$a = 7.7544\,(2)$ Å
$b = 31.6493\,(10)$ Å
$c = 13.2174\,(4)$ Å
$\beta = 93.004\,(1)°$
$V = 3239.4\,(2)$ Å^3
$Z = 4$
$D_x = 1.537$ Mg m^{-3}
D_m not measured

$\mu = 0.597$ mm^{-1}
$T = 150$ K
Block
$0.3 \times 0.2 \times 0.1$ mm
Yellow

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.768$, $T_{\max} = 0.942$
16 761 measured reflections

4669 independent reflections
2852 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.103$
$\theta_{\max} = 25°$
$h = -8 \rightarrow 8$
$k = -35 \rightarrow 32$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.105$
$S = 1.064$
4665 reflections
529 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.5595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.360$ e Å^{-3}
$\Delta\rho_{\min} = -0.368$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Mn1—O7	2.127 (3)	Mn1—N2	2.273 (4)
Mn1—N1	2.228 (4)	N1—C2	1.363 (5)
Mn1—N5	2.249 (4)	N1—S1	1.644 (4)
Mn1—N3	2.253 (4)	S2—N6	1.624 (4)
Mn1—N4	2.259 (4)	N6—C29	1.368 (6)
O7—Mn1—N1	90.74 (13)	N3—Mn1—N4	96.67 (14)
O7—Mn1—N5	163.11 (14)	O7—Mn1—N2	92.92 (13)
N1—Mn1—N5	95.52 (13)	N1—Mn1—N2	95.49 (14)
O7—Mn1—N3	90.92 (14)	N5—Mn1—N2	102.04 (14)
N1—Mn1—N3	168.06 (14)	N3—Mn1—N2	72.61 (14)
N5—Mn1—N3	86.20 (14)	N4—Mn1—N2	168.69 (14)
O7—Mn1—N4	90.80 (14)	C2—N1—S1	111.3 (3)
N1—Mn1—N4	95.13 (13)	C29—N6—S2	111.7 (3)
N5—Mn1—N4	73.06 (14)		

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

JAKH thanks the Royal Society for a Leverhulme Trust Senior Research Fellowship, while DTS thanks the Students' Research Fund of the Chemistry Department, University of Botswana, and CB thanks the EPSRC, UK, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1256). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 332-334

Bis(1,3-propanediamine-*N*,*N*′)bis(thiocyanato-*N*)nickel(II)

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(*Received 19 May 1998; accepted 15 October 1998*)

Abstract

The title compound, $[Ni(NCS)_2\{H_2N(CH_2)_3NH_2\}_2]$, (I), is an octahedral complex of nickel(II) in which the thiocyanate ligands are bonded through nitrogen in a *cis* arrangement, while the 1,3-propanediamine ligands are *N*,*N*′-bidentate. The molecule lies on a crystallographic twofold axis. The coordination geometry about the metal deviates only slightly from ideal [Ni—N distance range 2.118 (3)–2.143 (3) Å, *cis*-N—Ni—N angle range 85.9 (1)–95.3 (1)° and *trans*-N—Ni—N angle range 171.9 (1)–178.3 (3)°]. The molecules pack in a non-centrosymmetric arrangement and have been determined to possess the Λ configuration. The structural features of (I) are compared to those of related *N*-substituted 1,3-propanediamine complexes.

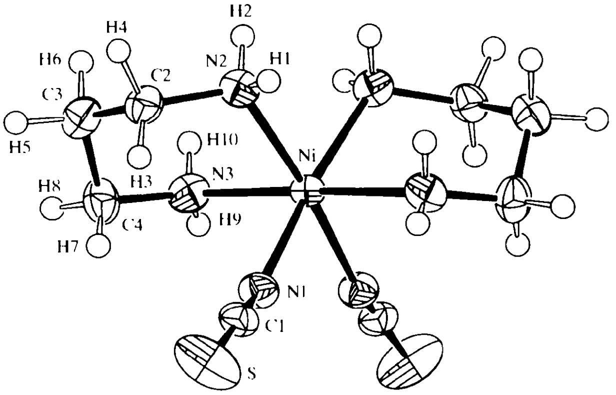
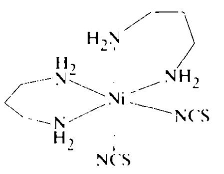


Fig. 1. *ORTEP*II (Johnson, 1976) view of a molecule of (I) showing the atom-labeling scheme. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

Comment

The conformation of six-membered rings formed by the bidentate coordination of 1,3-propanediamine to transition metals has long been of theoretical interest (Gollogly & Hawkins, 1972). In spite of this attention, only a modest number of such complexes have been structurally characterized. Recently, a number of bis(*N*-substituted-1,3-propanediamine) complexes of nickel(II) have been studied because of their ability to undergo solid-state phase transitions (Mukherjee *et al.*, 1990; Pariya *et al.*, 1995; Ghosh *et al.*, 1997). Our interest in the nickel(II)–1,3-propanediamine–thiocyanate system was prompted by the discovery of a series of hydrocarbon inclusion compounds of bis(ethylenediamine)bis(thiocyanato-*N*)nickel(II) (Squattrito *et al.*, 1996).

The title compound, (I), finds the Ni^{II} ion in a fairly regular octahedral environment (Fig. 1) of six N atoms



(I)

at distances and angles that are in the range of those found in similar complexes (Mukherjee *et al.*, 1990; Ghosh *et al.*, 1997). The thiocyanate ligands are in a *cis* arrangement and the molecule has crystallographic C_2 symmetry, with the rotation axis bisecting the N1—Ni—N1 and N2—Ni—N2 angles. The six-membered chelate rings are in the stable chair conformation [torsion angles Ni—N3—C4—C3 65.5 (5) and Ni—N2—C2—C3 −59.9 (3)°].

Thermal studies of a bis(1,3-propanediamine)bis(thiocyanato-*N*)nickel(II) complex not positively identified as *cis* or *trans* indicate the existence of several solid phases possibly differing in the conformations of the chelate rings (De *et al.*, 1984). Among related [NiL_2(NCS)$_2$] complexes, the *cis*-thiocyanate geometry has been found for L = *N*-methyl-1,3-propanediamine (Mukherjee *et al.*, 1990), while *trans* geometries were observed for L = *N*,*N*-dimethyl-1,3-propanediamine (Ghosh *et al.*, 1997) and N^1-isopropyl-2-methyl-1,2-propanediamine (Pariya *et al.*, 1995). These examples suggest that the *trans* geometry is favored when the amine ligand is more bulky. Still, it is surprising that the unsubstituted 1,3-propanediamine complex favors the *cis*-thiocyanate isomer, since the bis(ethylenediamine) complex crystallizes preferentially as the *trans* isomer under nearly identical conditions (Squattrito *et al.*, 1996).

Compound (I) crystallizes in the non-centrosymmetric space group *Iba*2, with the Ni^{II} atom on the twofold rotation axis. Brock & Dunitz (1994) have pointed out that this type of symmetry leads to effective packing of homochiral molecules with partially concave surfaces (so-called 'bean-shaped' molecules). The packing is sufficiently strong to keep the material from melting until 483 K. As noted earlier, our original interest in this system stemmed from the possibility of finding inclusion chemistry similar to that of bis(ethylenediamine)bis(thiocyanato-*N*)nickel(II) (Squattrito *et al.*, 1996), however, compound (I) failed to display any tendency to include small aromatics in its crystal structure. The very different packing in (I) may explain this result.

Determination of the absolute configuration shows that (I) exists as the Λ isomer. As required by the crystallographic symmetry, the six-membered rings are positioned so that the chairs fold towards the same side of the molecule (*i.e.* the middle C atom is pointing away from the NCS ligand). The most closely related complex, bis(*N*-methyl-1,3-propanediamine)bis(thiocyanato-*N*)nickel(II) (Mukherjee *et al.*, 1990), crystallizes in a centrosymmetric space group on a general position. The Λ isomer of this molecule has the chelate rings folded in opposite directions, with one of the middle C atoms directed towards the adjacent NCS ligand and the other directed away. It has been suggested that thermal transitions in these materials involve changes in the folding of the rings and that the different conformations are relatively close in energy, thus leading to a diverse structural chemistry in these systems.

Experimental

A 2.9 g sample of $Ni(NO_3)_2{\cdot}6H_2O$ was combined with 4.0 g of KSCN in 35 ml of water. A total of 1.5 ml of 1,3-diaminopropane was added dropwise. The resulting solution was buffered by the dropwise addition of 2-aminoethanol until the pH was *ca* 11.8, followed by saturated aqueous citric acid until the pH decreased to *ca* 8.6. Crystals up to 2 mm in size grew from this solution over a period of several days upon partial evaporation of the solvent.

Crystal data

$[Ni(NCS)_2(C_3H_{10}N_2)_2]$
$M_r = 323.11$
Orthorhombic
*Iba*2
$a = 7.579\,(2)$ Å
$b = 17.550\,(2)$ Å
$c = 11.111\,(5)$ Å
$V = 1477\,(1)$ Å^3
$Z = 4$
$D_x = 1.452$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 19 reflections
$\theta = 16.4$–$19.8°$
$\mu = 1.58$ mm^{-1}
$T = 296$ K
Plate
0.30 × 0.30 × 0.08 mm
Blue–violet

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.775$, $T_{\max} = 0.881$
1526 measured reflections
1526 independent reflections

1370 reflections with $I > 0$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.050$
$S = 2.12$
1370 reflections
107 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.67$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute structure: Flack (1983); refined using a complete set of Friedel pairs
Flack parameter = −0.019 (16)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0	0	0	0.0241 (1)
S	0.45789 (10)	0.12160 (6)	0.2287 (1)	0.0654 (3)
N1	0.1546 (3)	0.0546 (2)	0.1334 (3)	0.0329 (9)
N2	0.1270 (3)	0.0671 (2)	−0.1359 (3)	0.0323 (9)
N3	−0.1948 (3)	0.0867 (2)	0.0028 (4)	0.0343 (7)
C1	0.2825 (4)	0.0811 (2)	0.1718 (3)	0.0319 (9)
C2	0.1456 (4)	0.1502 (2)	−0.1146 (3)	0.034 (1)
C3	−0.0303 (5)	0.1900 (2)	−0.0986 (3)	0.039 (1)
C4	−0.1341 (4)	0.1661 (2)	0.0126 (5)	0.0394 (10)

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

Ni—N1	2.118 (3)	N2—C2	1.484 (4)
Ni—N2	2.143 (3)	N3—C4	1.471 (4)
Ni—N3	2.121 (2)	C2—C3	1.515 (5)
S—C1	1.635 (3)	C3—C4	1.523 (6)
N1—C1	1.157 (4)		
N1—Ni—N1^{i}	91.2 (2)	N3—Ni—N3^{i}	178.3 (3)
N1—Ni—N2	89.8 (1)	Ni—N1—C1	154.6 (3)
N1—Ni—N2^{i}	171.9 (1)	Ni—N2—C2	118.0 (2)
N1—Ni—N3	92.8 (1)	Ni—N3—C4	117.6 (2)
N1—Ni—N3^{i}	86.0 (1)	S—C1—N1	177.5 (3)
N2—Ni—N2^{i}	90.4 (2)	N2—C2—C3	112.9 (3)
N2—Ni—N3	85.9 (1)	C2—C3—C4	115.0 (3)
N2—Ni—N3^{i}	95.3 (1)	N3—C4—C3	111.3 (4)

Symmetry code: (i) $-x, -y, z$.

All H atoms were located on difference electron-density maps and their B_{iso} values set to 1.2 times those of the attached atoms at the time of their inclusion. A complete set of Friedel mates was measured and was used in the absolute configuration determination.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

This work was supported by a grant from the Faculty Research and Creative Endeavors Committee of Central Michigan University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1148). Services for accessing these data are described at the back of the journal.

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