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trans-Bis[*N*-(2-hydroxyethyl)ethylenediamine-κ^2N,N']bis(isothiocyanato-κN)nickel(II)

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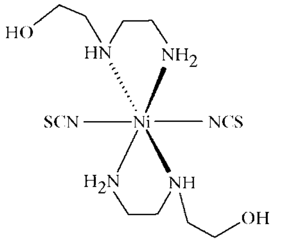
The crystal structure of the title compound, $[Ni(NCS)_2(C_4H_{12}N_2O)_2]$, has two crystallographically independent half-molecules in the asymmetric unit, with each Ni atom residing on a centre of symmetry. The two molecules exhibit similar coordination geometry but display differences with regard to other structural features. Each Ni^{II} centre is octahedrally coordinated by two mutually *trans* chelating hydroxyethylethylenediamine ligands and two mutually *trans* isothiocyanate ions. The two independent molecules form chains through different types of non-covalent interactions. In the case of one of the molecules, only NCS and free OH groups participate in hydrogen bonding, while in the chain based on the second molecule, the NCS, NH, NH_2 and free OH groups are involved in intermolecular hydrogen bonding. The two chains interact with one another through hydrogen bonding, forming planar sheets. The third packing direction is mediated only by van der Waals interactions.

Comment

Studies on the synthesis, structures and properties of metal complexes containing ambidentate ligands are of interest for a number of reasons, some of which involve controlling the reactivities of the coordination sites in the metal complexes. Many transition metal complexes of this type have been synthesized and their structures and physical properties, as well as the linkage isomerization reactions of the ambidentate units, have been investigated (Kabesova *et al.*, 1995; Buckingham, 1994; Burmeister, 1990). The coordination mode of an ambidentate ligand depends strongly on the nature of the central metal and the adjacent ligands. In this context, we have undertaken a study of the effect of *N*-(2-hydroxyethyl)ethylenediamine (hydet-en) on the coordination behaviour of thiocyanate ions in nickel complexes. Hydet-en, with three donor sites, has been the subject of few studies (Yilmaz *et al.*, 2002; Karadag *et al.*, 2004), and its coordination behaviour is, therefore, not well characterized. The present paper reports the synthesis and crystal structure determination of the title compound, $[Ni(NCS)_2(C_4H_{12}N_2O)_2]$, (I).



(I)

An *ORTEP*III (Burnett & Johnson, 1996) view of the molecular structure of (I) is shown in Fig. 1. The structure has two crystallographically independent molecules, which exhibit similar coordination geometry about the metal centre but which show differences in other structural features.

Each Ni^{II} centre lies on a centre of symmetry and is octahedrally coordinated by two mutually *trans* hydet-en ligands and two mutually *trans* isothiocyanate ions. The hydet-en ligand chelates through its two amine N atoms, while the ethanol groups of this ligand are uncoordinated, as was observed in the copper and cadmium saccharin complexes with the hydet-en ligand (Yilmaz *et al.*, 2002) and a cyano-bridged Zn^{II}/Ni^{II} complex (Karadag *et al.*, 2004). The isothiocyanate ions in each molecule act as N-donor ligands, as reported for other similar structures (Xu *et al.*, 2003; Yilmaz *et al.*, 2000). In each molecule, the coordinated amine N atoms of two hydet-en ligands form the equatorial planes ($N1/N2/N1^{ii}/N2^{ii}$ and $N4/N5/N4^{i}/N5^{i}$), while the N atoms of the isothiocyanate ions are located in the axial positions (symmetry codes as in the caption to Fig. 1). The dihedral angle between the equatorial planes of the two molecules is 27.6 (1)°.

The ring puckering of the five-membered chelate rings is similar in the two molecules. While both rings can best be characterized as being twisted about the C—C bond (as analysed by *PLATON*; Spek, 2003), the situation for molecule *A* (the molecule containing Ni1) is not so clear, since the

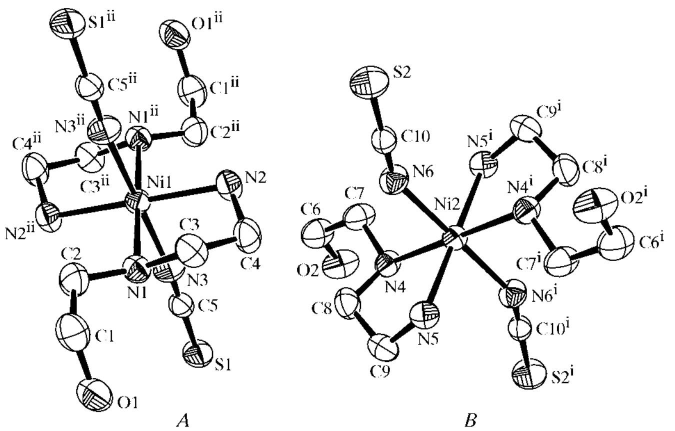


Figure 1
An *ORTEP*III (Burnett & Johnson, 1996) view of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. All H atoms have been omitted for clarity. [Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, 1 - y, -z$.]

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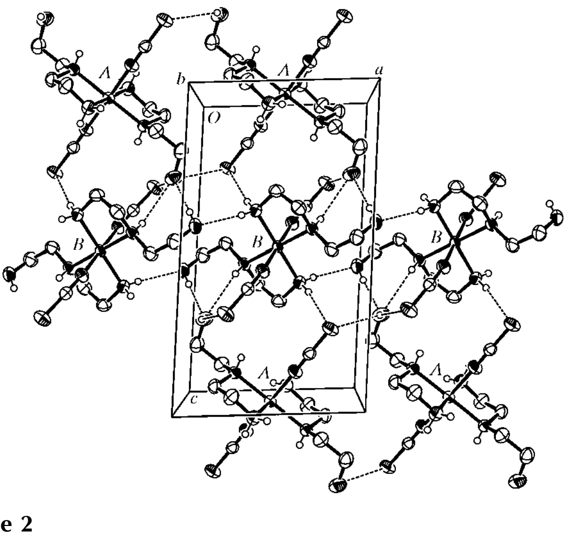

Figure 2
Hydrogen bonding involving molecules *A* (containing Ni1) and *B* (containing Ni2), viewed along the *b* axis. Dashed lines illustrate the hydrogen bonds. Methylene H atoms have been omitted for clarity.

displacement ellipsoids of atoms C3 and C4 are elongated perpendicular to the plane of the other three atoms, raising the possibility of slight conformational disorder.

Small but statistically significant differences between the geometric parameters involving the Ni atoms of the two independent molecules reflect their different packing environments (Table 1). The Ni—N_{amine} bond distances for molecule *A* are slightly longer than the corresponding bond lengths in molecule *B* (containing Ni2), while the Ni—N_{NCS} bond for molecule *A* is slightly shorter than that for molecule *B*. The five-membered chelate ring gives rise to the usual considerable distortion from ideal octahedral geometry, with bite angles of 82.59 (7) and 83.29 (7)° for molecules *A* and *B*, respectively. The observed geometries are, however, generally consistent with those observed in related di- and triethanolamine complexes of Ni^{II} (Hursthouse *et al.*, 1990; İçbudak *et al.*, 1995). The NCS groups are almost linear [178.7 (2)° for molecule *A* and 178.5 (2)° for molecule *B*]. Nevertheless, pronounced bending at the N atom is observed in molecule *B* [Ni2—N6—C10 = 150.51 (18)°], while the Ni1—N3—C5 angle in molecule *A* is 174.75 (19)°, similar to those observed in the mixed-ligand diethanolamine–Ni^{II} complex of isothiocyanate (Yilmaz *et al.*, 2000).

The hydrogen-bonding schemes (Table 2) are different for the two molecules. Only the NCS and free OH groups participate in hydrogen bonding in molecule *A*, whereas the NCS, NH, NH_2 and free OH groups in molecule *B* are all involved in intermolecular hydrogen bonding. The two molecules form two parallel chains, which are connected to one another *via* hydrogen bonding, as shown in Fig. 2. Hydrogen bonding between an H atom of an NH_2 group and an OH group connects successive *B* molecules into one chain. The other chain, formed by *A* molecules, is linked by one fork of a bifurcated hydrogen bond in which the H atom of an OH group of molecule *A* serves as a donor both to an S atom of the next molecule *A* in the chain and to an S atom of molecule *B* in a neighbouring chain. Other hydrogen bonds link the chains to one another. These bonds involve H atoms of the NH_2 groups in molecules *B* acting as donors to the S atoms in molecules *A*; in addition, the H atoms of the NH and OH groups in molecule *B* donate to an OH group in molecule *A*. The chains are thus linked to form sheets, which in turn are stacked with only van der Waals interactions between them.

Experimental

Solid KSCN (10 mmol, 097 g) was added slowly with continuous stirring to a solution of $NiCl_2 \cdot 6H_2O$ (5 mmol, 1.19 g). This solution was then mixed with a solution of *N*-(2-hydroxyethyl)ethylenediamine (10 mmol, 1.04 g) in distilled water and the reaction mixture was stirred for about 2 h. Violet crystals suitable for X-ray analysis were obtained by slow evaporation of the resulting solution at room temperature.

Crystal data

$[Ni(NCS)_2(C_4H_{12}N_2O)_2]$
$M_r = 383.18$
Monoclinic, $P2_1/c$
$a = 8.3891$ (7) Å
$b = 13.8940$ (8) Å
$c = 14.5530$ (12) Å
$\beta = 94.025$ (7)°
$V = 1692.1$ (2) $Å^3$
$Z = 4$
$D_x = 1.504$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 351 reflections
$\theta = 2.0$–29.3°
$\mu = 1.41$ mm^{-1}
$T = 293$ (2) K
Prism, violet
0.31 × 0.25 × 0.21 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{min} = 0.698$, $T_{max} = 0.770$
32 390 measured reflections
4605 independent reflections
2777 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 29.3°$
$h = -11 \rightarrow 11$
$k = -19 \rightarrow 17$
$l = -20 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.077$
$S = 0.94$
4605 reflections
226 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e $Å^{-3}$
$\Delta\rho_{min} = -0.50$ e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0081 (6)

Table 1
Selected geometric parameters (Å, °).

N1—Ni1	2.1542 (17)	N4—Ni2	2.1316 (17)
N2—Ni1	2.0986 (19)	N5—Ni2	2.0952 (18)
N3—Ni1	2.0782 (18)	N6—Ni2	2.1057 (18)
C5—N3—Ni1	174.75 (19)	$N3^{ii}$—Ni1—N2	89.86 (9)
C10—N6—Ni2	150.51 (18)	N5—Ni2—N6	91.29 (8)
N3—Ni1—N2	90.14 (9)	N5—Ni2—N4	83.29 (7)
N3—Ni1—N1	89.37 (7)	N6—Ni2—N4	92.15 (7)
N2—Ni1—N1	82.59 (7)	N5—Ni2—$N6^{i}$	88.71 (8)
$N2^{ii}$—Ni1—N1	97.41 (7)	$N5^{i}$—Ni2—N4	96.71 (7)
N3—Ni1—$N1^{ii}$	90.63 (7)	N6—Ni2—$N4^{i}$	87.85 (7)
N1—C3—C4—N2	58.3 (3)	N4—C8—C9—N5	55.9 (3)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, 1 - y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*B*···O2^{iii}	0.86 (3)	2.26 (3)	3.082 (3)	158 (3)
N5—H5*A*···S1^{iv}	0.93 (3)	2.71 (3)	3.634 (2)	170 (2)
N4—H2N···O1^{iv}	0.83 (3)	2.60 (2)	3.261 (3)	137 (2)
O1—H1O···S1^{iii}	0.82 (3)	2.96 (3)	3.539 (2)	130 (3)
O1—H1O···S2^{v}	0.82 (3)	2.74 (3)	3.450 (2)	147 (3)
O2—H2O···O1^{iv}	0.79 (3)	2.03 (3)	2.817 (3)	177 (3)

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

H atoms of the OH, NH and NH_2 groups were found in a difference map and their parameters were refined freely. The bond distances and $U_{\rm iso}$(H) values were in the ranges 0.79 (3)–0.82 (3) Å and 0.079 (11)–0.087 (13) Å^2 for the OH groups, 0.83 (3)–0.86 (2) Å and 0.044 (7)–0.047 (7) Å^2 for the NH groups, and 0.85 (3)–0.93 (3) Å and 0.056 (8)–0.073 (10) Å^2 for the NH_2 groups. Other H atoms were introduced at idealized positions and were allowed to ride on their parent atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1069). Services for accessing these data are described at the back of the journal.

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