Synthesis of Conformational Isomers, Thermally Induced Isomerism, and Crystal Structure of *cis*-Di-isothiocyanatobis(*N*-methylpropane-1,3-diamine)nickel(II)†

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Two isomers, (**1**) and (**1a**), of $[NiL_2(NCS)_2]$ (L = *N*-methylpropane-1,3-diamine) have been synthesised. Isomer (**1**) undergoes an irreversible endothermic solid-state phase transition (383—413 K, ΔH = 8.1 kJ mol^{-1}) transforming into species (**1a**). This isomerisation also takes place on crystallisation from methanol, ethanol, chloroform, or acetonitrile. Species (**1a**) has been characterised by *X*-ray crystallography. The crystals are monoclinic, space group $P2_1/c$ with four formula units in a unit cell of dimensions a = 8.136(2), b = 13.057(2), c = 15.235(3) Å, and β = 90.75(1)°. The structure has been solved by Patterson and successive Fourier syntheses and refined by block-diagonal least-squares calculations to R = 0.048 and R' = 0.061 for 2 311 reflections. The metal atom co-ordination is nearly octahedral with the two thiocyanate groups in *cis* position. The overall configuration and conformation of the complex molecule is Λ_{pp} (two chairs fold in the same rotational direction). Isomer (**1**) probably exists in the Λ_{pa} form (two chairs fold apart from each other).

The conformations of five- and six-membered chelate rings in transition-metal complexes have been studied extensively.[1] It has been found that six-membered rings, especially those formed by 1,3-propanediamine (tn) have either a stable, symmetrical chair or a skew-boat conformation. The other possible conformation, the symmetrical boat form, is rarely found in metal diamine complexes.

In 1971, Geue and Snow[2] determined the structure of *cis*-$[Co(tn)_2(CO_3)]ClO_4$ to study the conformations of *cis*-arranged six-membered rings. They found that both the tn chelate rings have chair conformations. Two chairs which are *cis* to one another have three possible spatial arrangements. On the basis of the relative energies of the different conformers with a particular configuration (say Λ) about the metal ion, the order of stabilities is as follows: Λ_{pa} (two chairs fold apart from each other) > Λ_{pp} (two chairs fold in the same rotational direction) > Λ_{ap} (two chairs fold towards each other), where p and a are chair ring conformers which fold such that the central carbon atom defines a rotation direction parallel or antiparallel to the direction defined by the metal ion.[3] Geue and Snow[2] also calculated the metal strain energy of three possible forms of *cis*-$[Co(tn)_2(CO_3)]ClO_4$ and showed that the Λ_{ap} conformer is less stable than the Λ_{pp} and Λ_{pa} forms by 20.1 and 13.4 kJ mol^{-1}, respectively.

Several complexes ML_2X_2 (M = Cu^{II} or Ni^{II}, L = *NN*-diethylethane-1,2-diamine, X = anion) exhibit continuous or discontinuous thermochromism, depending on the anion selected. For the discontinuously thermochromic complexes, differential scanning calorimetry (d.s.c.) experiments show that the thermochromism is accompanied by an endothermic transition.[4b,5] It was initially thought that the thermochromism was due to increased axial interaction of the anion.[5,6] However, in 1979 Grenthe *et al.*[7] reported on the basis of single-crystal *X*-ray analysis of both phases of bis(*NN*-diethylethane-1,2-diamine)copper(II) perchlorate that the thermochromism was due to a sudden decreased strength of the in-plane ligand field caused by conformational changes in the ring system. It has been observed in the case of nickel(II) complexes which show thermochromism that the red shift is not as dramatic as that observed for the copper(II) complexes.[4a] As a result, in some cases the conformational changes that may occur in the diamine chelate rings of bis(diamine)nickel(II) complexes cannot be detected by visual colour changes. Rather a simultaneous thermal gravimetry–differential thermal analysis (t.g.–d.t.a.) and/or d.s.c. technique would be very helpful to detect such changes, as they are generally accompanied by an endothermic transition without any mass loss.[4b,5] Such an attempt was made first in this laboratory[8] for diamine complexes of $Ni(SCN)_2$ and the observed endothermic phase transitions were related to the conformational changes of the diamine chelate ring on the basis of either enthalpy changes [8a,b,d] or *X*-ray crystallographic data.[8c] The present paper reports the syntheses of two conformational isomers of *cis*-di-isothiocyanatobis(*N*-methylpropane-1,3-diamine)nickel(II), thermally induced conformational changes in the solid state, and crystal structure analysis of one isomer.

Experimental

N-Methylpropane-1,3-diamine(L) was purchased from Fluka in high-purity grade and used as received.

Preparation of Complexes.—The complex $[NiL_2(NCS)_2]$ (**1**) was prepared by adding the diamine (L) (2 mmol) dropwise to nickel(II) thiocyanate (1 mmol) dissolved in methanol (10 cm^3) at *ca.* 233 K. The resultant solution was stirred for 1 h on a methanol-bath at *ca.* 233 K. The desired blue complex separated

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† *Supplementary data available* (No. SUP 56783, 3 pp.): i.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

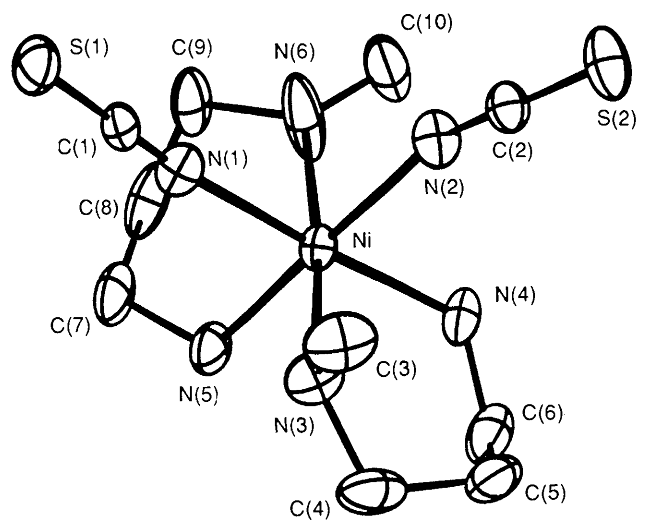

Figure 1. ORTEP plot of $[NiL_2(NCS)_2]$ (**1a**) with labelling of the non-hydrogen atoms

Table 1. Positional parameters and their estimated standard deviations (e.s.d.s) for $[NiL_2(NCS)_2]$ (**1a**)

Atom	*x*	*y*	*z*
Ni	0.197 99(7)	0.031 03(4)	0.225 14(4)
S(1)	0.290 5(2)	−0.310 2(1)	0.122 2(1)
S(2)	−0.316 2(2)	−0.122 7(1)	0.304 8(1)
N(1)	0.266 6(5)	−0.102 6(3)	0.162 8(3)
N(2)	−0.042 8(5)	−0.026 2(3)	0.232 7(3)
N(3)	0.274 3(6)	−0.040 9(3)	0.344 1(3)
N(4)	0.111 0(5)	0.162 8(3)	0.289 4(3)
N(5)	0.433 3(5)	0.096 5(4)	0.214 6(3)
N(6)	0.134 3(7)	0.087 9(7)	0.098 2(4)
C(1)	0.276 9(5)	−0.189 3(4)	0.145 1(3)
C(2)	−0.158 7(6)	−0.064 9(4)	0.262 1(3)
C(3)	0.186 8(8)	−0.133 4(5)	0.370 1(4)
C(4)	0.310 3(8)	0.025 5(5)	0.421 2(4)
C(5)	0.176 8(7)	0.104 2(6)	0.440 2(4)
C(6)	0.175 0(8)	0.192 1(5)	0.375 1(4)
C(7)	0.516 8(7)	0.089 1(5)	0.127 9(4)
C(8)	0.418 5(9)	0.135 9(5)	0.054 6(4)
C(9)	0.263 3(7)	0.080 2(5)	0.030 7(4)
C(10)	0.004 4(8)	0.141 5(7)	0.079 9(4)

Table 2. Selected bond distances (Å) and angles (°) in $[NiL_2(NCS)_2]$ (**1a**) with e.s.d.s in parentheses

Ni–N(1)	2.066(4)	S(2)–C(2)	1.630(5)
Ni–N(2)	2.101(4)	N(1)–C(1)	1.168(7)
Ni–N(3)	2.126(4)	N(2)–C(2)	1.164(6)
Ni–N(4)	2.106(4)	N(3)–C(3)	1.460(8)
Ni–N(5)	2.105(5)	N(3)–C(4)	1.486(7)
Ni–N(6)	2.130(6)	N(6)–C(9)	1.481(8)
S(1)–C(1)	1.621(5)	N(6)–C(10)	1.295(9)
N(1)–Ni–N(2)	89.0(2)	N(1)–Ni–N(4)	175.9(1)
N(1)–Ni–N(3)	86.6(2)	N(2)–Ni–N(5)	176.6(2)
N(1)–Ni–N(5)	93.2(2)	N(3)–Ni–N(6)	173.2(2)
N(1)–Ni–N(6)	86.6(2)	N(4)–Ni–N(6)	93.3(2)
N(2)–Ni–N(3)	93.3(2)	N(5)–Ni–N(6)	90.0(2)
N(2)–Ni–N(4)	86.9(2)	Ni–N(1)–C(1)	161.0(4)
N(2)–Ni–N(6)	87.6(2)	Ni–N(2)–C(2)	159.4(4)
N(3)–Ni–N(4)	93.5(2)	S(1)–C(1)–N(1)	179.0(5)
N(3)–Ni–N(5)	89.3(2)	S(2)–C(2)–N(2)	177.7(5)
N(4)–Ni–N(5)	90.9(2)		

and was washed with methanol and dried in a desiccator (Found: C, 34.5; H, 6.6; N, 23.8; Ni, 16.8. Calc. for $C_{10}H_{24}N_6NiS_2$: C, 34.2; H, 6.8; N, 23.9; Ni, 16.7%), $\mu_{eff.}$ 3.27, $\lambda_{max.}$ 580 and 362 nm.

The complex $[NiL_2(NCS)_2]$ (**1a**) was prepared by the above procedure at ambient temperature (*ca.* 298 K). It was also obtained by recrystallisation of complex (**1**) from methanol, ethanol, chloroform, or acetonitrile (Found: C, 34.3; H, 6.9; N, 23.9; Ni, 16.8%), $\mu_{eff.}$ 3.23, $\lambda_{max.}$ 578 and 362 nm.

A crystal suitable for *X*-ray analysis was obtained from a methanolic solution kept at room temperature (*ca.* 298 K).

Physical Measurements.—Elemental analyses were carried out using a 240C Perkin-Elmer analyser. Infrared spectra of KBr discs and electronic spectra of mulls (Nujol) were recorded with Perkin-Elmer IR 783 and Philips Scientific SP 8-150 spectrophotometers, respectively. The effective magnetic moments were evaluated from magnetic susceptibility measurements with an EG and G PAR 155 vibrating-sample magnetometer at room temperature. *X*-Ray powder-diffraction patterns were obtained with a Philips XRD diffractometer (PW 1730/1710) using Cu-K_α radiation.

Solid-state thermal investigations were carried out 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.

Crystallography.—Crystal data. $C_{10}H_{24}N_6NiS_2$ (**1a**), M = 351.2, monoclinic, space group $P2_1/c$, $a = 8.136(2)$, $b = 13.057(2)$, $c = 15.235(3)$ Å, $\beta = 90.75(1)°$, $U = 1\,618$ Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $T = 165$ K, $Z = 4$, $D_c = 1.44$ g cm^{-3}, dark blue crystal, dimensions 0.2 × 0.2 × 0.15 mm, $F(000) = 744$, $\mu(\text{Mo-}K_\alpha) = 14.48$ cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω—2θ mode, graphite-monochromated Mo-K_α radiation; 3 114 unique reflections ($1 < \theta < 25°$, $\pm h, k, l$) giving 2 311 with $I > 2\sigma(I)$. No absorption correction. No significant decay of intensity controls during data collection.

Structure analysis and refinement. Heavy-atom method. Block-diagonal least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions (methyl hydrogen atoms excepting one from difference map) with individual isotropic thermal parameters. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.02\,F_o^{\,2}]$, with $\sigma(F_o)$ from counting statistics. Final R and R' values were 0.048 and 0.061. Maximum, minimum peak height in final Fourier difference map, ± 0.7 e Å^{-3}. Sources of scattering factor data (Ni atom treated as anomalous scatterer with $\Delta f' = 0.285$, $\Delta f'' = 1.113$) and programs (run on a Burroughs 6700 computer at the Regional Computer Centre, Calcutta) are given in refs. 9 and 10.

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

Results and Discussion

Crystal and Molecular Structure of Complex (**1a**).—The crystal contains discrete monomeric units. An ORTEP plot of (**1a**) with labelling of the non-hydrogen atoms is shown in Figure 1. Table 1 gives the positional parameters, Table 2 selected bond lengths and angles. The geometry around the metal atom is close to octahedral, N–Ni–N angles lying within ± 3.5° of the value expected (90°) for ideal octahedral symmetry, with the two thiocyanate groups in *cis* position. The overall configuration and conformation of complex (**1a**) is Λ_{pp}, *i.e.* the two six-membered diamine chelate rings, ring 1 formed by Ni, N(3), N(4), C(4), C(5), C(6), and ring 2 defined by Ni, N(5), N(6),

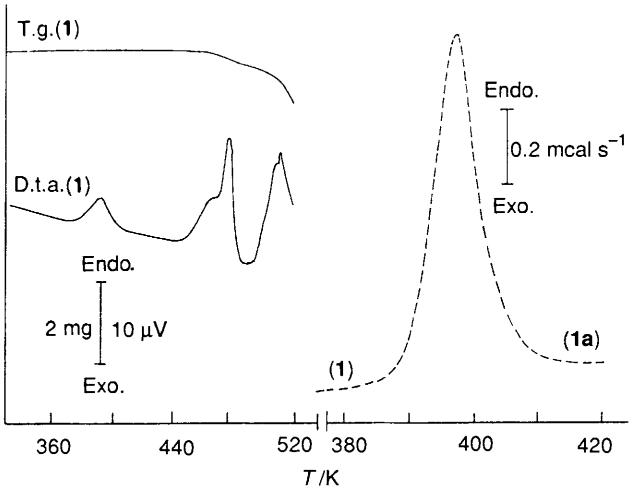

Figure 2. T.g.–d.t.a. (weight taken = 12.4 mg) (——) and d.s.c. (weight taken = 8.36 mg) (– – –) curves for $[NiL_2(NCS)_2]$ (1); cal = 4.184 J

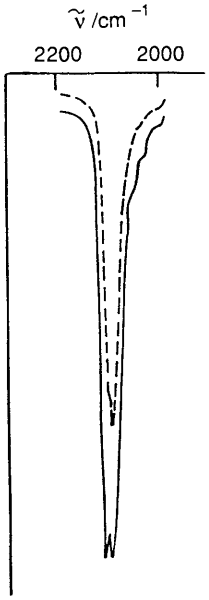

Figure 3. I.r. spectra of complexes (1) (——) and (1a) (– – –) in KBr

Table 3. Prominent lines (*d*/Å) in the *X*-ray powder patterns of the complexes $[NiL_2(NCS)_2]$

(1)	(1a)
8.76vs, 7.63ms, 7.08vs, 6.58s,	7.69s, 7.02w, 6.66ms, 6.42vs,
6.33m, 5.83mw, 5.66m, 5.26ms,	6.11w, 5.61m, 5.52vw, 5.01m,
5.10w, 4.95w, 4.82mw, 4.71mw,	4.90w, 4.30w, 4.11ms, 4.04m,
4.53w, 4.37mw, 4.09w, 4.04w,	3.89ms, 3.82ms, 3.61mw, 3.48m,
3.90s, 3.80w, 3.65mw, 3.53ms,	3.40w, 3.34ms, 3.19mw, 3.08w,
3.43mw, 3.30vs, 3.17m, 3.05mw,	2.95w, 2.89vw, 2.79w, 2.72w,
2.96vw, 2.91mw	2.68vw, 2.64w

vs = Very strong, s = strong, m = medium, and w = weak.

C(7), C(8), C(9), are in chair conformation and folded in the same rotational direction parallel to the direction (clockwise) defined by the metal ion. Chelate ring 2 is significantly flattened compared to ring 1; the torsion angle sum for ring 2 is 336.8° and that for ring 1 is 292.9°.

All the bond distances except N(6)–C(10) and angles are consistent with similar systems.[8c,11] The bond N(6)–C(10) of 1.295(9) Å is unusually short compared to N(3)–C(3) [1.460(8) Å]. To verify this unexpected result, the structure was redetermined using intensity data collected independently by one of the authors (A. K. M.) at the Crystallography Department of Birkbeck College, London. Refinement converged to $R = 0.058$, $R' = 0.065$ with N(6)–C(10) 1.31(2) Å. Shortening of this bond distance and the fact that the four atoms Ni, N(6), C(9), and C(10) display a planar geometry with none of them deviating from the least-squares plane by more than 0.67(8) Å apparently indicates a double-bond nature of N(6)–C(10). However, such an assumption has no chemical justification. In view of the large value of U_{22} (0.158 Å^2) for C(10), a better explanation of the shortness of this bond may be an unresolved disorder of C(10), the observed position being the mean of two positions, one slightly above and the other slightly below the mean plane through Ni, N(6), C(9), and C(10).

Complex (1) undergoes an endothermic irreversible phase transition (383—413 K, $\Delta H = 8.1$ kJ mol^{-1}) without any mass loss as is evident from the simultaneous t.g.–d.t.a. and d.s.c. studies (Figure 2). The species isolated after the phase transition appears identical to (1a) as it has an identical i.r. spectrum and *X*-ray powder diffraction pattern. Considering the crystal structure of (1a) and the appearance of similar ν(CN) and ν(CS) bands in the i.r. spectra of the two isomers (Figure 3) it is suggested that in complex (1) also the thiocyanate groups are N-bonded and in *cis* position[12] as in (1a). The electronic spectral and magnetic data for these two isomers suggest they have an identical NiN_6 chromophore. On the other hand, the dissimilarity in the i.r. spectra of the diamine vibrations of the complexes as well as in the *X*-ray powder diffraction patterns (Table 3) indicates that these two isomers probably differ only in their chelate ring conformations.[8] Complex (1) exists in a low-energy state (8.1 kJ mol^{-1}) as it is converted into (1a) with an endothermic phase transition. Consequently complex (1) is expected to possess the Λ_{pa} conformational form. Earlier, we reported thermally induced conformational changes of *trans*-$[NiL_2(NCS)_2]$ (L = tn,[8a] *NN*-dimethylpropane-1,3-diamine,[8b] or *NN'*-dimethylethane-1,2-diamine[8c]) and *trans*-$[Ni(tn)_2(NO_2)_2]$,[8d] where the transformed species (isolated after the phase transition) were observed to revert to their respective original forms either on crystallisation[8b,d] or merely on keeping in a humid atmosphere for a few hours.[8a,c] However, in the present case, isomer (1a) is very stable and once formed cannot be converted into any other isomers. Complex (1), though existing in a low-energy state, on crystallisation transforms to the higher-energy form, (1a). This is probably due to the fact that less-favoured conformations may exist in the crystals owing to intermolecular forces and the release of energy on lattice formation.[13] Where the isomers differ in energy only by a few kJ mol^{-1}, the one found in the crystals will depend largely on the requirements of the crystal lattice. In this context a question may arise regarding the purity of isomer (1). From the *X*-ray powder patterns (Table 3) of (1) we could find no evidence for the presence of (1a), some of the strong lines of (1a) being totally absent.

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