Thermally Induced Phase Transition and *X*-Ray Crystal Structure of Bis(*N,N'*-dimethyl-1,2-ethanediamine)di-isothiocyanatonickel(II)†

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The complex $[Ni(MeNHCH_2CH_2NHMe)_2(NCS)_2]$ (**1**) has been synthesised and characterised by *X*-ray crystallography. It undergoes an irreversible endothermic phase transition (452.5—468.5 K, ΔH = 13.4 kJ mol^{-1}) to species (**2**) which reverts to (**1**) in a humid atmosphere. Complex (**1**) crystallises in the monoclinic space group $C2/c$ with a = 13.069(2), b = 9.783(3), c = 15.074(4) Å, β = 111.40(2)°, and Z = 4. The structure has been solved by Patterson and successive Fourier methods and refined to R = 0.032 for 1 240 independent observed reflections. The co-ordination around the nickel atom, lying on a crystallographic inversion centre, is close to octahedral with the two thiocyanate N atoms in *trans* position. The chelate rings exist in the δλ conformation. For complex (**2**), $a = b$ = 8.16(3), c = 7.53(2) Å, $\alpha = \beta$ = 107.0(2), γ = 73.6(3)°, and Z = 1. Crystallographic and i.r. spectroscopic data suggest a non-centrosymmetric structure for (**2**) with a qualitative change in the conformation of the complex to δδ or λλ.

The conformations of five- and six-membered diamine chelate rings in metal complexes are well documented.[1–13] Their relative stabilities were calculated from the intramolecular non-bonded interactions. However little has been accomplished as regards the phase changes of this type of compound in the solid state. Recently, phase changes of some nickel(II) diamine complexes have been reported by us,[14–16] on the basis of an analysis of the general stereochemistry of chelate compounds and the stereospecific effects of the individual chelate rings in complex ions. However, any discussion relating to the conformations of complexes is speculative, unless supported by crystal-structure analysis. The present paper reports the results of an *X*-ray crystallographic study on $[NiL_2(NCS)_2]$ (L = *N,N'*-dimethyl-1,2-ethanediamine) and a thermally induced phase transition in the crystal.

Experimental

All the chemicals used were A.R. grade. Carbon, H, and N were estimated by a 240 C Perkin-Elmer elemental analyser. Phase transitions, i.r. spectra (KBr disc), electronic spectra (mull), and effective magnetic moments at room temperature were recorded by apparatus reported earlier.[14,15]

Preparation of $[NiL_2(NCS)_2]$ (**1**).—The diamine (*ca.* 2 mmol) was added dropwise to nickel thiocyanate (1 mmol) dissolved in ethanol–water (9:1). The resulting mixture was stirred vigorously for 1 h and kept overnight. The shiny pink crystals which separated were washed with ethanol, recrystallised from ethanol–water (9:1), and dried in air (Found: C, 34.1; H, 6.6; N, 24.0; Ni, 16.8. Calc. for $C_{10}H_{24}N_6NiS_2$: C, 34.2; H, 6.8; N, 23.9; Ni, 16.7%).

Structure Determination of $[NiL_2(NCS)_2]$ (**1**).—A single crystal (0.2 × 0.15 × 0.1 cm) was mounted on a glass fibre using low-temperature adhesive. Preliminary Weissenberg photographs yielded approximate cell dimensions. Systematic absences of *X*-ray reflections showed that the crystals belonged to one of the monoclinic space groups Cc or $C2/c$. An examination of the *X*-ray intensities following data collection strongly suggested a centrosymmetric structure and the chosen space group $C2/c$ (C^6_{2h}) was confirmed by a successful analysis. To maximise the chances of locating H atoms, a low-temperature study was performed by transferring the same crystal to an Enraf–Nonius CAD-4 diffractometer and cooling slowly to 185 K in a stream of cold nitrogen. The final cell dimensions were obtained from the least-squares fit of 25 strong reflections, well distributed in reciprocal space.

Crystal data. $C_{10}H_{24}N_6NiS_2$, M = 175.59, monoclinic, space group $C2/c$, a = 13.069(2), b = 9.783(3), c = 15.074(4) Å, β = 111.40(2)°, U = 1 794.4(8) Å^3, D_m(flotation) = 1.30, Z = 4, D_c = 1.30 g cm^{-3}, $F(000)$ = 744, graphite-monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 12.98 cm^{-1}.

Collection and reduction of data. Three-dimensional intensity data ($+h$, $+k$, $\pm l$) were recorded using ω—2θ scans in the range $1 < \theta < 25°$. Two standard reflections were remeasured once in every hour of *X*-ray exposure but subsequent analysis showed no crystal decomposition or movement. Data were corrected for Lorentz and polarisation effects but not for absorption. After data processing, 1 240 of 1 743 independent reflections measured had $F_o > 4\sigma(F_o)$ and these were used for structure solution and refinement.

Structure analysis and refinement. The structure was solved by the heavy-atom method and refined by block-diagonal least squares. The Ni atom was located at a crystallographic inversion centre (0.25, 0.25, 0.5), so that only one chelated diamine and one isothiocyanate group are independent. The positions of all non-hydrogen atoms were determined from successive Fourier syntheses. The hydrogen atoms of the Me groups were located in the difference synthesis; other H atoms were placed

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: cal = 4.184 J.

Table 1. Positional parameters for $[NiL_2(NCS)_2]$ (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni*	0.25	0.25	0.50	H(2)	0.075(2)	0.031(3)	0.377(2)
S(1)	0.636 3(1)	0.163 1(1)	0.652 4(1)	H(3)	0.138(3)	−0.087(4)	0.361(2)
N(1)	0.411 7(2)	0.202 4(3)	0.578 2(2)	H(4)	0.279(2)	0.022(3)	0.440(2)
N(2)	0.229 1(2)	0.041 9(3)	0.456 0(2)	H(5)	0.311(3)	−0.025(3)	0.590(2)
N(3)	0.205 2(2)	0.177 8(3)	0.613 6(2)	H(6)	0.205(2)	−0.116(3)	0.526(2)
C(1)	0.504 5(2)	0.185 4(3)	0.609 4(2)	H(7)	0.170(3)	−0.021(3)	0.653(2)
C(2)	0.136 1(3)	0.006 9(5)	0.370 2(3)	H(8)	0.095(2)	0.063(3)	0.543(2)
C(3)	0.229 6(3)	−0.034 7(4)	0.541 2(3)	H(9)	0.272(2)	0.162(3)	0.665(2)
C(4)	0.161 7(3)	0.039 3(4)	0.587 2(3)	H(10)	0.060(2)	0.280(3)	0.595(2)
C(5)	0.129 8(3)	0.260 6(4)	0.645 1(2)	H(11)	0.107(3)	0.214(4)	0.691(3)
H(1)	0.148(3)	0.051(3)	0.315(2)	H(12)	0.164(3)	0.365(3)	0.670(2)

* Occupancy 0.5.

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

Ni–N(1)	2.063(2)	Ni–N(2)	2.127(3)
Ni–N(3)	2.123(3)	S(1)–C(1)	1.619(3)
N(1)–C(1)	1.142(3)	N(2)–C(2)	1.457(4)
N(2)–C(3)	1.485(6)	N(3)–C(4)	1.467(5)
N(3)–C(5)	1.480(5)	C(3)–C(4)	1.497(7)
N(2)–Ni–N(3)	83.7(1)	N(1)–Ni–N(3)	89.5(1)
N(1)–Ni–N(2)	87.2(1)	Ni–N(1)–C(1)	168.8(2)
Ni–N(2)–C(3)	104.7(2)	Ni–N(2)–C(2)	118.2(2)
C(2)–N(2)–C(3)	112.9(3)	Ni–N(3)–C(5)	119.2(2)
Ni–N(3)–C(4)	106.4(2)	C(4)–N(3)–C(5)	110.8(3)
S(1)–C(1)–N(1)	179.1(3)	N(2)–C(3)–C(4)	109.9(3)
N(3)–C(4)–C(3)	109.6(3)		

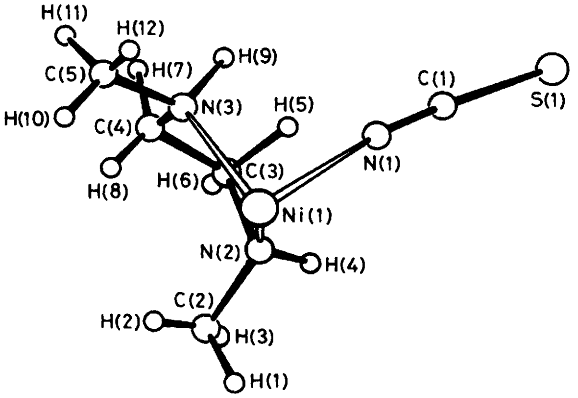

Figure 1. View of the asymmetric unit of complex (**1**) down the *b* axis with the atom-numbering scheme

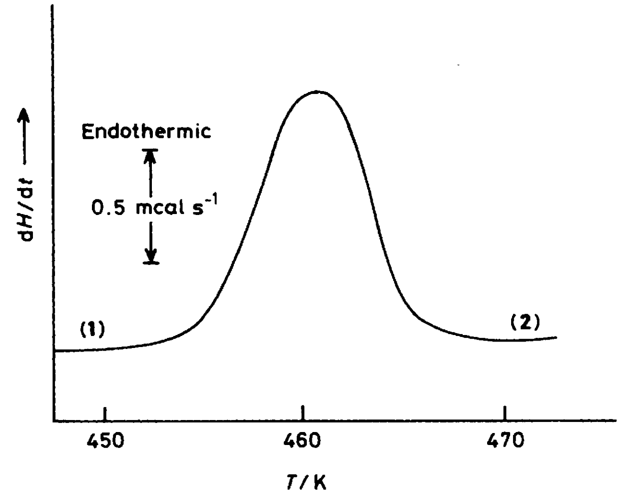

Figure 2. D.s.c. curves showing the transformation of complex (**1**) (6.34 mg) into (**2**)

in geometrically calculated positions. All atoms were refined anisotropically, with the exception of the H atoms included in the refinement with individual isotropic thermal parameters. The refinement converged at $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.032$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/w|F_o|^2]^{\frac{1}{2}} = 0.040$ with weights given by $w^{-1} = [\sigma^2(F_o) + 0.02|F_o|^2]$. The Ni atom was treated as an anomalous scatterer with $\Delta f' = 0.285$ and $\Delta f'' = 1.113$.[17] In the final cycle of refinement the largest shift/estimated standard deviation (e.s.d.) was 0.96 (for a H parameter). The final Fourier difference map was featureless with the maximum/minimum peak height ± 0.4 e Å^{-3}.

Final positional parameters with their estimated standard deviations are given in Table 1, selected bond distances (Å) and angles (°) in Table 2. All the calculations were carried out on a Burroughs 6700 computer at the Regional Computer Centre, Calcutta with the programs *X*-RAY ARC,[18] NORMAL-EXFFT-SEARCH of the MULTAN 78[19] package, and PARST.[20] Atomic scattering factors were taken from ref. 17.

Results and Discussion

A view of the asymmetric unit of complex (**1**) along the *b* axis with the atom numbering scheme is shown in Figure 1. The geometry around the metal atom is as close to octahedral as the ligand bite permits, the diamine N atoms and nickel lying in a plane with the two thiocyanate N atoms in *trans* position. The Ni–N(diamine), –N(thiocyanate) bond distances, Ni–N(2) 2.127(3), Ni–N(3) 2.123(3), and Ni–N(1) 2.063(2) Å, are consistent with similar systems.[21–23] All other bond distances and angles have the usual values. Both the methyl C atoms are *cis* with respect to the chelate ring, the corresponding deviations of C(2) and C(5) from the plane defined by Ni, N(2), and N(3) being 1.204(4) and 0.852(3) Å respectively. Of the three possible conformations (δδ, λλ, and δλ) of the two chelate rings, δδ and λλ are optical isomers with the same relative strain energy and since the molecule has a centre of inversion it exists in the δλ conformation.[24]

Complex (**1**) undergoes an irreversible endothermic phase transition upon heating in the range 452.5—468.5 K (ΔH = 13.4 kJ mol^{-1}; peak temperature 461.0 K) and is transformed to species (**2**) (Figure 2) which reverts to (**1**) on keeping in a humid

Table 3. I.r. spectral data (cm^{-1}) of nickel(II) diamine complexes

Compound	ν(NH)	$\nu(CH_3)$ + $\nu(CH_2)$	ν(CN)	$\delta(CH_2)$	$\rho_w(CH_2)$	τ(NH) + ρ_w(NH) + $\tau(CH_2)$	Stretching vibrations of skeleton ν(C–N) + ν(C–C)	$\rho_r(CH_2)$	ν(CS)
(**1**)	3 250s, 3 225s	2 985m, 2 960(sh), 2 940m, 2 910m, 2 850m, 2 800w	2 090vs	1 470m, 1 458s, 1 445s, 1 430m, 1 410w	1 364vw, 1 343w	1 275m, 1 267(sh), 1 210vw, 1 167vw, 1 143m, 1 132m	1 086m, 1 064m, 1 025s, 1 005(sh), 1 000s, 966s, 953s	852s, 817w	780m
(**2**)	3 220s	2 985w, 2 960m, 2 915m, 2 862m, 2 800w	2 090vs	1 470(sh), 1 460(sh), 1 450s, 1 428(sh), 1 410m	1 363vw, 1 342w	1 275m, 1 225vw, 1 208vw, 1 165vw, 1 141m	1 090m, 1 069s, 1 052m, 1 030m, 1 010s, 990s, 970s, 960s, 932s, 912(sh)	855s, 830m, 810w	780m

sh = Shoulder, v = very, s = strong, m = medium, and w = weak.

atmosphere (relative humidity 70—80%), but not when kept in a desiccator. This suggests that the conversion (**2**) $\longrightarrow$ (**1**) is catalysed by the moisture present in the atmosphere. A similar type of moisture-catalysed isomerisation was reported earlier.[14] The i.r. spectra (Table 3) of species (**2**) shows similarity in the region of ν(CN) and ν(CS)* with (**1**), and it can be tentatively concluded that the thiocyanate groups here also are N-bonded and in *trans* position. The configuration of the donor atoms around the metal ion is expected to be the same in (**1**) and (**2**) as is evident from their magnetic moments and absorption bands [for (**1**), $\mu_{eff.} = 3.28$, $\lambda_{max.} = 545$ and 345 nm; for (**2**), $\mu_{eff.} = 3.32$, $\lambda_{max.} = 560$ and 355 nm]. The small deviations in $\lambda_{max.}$ may be due to the confliction of normal angles between metal–ligand bonds,[1] and is corroborated by the fact that the i.r. spectra (Table 3) of (**2**) differ from (**1**) in the region of ν(NH), $\delta(CH_2)$, skeletal [ν(C–C) and ν(C–N)], and $\rho_r(CH_2)$ vibrations indicating some changes in the spatial arrangement of the chelate rings during isomerisation.[14]

In order to explain the above phenomenon several single crystals of complex (**1**) were placed in thin glass capillaries and heated to 190 °C at a rate of 0.5 °C min^{-1} in an atmosphere of nitrogen gas, at which temperature the capillaries were sealed. Oscillation and Weissenberg photographs of a single-crystal specimen of (**2**) thus obtained revealed the following cell parameters: $a = 8.16(3)$, $b = 8.16(3)$, $c = 7.53(2)$ Å, $\alpha = 107.0(2)$, $\beta = 107.0(2)$, and $\gamma = 73.6(3)°$. These correspond to those of the reduced primitive cell of the monoclinic C-centred lattice of (**1**), except for a halving of the parameter *c*. The unit cell of (**2**), with $U = 446.7$ Å^3, is a quarter of that of the C-centred cell of (**1**) and contains only one molecule of complex ($Z = 1$). Thus in (**2**) all the molecules are related by translational symmetry and are identically oriented. In (**1**) the pair of molecules with Ni situated respectively at 0.25, 0.25, 0.5 and 0.75, 0.25, 0.0 are related by a two-fold axis of rotation. This symmetry element has now vanished, resulting in a lower, triclinic, symmetry for (**2**). The question of whether Ni still occupies a centre of symmetry in (**2**), *i.e.* whether the space group is $P\bar{1}$ or $P1$, may be settled by the following considerations. Since the conformation of complex (**1**) has been established to be δλ the conformations of the complexes (**1**) and (**2**) may be described by considering their relative orientations as δλ and λδ. Now if the Ni atoms still occupy centres of symmetry in (**2**), *i.e.* if the space group is $P\bar{1}$, all the molecules must have identical conformation and orientation, either δλ or λδ. This means that the changes in the ligands, indicated by the spectroscopic study, occur in only half the number of molecules in the structure, the other half remaining unaffected during the structural transition. This is a highly improbable situation. It appears more reasonable to conclude that all the molecules are equally affected during transition, adopting either a δδ or λλ conformation and consequently their centrosymmetric nature is destroyed, resulting in a space group $P1$ for the structure of (**2**). Thus, the structural transition brings about a qualitative change in the conformation of the complex.

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* The ν(CS) band is identified by comparison with that of $[NiL_2Cl_2]$ and $[NiL_2Br_2]$.[16]

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