Cl3—Hg1—Cl2	163.6 (2)	Cl1$^{\rm i}$—Hg1—Cl2$^{\rm ii}$	99.2 (2)
Cl3—Hg1—Cl1$^{\rm i}$	96.4 (2)	Cl1—Hg1—Cl2$^{\rm iii}$	97.5 (2)
Cl2—Hg1—Cl1$^{\rm i}$	95.9 (2)	Cl2—Hg1—Cl2$^{\rm iii}$	81.6 (2)
Cl3—Hg1—Cl1	97.3 (2)	Cl3—Hg1—Cl2$^{\rm iii}$	85.1 (2)
Cl2—Hg1—Cl1	93.9 (2)	Cl1$^{\rm i}$—Hg1—Cl2$^{\rm iii}$	174.1 (2)
Cl1—Hg1—Cl1$^{\rm i}$	88.0 (2)	Cl2$^{\rm ii}$—Hg1—Cl2$^{\rm iii}$	75.3 (2)
Cl1—Hg1—Cl2$^{\rm ii}$	172.5 (2)	Hg1$^{\rm iv}$—Cl1—Hg1	180.0 (3)
Cl2—Hg1—Cl2$^{\rm ii}$	83.3 (2)	Hg1$^{\rm v}$—Cl1—Hg1	88.0 (2)
Cl3—Hg1—Cl2$^{\rm ii}$	84.2 (2)	Hg1—Cl1—Hg1$^{\rm vi}$	92.0 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iv) $1+x, 1-y, -z$; (v) $1+x, y, z$; (vi) $x, 1-y, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
N1—H1A···Cl2	2.69	3.508 (3)	159
N1—H1A···Cl2$^{\rm i}$	3.13	3.517 (3)	111
N1—H1B···Cl3$^{\rm ii}$	2.74	3.374 (3)	132
N1—H1B···Cl3$^{\rm iii}$	2.85	3.466 (3)	131
N2—H2A···Cl3$^{\rm iv}$	2.63	3.346 (3)	142
N2—H2A···Cl2$^{\rm i}$	3.15	3.548 (5)	111

Symmetry codes: (i) $1+x, y, z$; (ii) $1+x, 1-y, -z$; (iii) $x, 1-y, -z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -z$.

The largest peaks and holes in the ΔF Fourier map are within 1.0 Å of the Hg1 atom site.

Data collection: *Kuma KM-4 Users Guide* (Kuma Diffraction, 1991). Cell refinement: *Kuma KM-4 Users Guide*. Data reduction: *Kuma KM-4 Users Guide*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation* (Siemens, 1989). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1294). Services for accessing these data are described at the back of the journal.

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Bis(N,N-dimethyl-1,3-propanediamine)bis(thiocyanato-N)nickel(II), NiL_2(NCS)$_2$, and its Solid-State Isomer [L = NH$_2$(CH$_2$)$_3$N(CH$_3$)$_2$]

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Abstract

The coordination polyhedron about the Ni$^{\rm II}$ atom in NiL_2(NCS)$_2$, (1), where L = NH$_2$(CH$_2$)$_3$N(CH$_3$)$_2$, is a distorted octahedron with the two thiocyanate N and the two unsubstituted N atoms of the ligand defining the equatorial plane; the two dimethylated N atoms occupy *trans*-axial positions. The six-membered chelate rings are in stable chair conformations. Complex (1), [Ni(C$_5$H$_{14}$N$_2$)$_2$(NCS)$_2$], undergoes a thermochromic solid-state phase transition producing an isomer, (2). With the cell volume of (2) approximately double that of (1) and the crystal system remaining triclinic, the space group of the isomer (2) is $P1$ or $P\bar{1}$.

Comment

Thermally induced solid-state phase transitions in nickel(II)–diamine complexes are documented in the literature (Mukherjee, Mukherjee, Ray, Ghosh & Ray Chaudhuri, 1990; Ihara, Satake, Suzuki & Uehara, 1991; Koner *et al.*, 1995; Pariya *et al.*, 1996). The probable mechanism of the phase transition in these complexes is mostly associated with the changes in the geometry of the metal coordination and/or the conformation of the diamine chelate rings (Ihara, Fukuda & Sone, 1987; Roy, Ghosh & Ray Chaudhuri, 1989; Pariya *et al.*, 1995). The present work was undertaken as part of our ongoing program studying the effect of diamine substituents on phase transition and to construct a hierarchy. A

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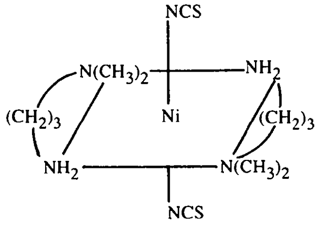
single-crystal X-ray structure analysis of [NiL_2(NCS)$_2$], (1), where L = *N,N*-dimethyl-1,3-propanediamine, and a powder diffraction study of its solid-state isomer, (2), are reported here.



(1)

An *ORTEP*II (Johnson, 1976) view of complex (1) with our atom-labelling scheme is shown in Fig. 1. The metal atom in complex (1) lies at the centre of inversion, hence, the crystallographic asymmetric units consist of half molecules. The coordination polyhedron around the Ni atom is best described as a distorted octahedron. The four ligand N atoms (N1, N2 and their centrosymmetrically related counterparts) define the equatorial plane and the two dimethylated N atoms (N3 and its centrosymmetric counterpart) are in *trans*-axial positions. The lengthening of the axial Ni—N3 distances [2.337 (2) Å] compared with the equatorial plane Ni—N bonds [Ni—N1 2.042 (2) and Ni—N2 2.108 (3) Å] define the tetragonal distortion of the metal coordination. Similar elongation of Ni—NR'_2 (R' = CH_3, C_2H_5) bond lengths are observed in several nickel(II)–diamine complexes with octahedral metal coordination (Table 3). Table 3 shows that the Ni—N bond distances increase in the order Ni—NH_2 < Ni—NHR < Ni—NR'_2. The six-membered chelate ring adopts a stable chair conformation, with Ni 0.891 (1) Å below and C3 0.702 (3) Å above the least-squares plane through the remaining endocyclic atoms; the maximum in-plane deviation is 0.000 (3) Å for C2.

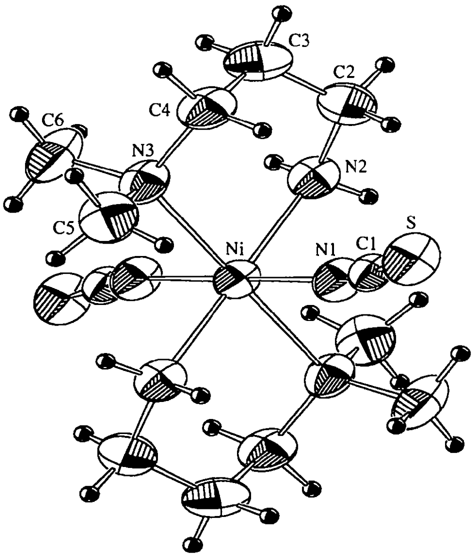


Fig. 1. *ORTEP*II (Johnson, 1976) view of a molecule of complex (1) with 50% probability ellipsoids and the atom-labelling scheme.

Complex (1) isomerizes to (2) (temperature range 383.0–397.5 K) in the solid state. Identical magnetic moment ($\mu_{\rm eff}$ = 3.28 BM) and electronic spectral band positions ($\lambda_{\rm max}$ = 678, 574 and 368 nm) in (1) and (2) indicate octahedral metal coordination in both the complexes. Though it is difficult to comment on the mechanism of phase transition (1 → 2) from the X-ray powder data, the following observations are noteworthy. The cell volume of the isomer (2) is approximately double that of (1) and the crystal system (triclinic) remains unchanged. The space group of the isomer (2) could be either $P1$ with the asymmetric unit consisting of two NiL_2(NCS)$_2$ units or $P\bar{1}$ with a centrosymmetric distribution of the molecules. The mechanism of phase transition (1 → 2) may be ascribed to the slight alteration in the crystal packing with or without any conformational changes of the diamine chelate ring.

Experimental

The title complexes (1) and (2) were synthesized according to the method of De & Ray Chaudhuri (1985). Diffraction quality single crystals of (1) were obtained on recrystallization from ethanol.

Compound (1)

Crystal data

[Ni($C_5H_{14}N_2$)$_2$(NCS)$_2$]
M_r = 379.23
Triclinic
$P\bar{1}$
a = 8.196 (5) Å
b = 9.315 (3) Å
c = 7.306 (2) Å
α = 107.50 (3)°
β = 112.93 (4)°
γ = 98.51 (3)°
V = 467.1 (3) Å^3
Z = 1
D_x = 1.348 Mg m^{-3}
D_m = 1.349 Mg m^{-3}
D_m measured by flotation in benzene–carbontetrachloride

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.26 mm^{-1}
T = 293 (2) K
Prism
0.50 × 0.35 × 0.25 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\rm min}$ = 0.624, $T_{\rm max}$ = 0.730
1731 measured reflections
1639 independent reflections

1551 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027
$\theta_{\rm max}$ = 25°
h = −9 → 8
k = −11 → 10
l = 0 → 8
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 0.988$
1639 reflections
153 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.1629P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.019$
$\Delta\rho_{\max} = 0.285$ e Å^{-3}
$\Delta\rho_{\min} = -0.450$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni	0	0	0	0.03683 (12)
S	0.32177 (8)	−0.18459 (6)	0.53333 (8)	0.0564 (2)
N1	0.1385 (2)	−0.0353 (2)	0.2752 (2)	0.0470 (4)
N2	0.2489 (2)	0.0399 (2)	−0.0253 (3)	0.0454 (4)
N3	0.0787 (2)	0.2725 (2)	0.1850 (2)	0.0467 (4)
C1	0.2166 (2)	−0.0942 (2)	0.3855 (3)	0.0375 (4)
C2	0.3144 (3)	0.1736 (2)	−0.0741 (4)	0.0561 (5)
C3	0.3461 (3)	0.3293 (2)	0.0946 (4)	0.0635 (6)
C4	0.1734 (3)	0.3646 (2)	0.0999 (4)	0.0540 (5)
C5	−0.0872 (4)	0.3260 (3)	0.1611 (5)	0.0617 (6)
C6	0.1971 (4)	0.3172 (3)	0.4170 (4)	0.0692 (7)

Table 2. *Selected geometric parameters (Å, °) for (1)*

Ni—N1	2.042 (2)	N3—C6	1.470 (3)
Ni—N2	2.108 (3)	N3—C5	1.481 (4)
Ni—N3	2.337 (2)	N3—C4	1.492 (4)
S—C1	1.629 (2)	C2—C3	1.502 (3)
N1—C1	1.152 (3)	C3—C4	1.512 (4)
N2—C2	1.478 (4)		
N1—Ni—N2	88.70 (9)	C6—N3—Ni	109.9 (2)
N1—Ni—N3	93.42 (7)	C5—N3—Ni	112.2 (2)
N2—Ni—N3	88.03 (9)	C4—N3—Ni	112.6 (1)
C1—N1—Ni	159.5 (2)	N1—C1—S	177.6 (2)
C2—N2—Ni	122.0 (2)	N2—C2—C3	111.6 (2)
C6—N3—C5	107.8 (2)	C2—C3—C4	115.7 (2)
C6—N3—C4	110.0 (2)	N3—C4—C3	116.4 (2)
C5—N3—C4	104.2 (2)		

Compound (2)

Crystal data

$[Ni(C_5H_{14}N_2)_2(NCS)_2]$
$M_r = 379.23$
Triclinic
$P\bar{1}$
$a = 7.94$ (1) Å
$b = 8.60$ (1) Å
$c = 14.36$ (2) Å
$\alpha = 93.95$ (3)°
$\beta = 97.26$ (2)°
$\gamma = 106.30$ (4)°
$V = 928$ (2) Å^3
$Z = 2$
$D_x = 1.357$ Mg m^{-3}
$D_m = 1.35$ Mg m^{-3}
D_m measured by flotation in benzene–carbontetrachloride
Cu $K\alpha_1$ radiation
$\lambda = 1.5406$ Å
Cell parameters from 37 reflections
$\theta = 5$–$25°$
$\mu = 1.81$ mm^{-1}
$T = 293$ (2) K
Powder
Blue

Table 3. *A comparison of Ni—NH$_2$, Ni—NHR and Ni—NR$'_2$ bond distances (Å) in octahedral nickel(II)–diamine complexes [R = CH$_3$, CH(CH$_3$)$_2$; R$'$ = CH$_3$, C$_2$H$_5$]*

	Ni—NH$_2$	Ni—NH*R*	Ni—N*R*$'_2$
$Ni(npda)_2(NCS)_2$[a]	2.117 (3)	2.146 (4)	
$Ni(N\text{-}metn)_2(NCS)_2$[b]	2.106 (4)	2.126 (4)	
	2.105 (5)	2.130 (6)	
$Ni(NCS)_2(NN\text{-}deen)_2$[c]	2.080 (3)		2.304 (3)
	2.086 (3)		2.331 (3)
$[Ni(H_2O)_2(NN\text{-}deen)_2].Cl_2$[d]	2.064 (3)		2.271 (3)
$NiL_2(NCS)_2$[e]	2.108 (3)		2.337 (2)

Notes: (*a*) npda = *N*^{1}-isopropyl-2-methyl-1,2-propanediamine (Pariya *et al.*, 1995); (*b*) metn = methylpropane-1,3-diamine (Mukherjee, Mukherjee, Ray, Ghosh & Ray Chaudhuri, 1990); (*c*) deen = diethylethylenediamine (Lever *et al.*, 1983); (*d*) Ihara, Satake, Fujimoto, Senda, Suzuki & Uehara (1991); (*e*) this work.

Table 4. *X-ray powder diffraction data for (2), λ = 1.5406 Å*

$d_{\rm obs}$	$d_{\rm calc}$	h	k	l	$I/I(0)$
8.195	8.201	0	1	0	100
7.101	7.117	−1	0	1	49
6.799	6.782	0	1	1	36
6.562	6.591	−1	1	0	18
6.070	6.081	−1	1	1	12
5.841	5.875	−1	1	−1	13
5.698	5.676	0	1	−2	30
5.605	5.603	−1	0	2	3
4.946	4.937	−1	1	2	10
4.870	4.883	1	1	0	1
4.808	4.808	1	0	2	19
4.710	4.721	0	0	3	15
4.398	4.399	1	1	1	23
4.276	4.300	0	1	−3	2
4.050	4.059	0	2	−1	6
3.941	3.950	−1	2	1	33
3.763	3.759	−1	1	−3	24
3.647	3.647	−2	1	−1	2
3.566	3.565	−2	1	2	6
3.289	3.296	−2	2	0	12
3.257	3.263	−2	1	−2	27
3.197	3.191	−2	0	3	7
3.164	3.165	−2	1	3	11
3.144	3.146	1	1	3	27
3.078	3.074	−1	2	3	15
3.040	3.041	−2	2	2	7
2.929	2.926	2	1	1	1
2.748	2.748	2	0	3	3
2.640	2.642	−3	1	1	3
2.450	2.450	−2	0	5	2
2.427	2.427	−3	1	3	2
2.403	2.404	2	0	4	2
2.381	2.381	−1	3	3	1
2.186	2.186	−3	3	1	2
2.013	2.012	−1	4	2	1
1.985	1.985	1	2	5	1
1.963	1.961	−3	2	−4	1

Density measurement of (1) indicated that there was one complex molecule per unit cell. Of the two possible space groups, $P1$ and $P\bar{1}$, the choice of the latter was favoured by a centrosymmetric distribution of E values, and was subsequently confirmed by a successful structure refinement. The structure of (1) was solved by a combination of Patterson and Fourier methods and refined (on F^2) through full-matrix least-squares calculations. Anisotropic refinements were performed for non-H atoms. The H atoms, located from the difference Fourier maps, were refined isotropically. All calculations were performed on a VAX3400 computer at the Computer Center, Indian Association for the Cultivation of Science. Since all attempts to obtain suitable single crystals of (2) failed, the complex was examined by X-ray powder diffraction. Accurate d_{hkl} spacings (Å) were obtained from the powder pattern recorded on a Seifert XRD-3000P diffractometer at 295 K operating at 30 kV and 30 mA with a 2° $\min^{-1}$ scan rate. The results are summarized in Table 4. The initial cell parameters have been determined from powder data and accurate lattice parameters were obtained by least-squares refinement (Gabe, Le Page, Charland, Lee & White, 1989).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989) for (1). Cell refinement: *CAD*-4 *Software* for (1). Data reduction: *CAD*-4 *Software* for (1). Program(s) used to solve structures: *SHELX*76 (Sheldrick, 1976) for (1). Program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993) for (1); *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1993) for (2). Molecular graphics: *ORTEP*II (Johnson, 1976) for (1). Software used to prepare material for publication: *SHELXL*93 for (1).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LI1152). Services for accessing these data are described at the back of the journal.

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[*N*,*N*′-Bis(2-thiobenzylidene)-1,2-phenylenediaminato]nickel(II)†

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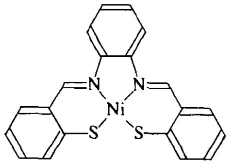
Abstract

The title compound, [$Ni(C_{20}H_{14}N_2S_2)$], was formed from a Schiff base reaction of 2-*tert*-butylthiobenzaldehyde with 1,2-phenylenediamine, followed by reaction with $Ni(BF_4)_2.6H_2O$. The square-planar NiN_2S_2 complex has Ni—N distances of 1.8992 (17) and 1.9014 (15) Å, and Ni—S distances of 2.1519 (6) and 2.1587 (6) Å. Molecules pack in layers with a tilt angle of 46.09 (1)°; the (001) packing plane is arranged so that the molecules in superimposed layers stack approximately perpendicular to each other.

Comment

Mononuclear NiN_2S_2 complexes are well known, but continue to be studied as models for the active sites in metalloenzymes, such as nickel hydrogenases (Ni-H_2ases) (Lancaster, 1988; Halcrow & Christou, 1994). The title complex, [Ni(tsalphen)], (I), and the related 4,5-dimethyl-1,2-phenylenediamino complex [Ni(tsaldimph)] (Henderson, Bouwman, Reedijk & Powell, 1996) were synthesized and characterized as part of research in modelling the active site of the Ni-H_2ase enzyme from *Desulfovibrio Gigas*, for which an X-ray structure was recently published (Volbeda *et al.*, 1995).



(I)

The title complex contains a square-planar Ni atom, coordinated by two imino N atoms and two thiolate S atoms. The asymmetric unit corresponds to one complete molecule. No use is made of the molecular

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† Alternative name: {2,2′-[1,2-phenylenebis(nitrilomethylidene)]diphenolato-*S*,*N*,*N*′,*S*′}nickel(II).

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