is interesting that on melting complex (2) transforms into the pink product although it does not show any exothermic transitions. It is, therefore, reasonable to assume that the transformation occurs simultaneously with melting at a relatively higher temperature (Table 1) in the case of complex (2).

Table 1. Results of thermal analyses

		Transformation		
Compound	Dehydration temperature range (°C)	Temperature range (°C)	Enthalpy change[a] ΔH/kJ mol^{-1}	Melting peak temperature[b] (°C)
(1) $[NiL_2(H_2O)_2][NO_3]_2$	47—83	112—157	−7.4	197
(2) $[NiL_2(NO_3)]NO_3$	—	—	—	201
(3) $[NiL_2(NO_3)_2]$	—	—	—	196
(4) $[NiL_2(H_2O)_2][NO_3]_2\cdot2H_2O$	32—85	98—146	−7.1	198

[a] ΔH was calculated by d.s.c. using indium metal as calibrant. [b] ΔH for melting could not be evaluated accurately, because decomposition of the complexes starts before completion of the melting peak.

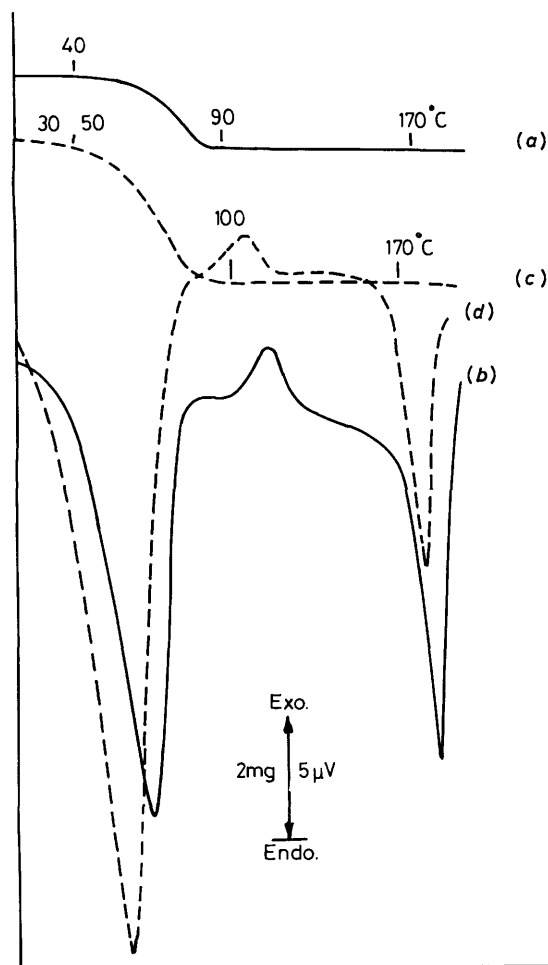**Figure 1.** T.g.a [(a) and (c)] and d.t.a. [(b) and (d)] curves for *cis*-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$ (1) (weight taken = 14.65 mg) and for *trans*-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$·2H$_2$O (4) (weight taken = 14.10 mg)

Magnetic Moments and Electronic Spectra.—The magnetic moments and electronic spectra of all the complexes are summarised in Table 2. The magnetic moments are typical of octahedral nickel(II). The electronic spectra in the near-i.r. region hve been used for the identification of *cis* or *trans* isomers.[3e,5,9] It is evident from the spectral patterns that complexes (1) and (2) possess a *cis* configuration as their *d–d* bands in the near-i.r. region do not show any splitting, whereas the appearance of two bands in the near-i.r. region of complexes (3) and (4) shows that they possess *trans*-octahedral geometry. The change in the electronic spectra corresponding to the

deaquation and phase transition of complex (1) are shown in Figure 2. The bright blue deaquated species has a spectral pattern identical with that of (1) except for a slight shift of band positions which indicates a partial exchange of ligands, while that of the pink product obtained by heating (1) at the temperature where the exotherm has been completed is characteristic of a *trans*-configuration. It is, therefore, logical to infer that complex (1) becomes anhydrous on heating, retaining its *cis* configuration, and on further heating isomerises to the *trans* configuration showing an exotherm in the d.t.a. profile.

It is interesting that although the species (4) possesses a *trans* configuration, on deaquation it transforms to *cis* as is evident from the respective electronic spectra in the near-i.r. region. On further heating it undergoes *cis* ⟶ *trans* isomerisation as in the case of complex (1).

I.r. Spectra.—The co-ordination mode of NO$_3^-$ was studied by i.r. spectroscopy in the region 1 700—1 800 cm^{-1} (Table 2) where a weak combination band of the ν_1 symmetric stretching and the doubly degenerate in-plane bending mode of NO$_3^-$ ion in a metallic complex appears.[10,11] Figure 3 represents the changes in i.r. spectra of complex (1) on dehydration and isomerisation. A relatively strong peak at 1 750 cm^{-1} assignable to the free NO$_3^-$ ions indirectly demonstrates the co-ordination of water molecules in (1). On the other hand, the dehydrated species shows three peaks at 1 761, 1 740, and 1 715 cm^{-1}. Of these the peak at 1 740 cm^{-1}, which appears nearly at the same position as that of the parent complex, suggests the presence of free NO$_3^-$ ions. The large separation (46 cm^{-1}) between the other two peaks indicates that the co-ordinated NO$_3^-$ ions are acting as bidentate ligands.[3e,5] Complex (2) and the deaquated species obtained from (4) have similar spectral patterns in this region. In contrast, the pink product obtained from complex (1) possesses two peaks at 1 761 and 1 747 cm^{-1} in the same region. The small difference (14 cm^{-1}) between the peaks indicates that the NO$_3^-$ ions in this complex are acting as unidentate ligands.[3e,11] Complex (3) and the pink species obtained from (4) also have unidentate NO$_3^-$ ions as is evident from their i.r. spectra.

Thermal Reactions.—Considering the electronic and i.r. spectral data, complexes (1), (2), (4), and (3) may be formulated as *cis*-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$, *cis*-[NiL$_2$(NO$_3$)]NO$_3$, *trans*-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$·2H$_2$O, and *trans*-[NiL$_2$(NO$_3$)$_2$], respectively. The thermal reaction of complex (1), therefore, can be represented as in equation (1), and that of (4) as in (2) (see Scheme).
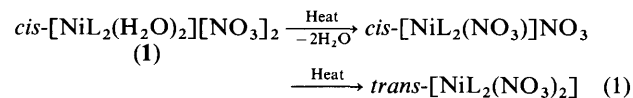
$$cis\text{-}[NiL_2(H_2O)_2][NO_3]_2 \xrightarrow[-2H_2O]{\text{Heat}} cis\text{-}[NiL_2(NO_3)]NO_3$$
$$(1)$$

$$\xrightarrow{\text{Heat}} trans\text{-}[NiL_2(NO_3)_2] \quad (1)$$

Table 2. Magnetic, electronic, and i.r. spectral (mull) data for the complexes

Compound		Colour	$\lambda_{max.}$/nm	$\mu_{eff.}$	I.r. (cm^{-1}) combination band $(\nu_1 + \nu_4)$ of NO$_3^-$
[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$	(1)	Light blue	929, 576	3.2	1 750
[NiL$_2$(NO$_3$)]NO$_3$ [a]		Deep blue	898, 571	3.1	1 761, 1 740, 1 715
[NiL$_2$(NO$_3$)$_2$] [b]		Pink	1 193, 748, 563	3.1	1 761, 1 747
[NiL$_2$(NO$_3$)]NO$_3$	(2)	Deep blue	896, 570	3.1	1 762, 1 738, 1 713
[NiL$_2$(NO$_3$)$_2$]	(3)	Pink	1 193, 748, 563	3.2	1 761, 1 748
[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$·2H$_2$O	(4)	Pinkish blue	1 066, 824, 568	3.1	1 756
[NiL$_2$(NO$_3$)]NO$_3$ [a]		Deep blue	898, 571	3.1	1 761, 1 739, 1 715
[NiL$_2$(NO$_3$)$_2$] [b]		Pink	1 193, 748, 563	3.2	1 761, 1 747

[a] Obtained after dehydration of the corresponding parent complexes. [b] Obtained after exothermic transformation of the corresponding dehydrated species.
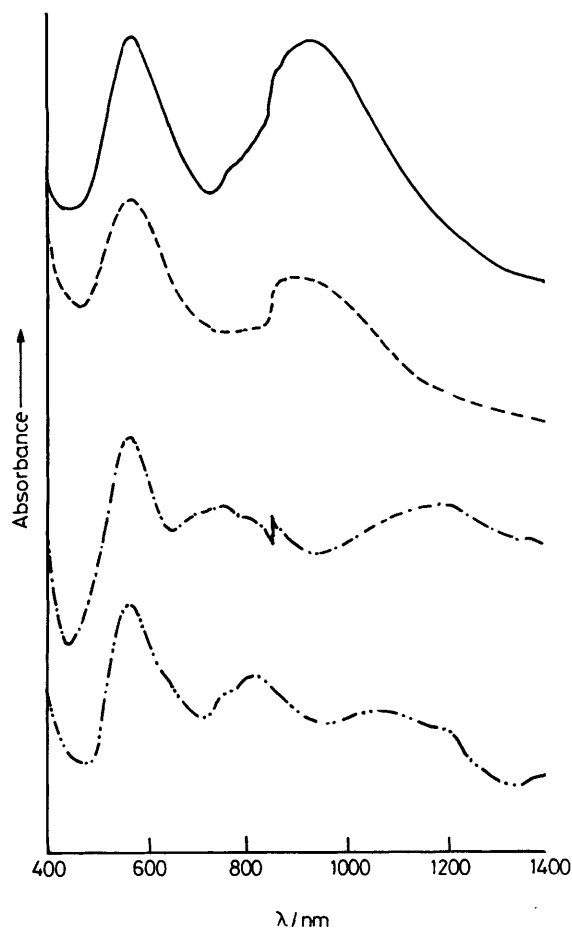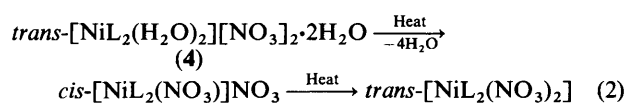

λ/nm

Figure 2. Electronic spectra (Nujol) of cis-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$ (1) (————), cis-[NiL$_2$(NO$_3$)]NO$_3$ obtained after deaquation of (1) (– – – –), trans-[NiL$_2$(NO$_3$)$_2$] obtained after exothermic phase transition of (1) (– · – · –), and trans-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$·2H$_2$O (4) (– ·· – ·· –)

$$\text{trans-[NiL}_2\text{(H}_2\text{O)}_2\text{][NO}_3\text{]}_2\text{·2H}_2\text{O} \xrightarrow[-4\text{H}_2\text{O}]{\text{Heat}}$$
(4)

$$\text{cis-[NiL}_2\text{(NO}_3\text{)]NO}_3 \xrightarrow{\text{Heat}} \text{trans-[NiL}_2\text{(NO}_3\text{)}_2\text{]} \quad (2)$$

Effect of Humidity.—The relative humidity has a remarkable effect on the composition (*i.e.* degree of hydration) and structure of the complex. To study this effect we have used two closed vessels of constant humidity *ca.* 90 and 60% and a P$_2$O$_5$
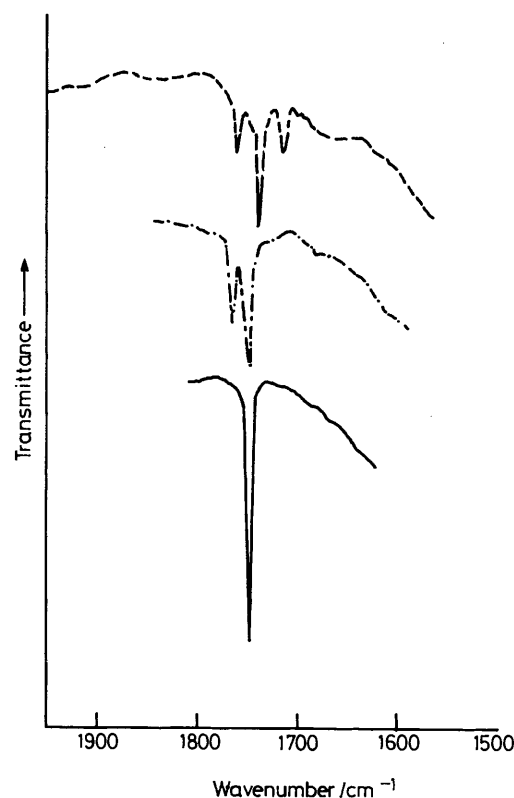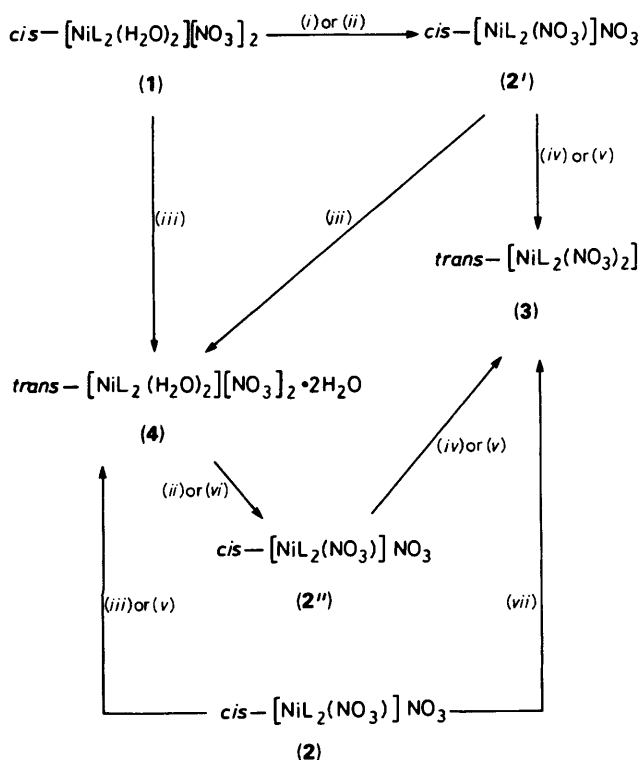

Figure 3. I.r. spectra (Nujol) showing the change of band positions of cis-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$ (1) (————), after deaquation (– – – –), and after transformation (– · – · –)

desiccator. Thermogravimetric analysis was used to measure the degree of hydration in all cases.

The bright blue crystals freshly removed from propan-2-ol (see Experimental section), after drying on a filter paper, show a water content of *ca.* 16.8% (equivalent to four water molecules). The corresponding d.t.a. curve shows a very small endotherm. At 60% humidity, water is lost readily from the freshly prepared crystals and ultimately the stable complex cis-[NiL$_2$-(H$_2$O)$_2$][NO$_3$]$_2$ is produced in 30 min. On the other hand, the water molecules are lost from the crystals rather slowly in a P$_2$O$_5$ desiccator and finally cis-[NiL$_2$(NO$_3$)]NO$_3$ results in *ca.* 12 h and is stable. However, at 90% humidity these crystals do not lose any water but the area under the endotherm due to loss of water increases gradually with time and by this process the complex is transformed to the considerably stable trans-[NiL$_2$(H$_2$O)$_2$][NO$_3$]$_2$·2H$_2$O (4) in *ca.* 48 h (Scheme).

The freshly prepared crystals of complex (2) does not show

$$cis-[NiL_2(H_2O)_2][NO_3]_2 \xrightarrow{(i) \text{ or } (ii)} cis-[NiL_2(NO_3)]NO_3$$

(1)   **(2')**

$trans-[NiL_2(NO_3)_2]$

(3)

$trans-[NiL_2(H_2O)_2][NO_3]_2 \cdot 2H_2O$

(4)

$cis-[NiL_2(NO_3)]NO_3$

(2'')

$cis-[NiL_2(NO_3)]NO_3$

(2)

(iii)   *(iii)*   *(iv) or (v)*   *(iv) or (v)*   *(ii) or (vi)*   *(iii) or (v)*   *(vii)*

Scheme. (i) 47—83 °C; (ii) P_2O_5 desiccator; (iii) 90% relative humidity; (iv) 112—157 °C; (v) 60% relative humidity; (vi) 32—85 °C; (vii) ca. 200 °C, with melting. The species (2), (2'), and (2'') are structurally and spectroscopically similar but differ in phase-transition temperature range (Table 1)

the exothermic phase transformation (see Thermal Analyses section) on keeping in a P_2O_5 desiccator for several days; the thermal profile remained unchanged. However if these crystals are kept at 60 or 90% humidity they gradually absorb water molecules and are finally transformed into (4). It is of great interest that this aquated (partially or fully) species on heating shows the exothermic *cis* ⟶ *trans* isomerisation like complexes (1) or (4) before melting and the transition temperature is highly dependent on the amount of water absorbed; the greater the amount of water absorbed the lower is the transformation temperature. In this process, on absorbing four molecules of water, complex (2) transforms to (4) and the transition temperature is decreased from the melting point to ca. 128 °C (Table 1).

Another interesting observation is that the deaquated *cis*-[NiL₂(NO₃)]NO₃ obtained from complex (1) or (4) can be stored in the P_2O_5 desiccator for several months. However, at 60% humidity it is transformed to *trans*-[NiL₂(NO₃)₂] (3) in ca. 24 h (Scheme). This observation clearly demonstrates that the water molecule present in the humid atmosphere catalyses this *cis* ⟶ *trans* isomerisation

Conclusion

The above results indicate that the deaquated *cis*-[NiL₂-(NO₃)]NO₃ obtained from complex (1) or (4) can be transformed into *trans*-[NiL₂(NO₃)₂] by two different ways: (i) at room temperature in the presence of humidity; and (ii) on heating at ca. 150 °C (Scheme). In the first case, the role of humidity *i.e.* water is found to be very significant for this *cis* ⟶ *trans* isomerisation. It takes only 0.5 h for complete transformation in the presence of 90% humidity, whereas the time at 60% humidity is ca. 12 h. This apparent involvement of

water in the isomerisation process suggests that an aquation–anation mechanism is probably operative here.[2b,7,12] In this Scheme aquation could result from the high effective concentration of water in the lattice due to its high mobility relative to the charged species. This would permit a large number of encounters between water molecules and *cis*-[NiL₂(NO₃)]⁺ followed by anation to bring about the isomerisation. The enhanced rate at higher humidity and the non-occurrence of isomerisation at room temperature in the absence of water corroborate the important catalytic role of the water molecule. However, in the second case, where the anhydrous salt isomerises exothermally on heating, water does not play any role in the isomerisation process. Consequently, the thermal energy is supposed to be effective in the intramolecular rearrangements such as bond rupture, twisting, and anation in order to facilitate the isomerisation.[2b,13]

It is to be noted that complex (2) does not show any isomerisation before melting whereas the anhydrous *cis* product obtained from (1) and (4) undergoes isomerisation at a temperature much below the melting point, although all these three compounds have the same structure. However, the melted product of complex (2) is found to be *trans* indicating that isomerisation occurs simultaneously with melting. This is probably due to the fact that the loss of water from (2) and (4) produces a large number of defects in the crystals. Since complexes near a defect are known to experience enhanced reactivity, their isomerisation is expected to occur at a lower temperature. This is also in accord with the gradual lowering of transformation temperature with increased amount of absorbed water.

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