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Dichlorobis(2,2′-diamino-4,4′-bi-1,3-thiazole-κ^2N,N')nickel(II) dihydrate

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Key indicators

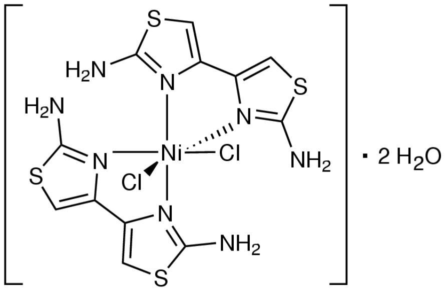
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
R factor = 0.045
wR factor = 0.101
Data-to-parameter ratio = 14.1

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

The Ni^{II} atom in the crystal structure of the title compound, $[NiCl_2(C_6H_6N_4S_2)_2]\cdot 2H_2O$, has a distorted *cis*-octahedral coordination, formed by two Cl atoms [Ni—Cl 2.4767 (17) and 2.4922 (17) Å] and four N atoms of two chelate bithiazole ligands [Ni—N 2.069 (5)–2.138 (5) Å]. The overlapped arrangement and short separation between parallel thiazole rings belonging to neighbouring complexes [3.47 (3) Å] suggest the existence of π–π stacking interactions. Short intermolecular S···S contacts [3.183 (3) Å] are also observed. The water molecules are involved in hydrogen bonds with the Cl ligands.

Comment

As metal complexes with 2,2′-diamino-4,4′-bithiazole (DABT) have been shown to exhibit interesting properties and promise potential applications in various fields (Waring, 1981; Fisher *et al.*, 1985; Sun *et al.*, 1997), a series of transition metal complexes with DABT ligands have been prepared in our laboratory. One such complex is the title compound, (I), and its crystal structure is presented here.



(I)

The crystal structure of (I) is built of *cis*-Ni(DABT)$_2$Cl$_2$ complexes and uncoordinated water molecules (Fig. 1). It is isostructural with the Co analogue reported earlier (Liu *et al.*, 2003). The Ni atom has a distorted *cis*-octahedral coordination, formed by two Cl atoms and four N atoms of two chelate DABT ligands (Table 1).

The N3,N4-bithiazole ligand in (I) is essentially planar, the dihedral angle between thiazole rings being 1.6 (3)°. The N1,N2-ligand shows substantial deviations from planarity, the dihedral angle formed by the planes of the rings being 11.1 (4)°. The latter value is comparable with the corresponding dihedral angles observed in both ligands of the Co analogue (10.2 and 8.4°). The C—NH$_2$ bond lengths are in the range 1.336 (7)–1.358 (7) Å, which suggests that the electron

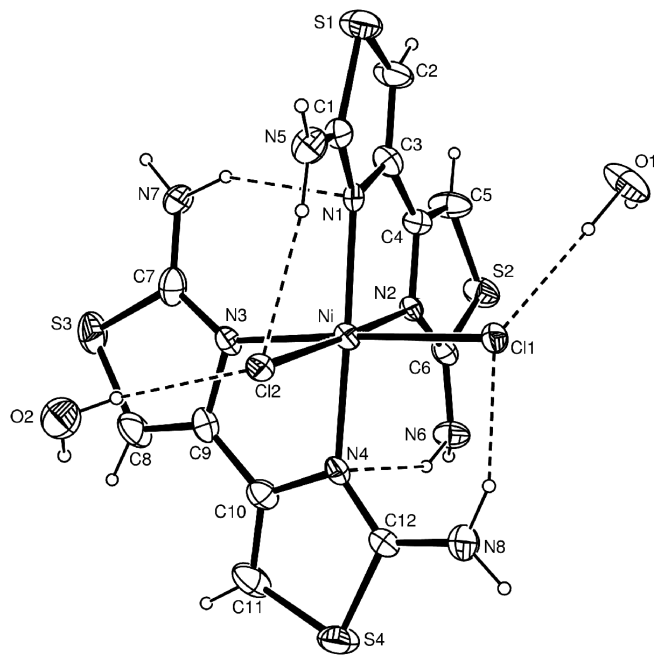


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

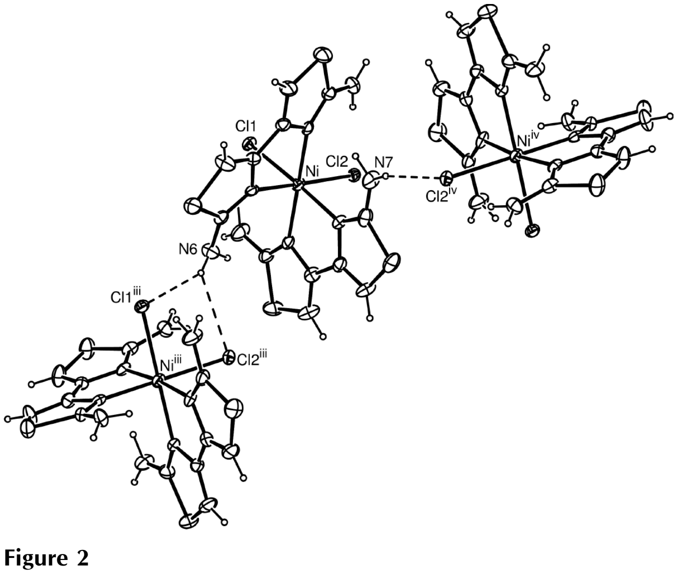


Figure 2
A fragment of the crystal packing of (I), showing the hydrogen bonding between complex molecules [symmetry codes: (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$].

pairs of the amino groups are involved in the π systems of the thiazole rings.

The crystal structure of (I) exhibits an extensive hydrogen-bonding system (Table 2). The amino groups of the DABT ligands participate in both intra- (Fig. 1) and intermolecular (Fig. 2) hydrogen bonding. The complex molecules are linked into infinite chains *via* N—H$\cdots$Cl hydrogen bonds (Fig. 2). Uncoordinated water molecules are hydrogen bonded to complex molecules, as shown in Fig. 1.

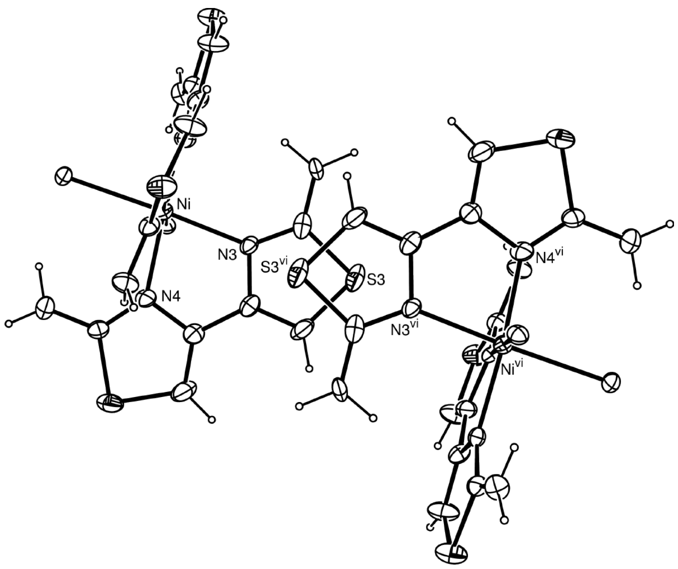


Figure 3
A fragment of the crystal packing of (I), showing the π–π stacking between DABT ligands [symmetry code: (vi) $2 - x, 1 - y, 1 - z$].

The bithiazole ligands belonging to molecules of (I) related by an inversion centre exhibit substantial overlap (Fig. 3). The separation of 3.47 (3) Å between parallel thiazole ligands suggests the existence of π–π interactions. There is also a short intermolecular S2$\cdots$S2^{vii} contact of 3.183 (3) Å [symmetry code: (vii) $1 - x, 1 - y, 1 - z$]

Experimental

Crystals of the title complex were obtained by a solution diffusion method using an H-shaped glass tube. Aqueous solutions of $NiCl_2\cdot6H_2O$ (0.1 *M*) and DABT (0.2 *M*) were introduced into the two branches of the H-shaped tube. Blue single crystals of (I) were obtained after 2 weeks.

Crystal data

$[NiCl_2(C_6H_6N_4S_2)_2]\cdot2H_2O$
$M_r = 562.18$
Monoclinic, $P2_1/c$
$a = 10.814\ (2)$ Å
$b = 13.534\ (3)$ Å
$c = 15.061\ (3)$ Å
$\beta = 106.561\ (14)^\circ$
$V = 2112.8\ (8)$ Å^3
$Z = 4$
$D_x = 1.767$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9868 reflections
$\theta = 3.0$–23.0°
$\mu = 1.59$ mm^{-1}
$T = 298\ (2)$ K
Prism, blue
0.22 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.710$, $T_{max} = 0.832$
10 682 measured reflections
3705 independent reflections
1887 reflections with $I > 2\sigma(I)$
$R_{int} = 0.086$
$\theta_{max} = 25.0^\circ$
$h = -12 \rightarrow 9$
$k = -16 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.101$
$S = 0.81$
3705 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N1	2.092 (5)	Ni—N4	2.069 (5)
Ni—N2	2.088 (5)	Ni—Cl1	2.4767 (17)
Ni—N3	2.138 (5)	Ni—Cl2	2.4922 (17)
N4—Ni—N2	95.70 (19)	N1—Ni—Cl1	86.32 (13)
N4—Ni—N1	173.99 (19)	N3—Ni—Cl1	177.45 (14)
N2—Ni—N1	79.79 (19)	N4—Ni—Cl2	86.10 (14)
N4—Ni—N3	79.79 (19)	N2—Ni—Cl2	178.00 (13)
N2—Ni—N3	89.16 (18)	N1—Ni—Cl2	98.35 (14)
N1—Ni—N3	96.08 (18)	N3—Ni—Cl2	90.32 (13)
N4—Ni—Cl1	97.75 (15)	Cl1—Ni—Cl2	90.19 (6)
N2—Ni—Cl1	90.41 (13)		

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯Cl1	0.95	2.28	3.233 (5)	176
O1—H1*B*⋯O2^{i}	0.96	1.95	2.810 (6)	148
O2—H2*A*⋯Cl2	0.86	2.32	3.142 (5)	159
N5—H5*A*⋯Cl2	0.96	2.33	3.227 (5)	155
N5—H5*B*⋯O1^{ii}	0.92	2.18	2.900 (6)	134
N6—H6A⋯N4	0.88	2.34	3.113 (7)	147
N6—H6*B*⋯Cl1^{iii}	0.84	2.61	3.353 (5)	148
N6—H6*B*⋯Cl2^{iii}	0.84	2.81	3.431 (5)	131
N7—H7*A*⋯N1	0.95	2.29	3.154 (7)	150
N7—H7*B*⋯Cl2^{iv}	0.97	2.44	3.356 (5)	156
N8—H8*A*⋯Cl1	0.98	2.18	3.101 (6)	156
N8—H8B⋯O2^{v}	0.93	2.15	2.977 (7)	147

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

The H atoms of the water molecules and amino groups were located in a difference Fourier map and included in the structure factor calculation with fixed positional parameters and with $U_{\rm iso}$(H) = 0.05 Å^2. The H atoms on C atoms were placed in calculated positions with C—H = 0.93 Å, and included in the final cycles of the refinement in the riding model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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