Isomerism in Bis(diethylenetriamine)nickel(II) Thiocyanate: Synthesis, Solid-state Interconversion and X-Ray Crystallographic Study of sym-*fac* and *mer* Isomers†

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Bis(diethylenetriamine)nickel(II) thiocyanate has been found to undergo a phase transition (162–180 °C, $\Delta H = 29.4$ kJ mol^{-1}) involving a low-temperature ordered system (sym-*fac* isomer **1**) and a high-temperature disordered system (*mer* isomer **2**). Both isomers have been synthesised and characterized by X-ray crystallography. Isomer **2** is metastable and reverts to **1** in the presence of a humid atmosphere (relative humidity *ca.* 60% or more) as heterogeneous catalyst. Isomer **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 7.240(2)$, $b = 8.225(3)$, $c = 8.766(3)$ Å, $\alpha = 63.27(2)$, $\beta = 74.07(4)$, $\gamma = 65.56(2)°$, $Z = 1$, $R = 0.024$. In the cationic unit, the ligand geometry around nickel(II) is nearly octahedral. Two chelating tridentate diethylenetriamine (dien) molecules with terminal amino groups in *cis* and secondary amino groups in *trans* position define the sym-*fac* geometry. Isomer **2** crystallizes in the cubic system, space group $F\bar{4}3m$, with $a = b = c = 12.373(3)$ Å, $Z = 4$, $R = 0.112$. The cation $[\mathrm{Ni(dien)_2}]^{2+}$ is three-fold disordered about the [111] direction and the two tridentate dien molecules are co-ordinated meridionally.

Thermally induced solid-state geometrical isomerism in bis(diamine) complexes of first-row transition metals is of great interest and has been studied by several workers.[1–4] However no such isomerism has been reported for bis(tridentate ligand) complexes.

The bis complexes of the tridentate ligand diethylenetriamine (dien) can exist in three geometrical isomers: meridional (*mer*), symmetrical facial (sym-*fac*) and unsymmetrical facial (unsym-*fac*). The isolation and characterization of these isomers for first-row transition metals are well documented.[5] The equilibrium distribution in solution[6] and molecular-mechanics studies[7–9] show that the difference in energy among them is only a few kJ mol^{-1}. Therefore, the possibility of thermally induced solid-state transformation of these isomers cannot be ruled out.[10] To investigate this, attempts have been made in this laboratory for several $\mathrm{Ni^{II}(dien)_2}$ complexes[5f] but none of them except the present one is found to undergo such isomerization.

Here we report the first ever example of such isomerization in sym-*fac*-bis(diethylenetriamine)nickel(II) thiocyanate which on heating in the solid state transforms into its *mer* isomer. The latter has also been synthesised from solution. Single-crystal X-ray analyses of both the sym-*fac* and *mer* isomers have been performed.

Experimental

All the chemicals used were AR grade and high-purity diethylenetriamine was obtained from Fluka and distilled before use. Analyses (C, H and N) were made by a 240 Perkin-Elmer elemental analyser. Infrared (in KBr) and electronic spectra (in Nujol) were recorded on Perkin-Elmer 783 and Philips Analytical SP8-150 spectrophotometers, respectively. The effective magnetic moments were evaluated from magnetic susceptibility measurements with an EG and G PAR 155 vibrating-sample magnetometer. X-Ray powder diffraction patterns were recorded by a Philips XRD diffractometer (PW 1730/1710) at 25 °C (relative humidity 30%) using Cu-Kα radiation. The thermally induced solid-state transformation was investigated with a Perkin-Elmer DSC-2 differential scanning calorimeter and a Shimadzu DT-30 thermal analyser. Indium metal was used as calibrant for the evaluation of enthalpy changes.

Preparations.—sym-*fac*-$[\mathrm{Ni(dien)_2}][\mathrm{SCN}]_2$ **1**. This complex was prepared by addition of dien (2–3 mmol) to a solution of nickel(II) thiocyanate (1 mmol) dissolved in ethanol–water (9 : 1, 10 cm^3). Shiny pink crystals separated on stirring the resulting mixture for 2–3 min. These were filtered off, washed with ethanol and dried in a desiccator (70% yield) (Found: C, 31.3; H, 6.9; N, 29.2; Ni, 15.1. $\mathrm{C_{10}H_{26}N_8NiS_2}$ requires C, 31.5; H, 6.8; N, 29.4; Ni, 15.4%). UV/VIS: $\lambda_{\max}$ 518 and 330 nm. μ_{eff} 3.1 μ_B. Recrystallization from methanol yielded pink rhombic crystals suitable for X-ray analysis.

mer-$[\mathrm{Ni(dien)_2}][\mathrm{SCN}]_2$ **2**. Diethylenetriamine (2–3 mmol) was added to a solution of nickel(II) thiocyanate (1 mmol) dissolved in methanol (10 cm^3). The resulting mixture was set aside without stirring at room temperature. After 4–5 d prismatic crystals appeared and were filtered off (40% yield) (Found: C, 31.4; H, 6.7; N, 29.5; Ni, 15.3. $\mathrm{C_{10}H_{26}N_8NiS_2}$ requires C, 31.5; H, 6.8; N, 29.4; Ni, 15.4%). UV/VIS: $\lambda_{\max}$ 520 and 330 nm. μ_{eff} 3.1 μ_B. Complex **2** was found to be unstable and reverted to **1** on keeping in a humid atmosphere (see Results and Discussion), thus making extremely difficult crystallographic data collection. Therefore, the crystal of **2** used

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, ppl. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

for X-ray intensity data collection was coated with an amorphous resin immediately after isolation.

X-Ray Data Collection, Structure Determination, and Refinement.—A suitable single crystal of complex **1** was mounted on a glass fibre using low-temperature adhesive. Diffraction measurements were made at 185 K with an Enraf–Nonius CAD-4 diffractometer equipped with a low-temperature device. Unit-cell dimensions were determined from the angular settings of 25 randomly selected reflections. Intensity data were collected by ω–2θ scans and corrected for Lorentz-polarization and absorption[11] factors. The structure was solved by the heavy-atom method and refined by full-matrix least squares based on *F*. The hydrogen atoms were located by Fourier-difference syntheses. The final refinement with anisotropic thermal parameters for all non-hydrogen atoms (hydrogen atoms were treated isotropically) converged to $R = 0.024$. Unit weights were assigned throughout. The final difference map showed maximum and minimum peak heights of +0.47 and −0.3 e Å^{-3} respectively. The crystal data are listed in Table 1 and atomic coordinates in Table 2.

Indexing of the X-ray powder pattern of complex **2** (*h*, *k*, *l* either all odd or all even) revealed a face-centred cubic system. After several unsuccessful attempts, the single-crystal diffraction data collection was finally performed on a Nicolet R3m/V automated diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Summaries of the crystal data and data collection parameters are listed in Table 1. Unit-cell dimensions were obtained by least-squares refinement of the angular settings of 15 reflections having 2θ 10–25 °. The data were corrected as for **1**. Systematic absences indicated possible space groups *F*23, *Fm*3, *F*432, *Fm*3*m* and $F\bar{4}3m$ of which the latter was confirmed by a successful structure solution. Owing to the remarkable disorder problem, a straightforward structure solution of **2** by routine use of the program package MULTAN 87[12a] or SHELX 86[12b] proved impossible. The structure was solved by a meticulous interpretation of the apparently flat Patterson map coupled with judicious symmetry considerations. Since the face-centred cubic cell contained four $[Ni(dien)_2]^{2+}$ cations and eight SCN^- anions it was logical to assume that the Ni atoms would occupy one of the four sets of $\bar{4}3m$ symmetry sites of the space group $F\bar{4}3m$. Positioning the Ni atom at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and considering the highest non-origin peak in the Patterson map at 0.315, 0.315, 0.315 to be due to the Ni–S interatomic vector (peaks due to Ni ··· Ni interactions coincided with the face centring) the coordinates of the S atom of one of the anions were obtained. The S atom of the remaining anion and the non-hydrogen atoms of the $[Ni(dien)_2]^{2+}$ cation, located from successive Fourier-difference maps, occupying different symmetry sites were found to be disordered. The observed 2:1 occupancy factor ratio between the two N-atom sites with coordinates *x*, *x*, *z* and $\frac{1}{4}, \frac{1}{4}, x$ respectively indicated that the former ones were primary nitrogens while the latter were the secondary nitrogens of the chelating diamine. Satisfactory refinement of such a structure with high degree of disorder was practically impossible. Isotropic constrained least-squares refinement with all observed data converged to $R = 0.112$. This high value could be attributed to the inability of locating the C and N atoms in the anions. A Fourier-difference map computed at this stage contained maximum and minimum peak heights of 0.59 and −0.44 e Å^{-3} respectively indicating that the main structural features of **2**, especially those of the cations, were correct. The atomic coordinates are listed in Table 3.

Calculations were carried out with programs SHELX 76,[12c] SHELX 86, MULTAN 87 and PARST[12d] on Vax Computer Stations at the University of York, and the Indian Association for the Cultivation of Science, Calcutta. Scattering factors and corrections for anomalous scattering for Ni were taken from ref. 13. Selected bond distances and angles for **1** and **2** are given in Tables 4 and 5.

Table 1 Crystallographic data* for sym-*fac*-$[Ni(dien)_2][SCN]_2$ **1** and *mer*-$[Ni(dien)_2][SCN]_2$ **2**

Crystal symmetry	Triclinic	Cubic
Space group	$P\bar{1}$	$F\bar{4}3m$
a/Å	7.240(2)	12.373(3)
b/Å	8.225(3)	12.373(3)
c/Å	8.766(3)	12.373(3)
α/°	63.27(2)	90
β/°	74.07(4)	90
γ/°	65.56(2)	90
U/Å^3	421.9(4)	1894(1)
Z	1	4
F(000)	202	808
D_c/g cm^{-3}	1.50	1.34
D_m/g cm^{-3}	1.48	1.37
Crystal size/mm	0.4 × 0.3 × 0.2	0.3 × 0.15 × 0.10
μ/cm^{-1}	13.3	11.8
T/K	185	291
Range 2θ/°	3–60	3–50
No. of reflections measured	2691	208
Criterion for observed data [$I \geqslant n\sigma(I)$]	2	all data
No. of observed data	2322	208
R	0.024	0.112
R′	0.024	0.112

* Details in common: $C_{10}H_{26}N_8NiS_2$; *M* 381.2; scan method ω–2θ.

Table 2 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for sym-*fac*-$[Ni(dien)_2][SCN]_2$ **1**

Atom	*x*	*y*	*z*
Ni*	0	0	0
N(1)	−0.0154(2)	0.2748(2)	−0.0233(2)
N(2)	0.1639(2)	0.0836(2)	−0.2455(2)
N(3)	−0.2441(2)	0.1238(2)	−0.1467(2)
N(4)	−0.3398(3)	−0.2066(3)	−0.1531(3)
C(1)	0.0574(3)	0.3837(2)	−0.2012(3)
C(2)	0.2218(3)	0.2510(3)	−0.2758(3)
C(3)	0.0451(3)	0.1056(3)	−0.3695(2)
C(4)	−0.1739(3)	0.1999(3)	−0.3322(2)
C(5)	−0.4144(2)	−0.2756(2)	−0.1985(2)
S	−0.5258(1)	−0.3687(1)	−0.2634(1)

* Occupancy 0.5.

Table 3 Atomic coordinates with e.s.d.s in parentheses for *mer*-$[Ni(dien)_2][SCN]_2$ **2**

Atom	*x*	*y*	*z*	Occupancy factor
Ni	0.25	0.25	0.25	0.0417
S(1)	0.567(2)	0.567(2)	0.567(2)	0.0417
S(2)	0.163(3)	0.773(7)	0.163(3)	0.0417
N(11)	0.365(1)	0.365(1)	0.278(6)	0.1667
N(21)	0.25	0.25	0.414(20)	0.0833
C(11)	0.375(3)	0.375(3)	0.401(6)	0.1667
C(21)	0.317(3)	0.317(3)	0.494(4)	0.1667

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Structure of sym-*fac*-$[Ni(dien)_2][SCN]_2$ **1**.—The crystal structure consists of discrete $[Ni(dien)_2]^{2+}$ cations and NCS^- anions. With the Ni atom lying at a crystallographic inversion centre, the asymmetric unit consists of one chelated triamine and one thiocyanate. An ORTEP[14] view with the atom labelling and ring numbering scheme is shown in Fig. 1. The Ni–N bond distances range between 2.096 (1) and 2.134(1) Å, consistent with similar systems.[15] The nickel environment is as nearly octahedral as the ligand bite angles permit, comprising six nitrogen atoms from two tridentate dien molecules with the terminal amino groups in *cis* and secondary amino groups in *trans* position. Complex **1** is therefore the sym-*fac* geometrical isomer. The conformation of the chelate rings according to the ring numbering scheme in Fig. 1 is λδ, λδ. This conformer was found to exist in sym-*fac*-$[Co(dien)_2]Br_3$[16] and calculated to possess lower strain energy than any other conformer of the cobalt(III) system. However, as Ni^{II} has M–N bond lengths similar to those of Co^{II}, the minimized strain energies of the nickel(II) isomers should be very close to those of the corresponding cobalt(II) isomers. In sym-*fac*-$[Co(dien)_2]^{2+}$ the λδ, λδ conformer has been calculated to have a strain energy 3 kJ mol^{-1} higher than that of the lowest-strain-energy conformer λλ, λλ. The less-favoured conformation may exist in crystals owing to intermolecular forces and the release of energy on lattice formation where the conformers differ in energy only by a few kJ mol^{-1}. Weak hydrogen bonding between the nitrogen atom of thiocyanate and one of the primary amino groups was observed [N(3) $\cdots$ N(4) 3.10, N(3)–H(N3B) 0.80, N(4)–H(N3B) 2.37 Å; N(4)–H(N3B)–N(3) 151°].

Structure of mer-$[Ni(dien)_2][SCN]_2$ **2**.—The crystal structure consists of disordered $[Ni(dien)_2]^{2+}$ cations and SCN^- anions. The asymmetric unit contains one Ni, two N, two C atoms of the cation and two SCN groups (anionic part), all lying on various special positions with adequate fractional occupancies. The nickel atom is surrounded by 18 (12 + 6 symmetry-related sites of x, x, z and $\frac{1}{4}, \frac{1}{4}, x$ types) nitrogen atom sites forming three groups of 4 + 2. Each group of nitrogen atoms displays a distorted-octahedral geometry, the N–Ni–N angles ranging between 80(1) and 180(1)° respectively. The two tridentate dien molecules with both terminal and secondary amino groups *trans* define complex **2** as a meridional isomer. The corresponding N atoms of the three NiN_6 chromophores are related by transformations $x, y, z \longrightarrow z, x, y \longrightarrow y, z, x$, leading to a three-fold disorder of the cation about the [111] direction. With such disordering the C,N positions could obviously be ascertained with limited accuracy. This led to an indeterminacy of the chelate ring conformation. An ORTEP view of the cation (without disorder) is shown in Fig. 2. Bond distances and angles of the cation are listed in Table 5. The observed Ni–N bond distances are in agreement with those in **1** and related systems.[15]

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for sym-*fac*-$[Ni(dien)_2][SCN]_2$ **1**

Ni–N(1)	2.134(1)	Ni–N(2)	2.110(1)
Ni–N(3)	2.096(1)	N(1)–C(1)	1.481(2)
N(2)–C(2)	1.493(2)	N(2)–C(3)	1.471(2)
N(3)–C(4)	1.479(2)	S–C(5)	1.647(2)
N(4)–C(5)	1.161(2)		
N(1)–Ni–N(2)	81.2(1)	N(1)–Ni–N(3)	92.6(1)
N(2)–Ni–N(3)	82.1(1)	Ni–N(1)–C(1)	110.1(1)
Ni–N(2)–C(2)	109.7(1)	Ni–N(2)–C(3)	107.4(1)
Ni–N(3)–C(4)	110.6(1)	S–C(5)–N(4)	178.5(2)

Table 5 Bond distances (Å) and angles (°) of the cation in *mer*-$[Ni(dien)_2][SCN]_2$ **2** with e.s.d.s in parentheses

Ni–N(11)	2.04(2)	Ni–N(21)	2.03(2)
N(11)–C(11)	1.53(10)	N(21)–C(21)	1.53(5)
C(11)–C(21)	1.53(8)		
N(11)–Ni–N(21)	80(1)	N(11)–Ni–N(13)	161(2)
N(21)–Ni–N(22)	180(1)	Ni–N(11)–C(11)	106(2)
Ni–N(21)–C(21)	130(2)	N(11)–C(11)–C(21)	132(3)
N(21)–C(21)–C(11)	91(3)		

Thermal Isomerization.—Complex **1** on heating shows an endothermic phase transition (162–180; peak 168 °C) in the differential thermal analysis (DTA) curve, whereas the thermal gravimetric analysis (TGA) curve remains flat (Fig. 3). The enthalpy change of this irreversible transformation was estimated to be 29.4 kJ mol^{-1} by differential scanning colorimetry (DSC). The colour of the species after the transition seems to be more intense than that of the species before the

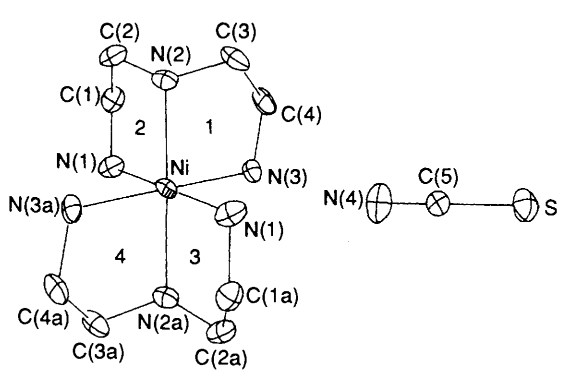

Fig. 1 An ORTEP view of complex **1** with the atom labelling and ring numbering scheme

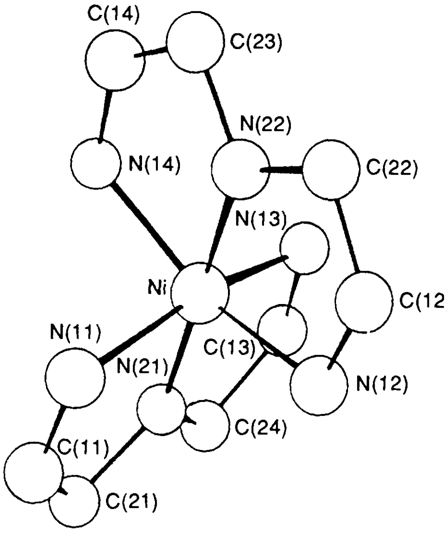

Fig. 2 An ORTEP view of cation (without disorder) in complex **2** with the atom labelling scheme

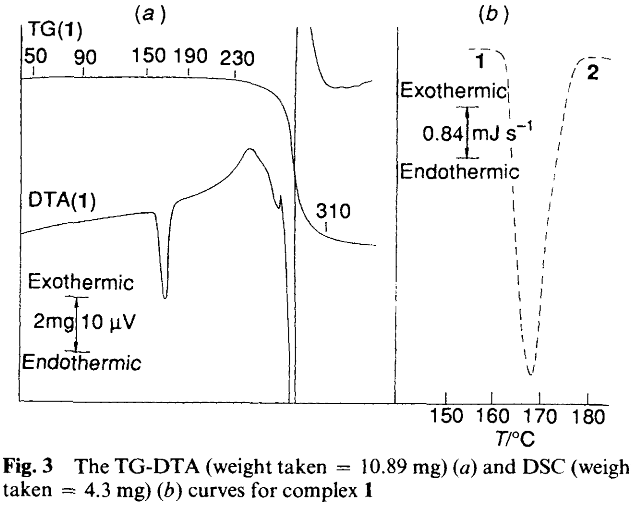

Fig. 3 The TG-DTA (weight taken = 10.89 mg) (*a*) and DSC (weight taken = 4.3 mg) (*b*) curves for complex **1**

transition. The IR spectra and X-ray powder diffraction patterns (Figs. 4 and 5) of the former species differ appreciably from those of **1** but are interestingly identical to those of **2**. Therefore, it is assumed that *mer*-[Ni(dien)$_2$][NCS]$_2$ **2** and the species formed after the phase transition are identical, *i.e.* the *fac* isomer on heating isomerizes endothermally to the *mer* isomer.

Magnetic Moments and Electronic Spectra.—The magnetic moment and electronic spectrum of complex **1** are typical of octahedral nickel(II) and those of **2** are very similar.

IR Spectra.—Searle and House[5e] used IR spectroscopy to characterize three possible geometric isomers of [Cr(dien)$_2$]$^{3+}$. The *fac* isomers have a band at 780 cm^{-1} which is absent for the *mer* isomer. Complex **1** shows the characteristic intense peak of a *fac* isomer at 780 cm^{-1} (Fig. 4). Complex **2** shows an intense peak at 890 cm^{-1}, a weak peak at 862 cm^{-1} and a broad band at *ca.* 1570 cm^{-1} all of which are characteristics of a *mer* isomer.[5e] Moreover the spectral pattern of **2** in the region 950–800 cm^{-1} is a replica of that of *mer*-[Ni(dien)$_2$]Cl$_2$·H$_2$O the structure of which has been determined by single-crystal X-ray crystallography.[17] Therefore, it is reasonable to conclude that in **2** the ligands are arranged meridionally. This was subsequently confirmed by single-crystal X-ray analysis.

Effect of Humidity.—Complex **2** is metastable and on keeping in a humid atmosphere reverts to **1**. Measurements of ΔH (by DSC) and X-ray powder diffraction patterns (Fig. 5) have been used to study the rate of reversion and to characterize the products. The X-ray powder pattern of **2** shows fewer lines than that of **1**. When **2** was kept in a humid atmosphere it showed all the strong characteristic lines of **1** in addition to the original lines, and the intensities of the lines corresponding to **1** increased while those of **2** decreased in the course of time. Finally the latter disappeared leaving only the lines of **1**, indicating complete reversion **2** $\longrightarrow$ **1**. The rate of reversion is dependent on the relative humidity. To study this we used three closed vessels of constant humidity,[18] *ca.* 90, 60 and 30%, and the results are shown in Table 6. It is clear that the higher is the humidity the faster is the rate of reversion. This indicates the apparent involvement of a water molecule although neither **1** nor **2** absorbs any water from the humid atmosphere. Therefore, the water molecule is acting as a heterogeneous catalyst.

Kinetic Analysis.—The rate equation for the non-isothermal solid-state reaction can be expressed[19,20] as in (1) where α is the

$$\ln [(\mathrm{d}\alpha/\mathrm{d}T)\beta] - \ln F(\alpha) = \ln A - (E/RT) \qquad (1)$$

fraction of the reaction after time t, $F(\alpha)$ is a function depending on the reaction mechanism, β is the linear heating rate, A is the pre-exponential factor, E the activation energy and R the gas constant. In this study the rate of reaction $[(\mathrm{d}\alpha/\mathrm{d}T)\beta]$ has been directly determined from the DSC measurements. A plot of $\ln [(\mathrm{d}\alpha/\mathrm{d}T)\beta] - \ln F(\alpha)$ against T^{-1} shows the best linearity over nearly the whole reaction range if $F(\alpha)$ is taken to be $1 - \alpha$ (Fig. 6).[19] The activation energy obtained from the plot is 748 ± 75 kJ mol^{-1}. A possible explanation for the observed high activation energy in the present system compared to that for geometrical isomerism in bis(diamine) complexes[20] ($\approx$325 kJ mol^{-1}) is as follows. In the latter case rearrangement of only one chelate ring is sufficient for *cis* $\rightleftharpoons$ *trans* isomerism, whereas for the proposed *fac* $\rightleftharpoons$ *mer* isomerization at least one chelate ring of each dien molecule needs to be rearranged in

Table 6 Reversion of *mer*-[Ni(dien)$_2$][SCN]$_2$ **2** to sym-*fac*-[Ni(dien)$_2$][SCN]$_2$ **1** at different relative humidities

Relative humidity (%)	Days exposed	Reversion (%)
90	14	90
90	30	100
60	14	2
60	30	5
30	30	0

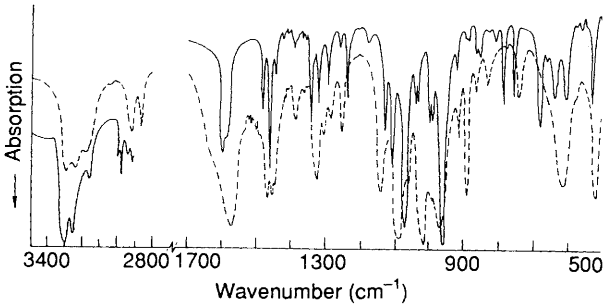

Fig. 4 Infrared spectra for complexes **1** (——) and **2** (– – – –)

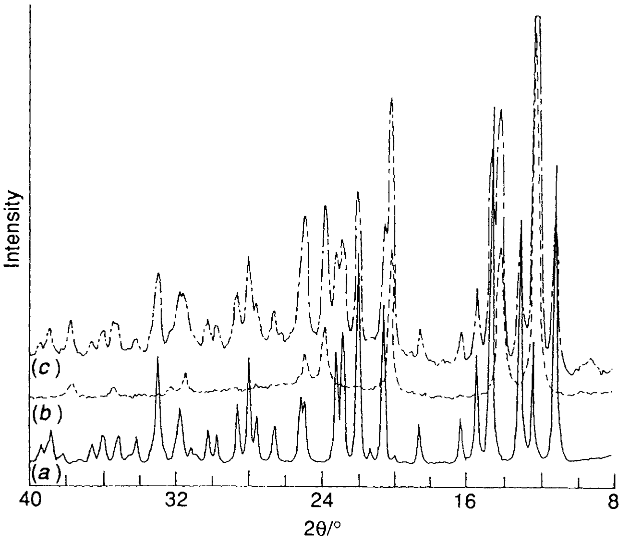

Fig. 5 X-Ray powder patterns for (*a*) complex **1**, (*b*) **2** and (*c*) the partially reverted product of **2**, kept at 90% relative humidity for 5 d

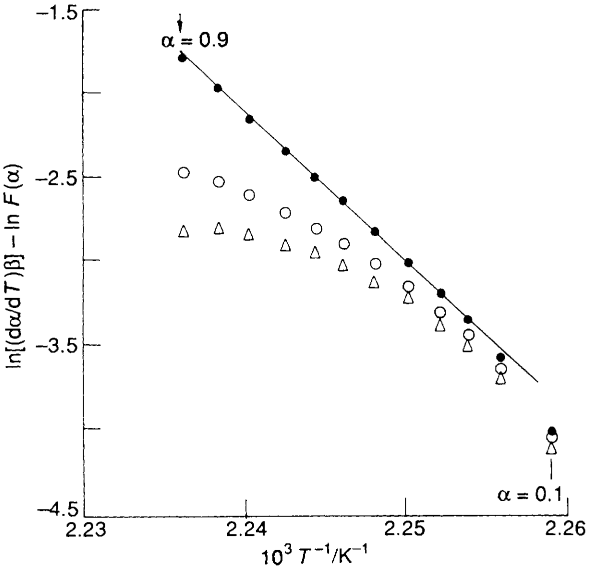

Fig. 6 Plots of $\ln [(\mathrm{d}\alpha/\mathrm{d}T)\beta] - \ln F(\alpha)$ *versus* T^{-1}. Among the nine models[20] of $F(\alpha)$ examined these three plots approach the best linearity. $F(\alpha) = (1 - \alpha)^n$ where $n = 1$ (●), $\frac{2}{3}$ (○) or $\frac{1}{2}$ (△)

the transition state. This indicates that the reaction occurs through a bond-rupture mechanism.[21] A similar mechanism has been suggested for sym-*fac* $\rightleftharpoons$ *mer* rearrangement of $[Co(dien)_2]^{3+}$ in solution.[22]

The results of this work can be summarized as follows. (*a*) Bis(diethylenetriamine)nickel(II) thiocyanate undergoes a phase transition involving a low-temperature ordered system (sym-*fac* isomer) and a high-temperature disordered system (*mer* isomer). (*b*) The *mer* isomer can also be synthesised from solution and is metastable. It reverts to the sym-*fac* isomer in a humid atmosphere (relative humidity *ca.* 60% or above) as heterogeneous catalyst. (*c*) The sym-*fac* $\rightleftharpoons$ *mer* isomerization for the dien system is reported here for the first time in the solid state.

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