

Bis(2,2'-diamino-4,4'-bi-1,3-thiazole- κ^2N,N')-(isothiocyanato- κN)(methanol)nickel(II) chloride

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Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.039

wR factor = 0.078

Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Ni}(\text{NCS})(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)(\text{CH}_4\text{O})]\text{Cl}$, consists of an Ni^{II} complex cation and a Cl^- anion. The Ni^{II} complex has an octahedral coordination, with the isothiocyanate and methanol ligands in *cis* positions. The diaminobithiazole ligands are each nearly planar, but the Ni^{II} atom is out of the planes of the thiazole rings, the deviations ranging from 0.113 (5) to 0.389 (4) \AA .

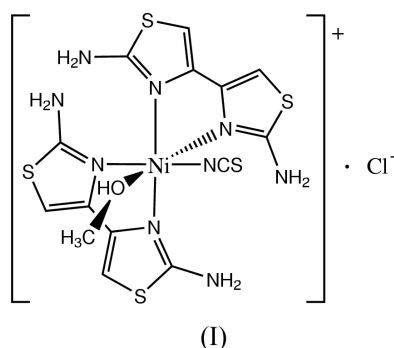
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Comment

The ligand 2,2'-diamino-4,4'-bi-1,3-thiazole (DABT) has been used to prepare metal complexes in our laboratory for their potential application in the field of soft magnetic materials (Sun *et al.*, 1997). X-ray structure determinations have revealed different degrees of non-planarity for the thiazole rings of DABT in transition metal complexes. We present here the structure of the title Ni^{II} complex, (I), which shows appreciable deviation of the Ni atom from the thiazole planes.



The molecular structure of (I) is shown in Fig. 1. Compound (I) consists of an Ni^{II} complex cation, with an octahedral coordination geometry, and a Cl^- counter-anion. One isothiocyanate anion and one methanol molecule coordinate to the Ni^{II} atom in a *cis* configuration. The $\text{Ni}-\text{N}9-\text{C}13$ bond angle of $165.1(3)^\circ$ is comparable with the values of 152.3 and 171.7° found in bis(isothiocyanato)(triazacyclododecane)-zinc(II) (Kimura *et al.*, 1992). The $\text{Ni}-\text{O}1$ bond of $2.156(2)\text{ \AA}$ is longer than the $\text{Ni}-\text{O}(\text{methanol})$ bond of $2.126(3)\text{ \AA}$ found in bis(methanol)-bis(nitrosophenylhydroxylamino)-nickel(II) (Okabe & Tamaki, 1995) and the $\text{Ni}-\text{O}(\text{water})$ bond of $2.128(3)\text{ \AA}$ found in an Ni^{II} complex of DABT with coordinated water (Luo *et al.*, 2004).

Two DABT ligands chelate to the Ni^{II} atom. Each DABT is nearly planar, the maximum deviations being $0.0625(16)$ (atom S2) and $0.084(2)\text{ \AA}$ (atom N5). The two DABT mean planes are nearly perpendicular to each other, with a dihedral angle of $73.78(7)^\circ$. It is notable that the Ni atom is not

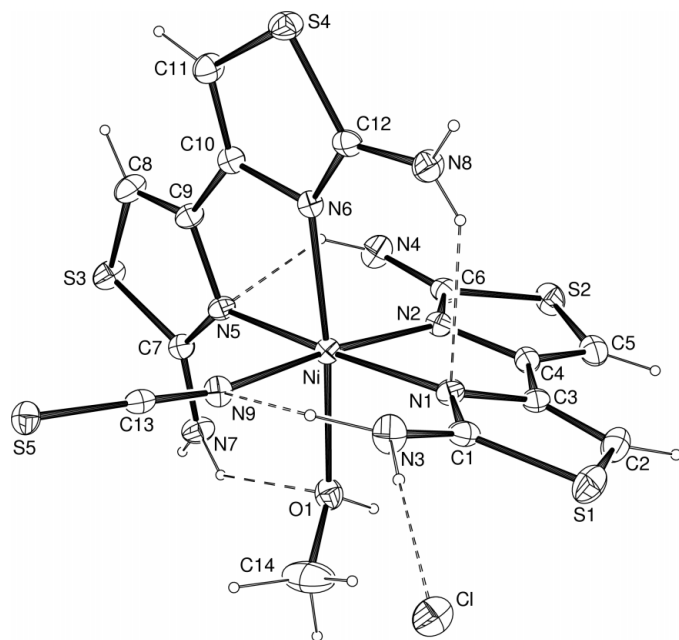


Figure 1
A view of the molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. Dashed lines indicate hydrogen bonds.

coplanar with the thiazole rings, the deviation ranging from 0.113 (5) (N5-thiazole) to 0.389 (4) Å (N1-thiazole).

Four intramolecular hydrogen bonds occur between the amino groups and neighbouring coordinated atoms (Fig. 1). Each Cl^- anion links to three complex cations *via* hydrogen bonds, as shown in Fig. 2. A short contact of 3.4003 (15) Å is observed between the Cl^- ion and atom S2($x + 1, \frac{1}{2} - y, z - \frac{1}{2}$).

Experimental

A methanol solution (60 ml) containing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.25 mmol) and DABT (2.5 mmol) was refluxed for 30 min. KSCN (2.5 mmol) was then added to the solution and the mixture was refluxed for 3 h, cooled to room temperature and filtered. Green crystals of (I) were obtained from the filtrate after 5 d.

Crystal data

$[\text{Ni}(\text{NCS})(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)(\text{CH}_4\text{O})]\text{Cl}$	$D_x = 1.706 \text{ Mg m}^{-3}$
$M_r = 580.82$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 11 826 reflections
$a = 8.6493$ (17) Å	$\theta = 1.6\text{--}25.0^\circ$
$b = 32.089$ (6) Å	$\mu = 1.47 \text{ mm}^{-1}$
$c = 8.3107$ (17) Å	$T = 298$ (2) K
$\beta = 101.42$ (3)°	Prism, green
$V = 2261.0$ (8) Å ³	$0.42 \times 0.36 \times 0.32 \text{ mm}$
$Z = 4$	

Data collection

Rigaku R-Axis RAPID diffractometer	4406 independent reflections
ω scans	2769 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.55, T_{\text{max}} = 0.63$	$\theta_{\text{max}} = 25.9^\circ$
12 745 measured reflections	$h = -9 \rightarrow 10$
	$k = -37 \rightarrow 39$
	$l = -9 \rightarrow 10$

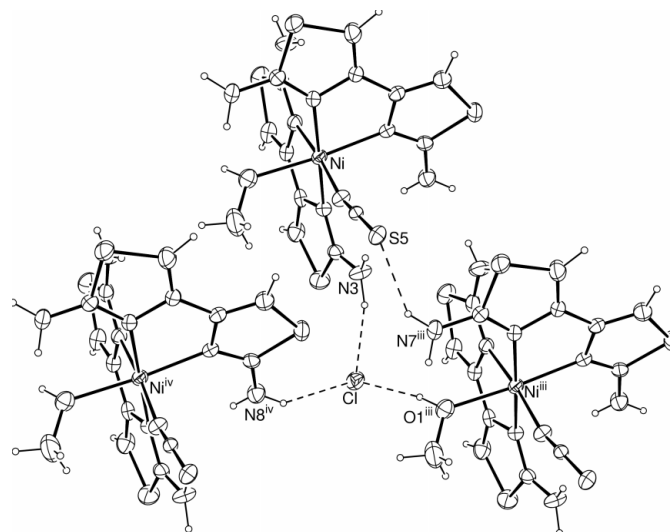


Figure 2
The hydrogen-bonded supramolecular structure of (I) [symmetry codes: (iii) $1 + x, y, z$; (iv) $x, y, z - 1$].

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2]$
$wR(F^2) = 0.078$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.85$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4406 reflections	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
281 parameters	$\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å).

Ni—O1	2.156 (2)	Ni—N6	2.096 (3)
Ni—N1	2.099 (3)	Ni—N9	2.055 (3)
Ni—N2	2.106 (3)	S5—C13	1.638 (4)
Ni—N5	2.087 (3)	N9—C13	1.169 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O1—H1 \cdots Cl ⁱ	0.97	2.06	2.994 (3)	163
N3—H3A \cdots Cl	0.96	2.22	3.152 (4)	166
N3—H3B \cdots N9	0.96	2.19	3.008 (5)	142
N4—H4A \cdots N5	0.92	2.38	3.089 (4)	134
N4—H4B \cdots N8 ⁱ	0.81	2.47	3.257 (5)	163
N7—H7A \cdots O1	0.95	2.13	2.923 (4)	140
N7—H7B \cdots S5 ⁱ	0.93	2.54	3.358 (3)	146
N8—H8A \cdots N1	0.82	2.48	3.181 (4)	145
N8—H8B \cdots Cl ⁱⁱ	0.89	2.39	3.171 (3)	146

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

The H atoms of the methanol and amino groups were located in a difference Fourier map and included in the structure factor calculations with fixed positional and isotropic displacement parameters, $U_{\text{iso}}(\text{H}) = 0.08 \text{ \AA}^2$. Other H atoms were placed in calculated positions, with $\text{C—H} = 0.93$ or 0.96 \AA , and were included in the final cycles of refinement in a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ of the carrier atom.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/

MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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