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Diaqua(2,2′-diamino-4,4′-bi-1,3-thiazole)-(malonato)nickel(II)

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The title complex, $[Ni(C_6H_6N_4S_2)(C_3H_2O_4)(H_2O)_2]$, has a distorted octahedral coordination geometry with the malonate dianion and diaminobithiazole chelating to the Ni^{II} atom in the equatorial plane, and two water molecules in the axial positions. Both the malonate and diaminobithiazole are planar, and are tilted out of the equatorial plane, with dihedral angles of 9.87 (5) and 11.65 (5)°, respectively.

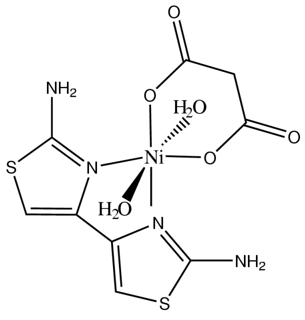
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.002 Å
R factor = 0.024
wR factor = 0.059
Data-to-parameter ratio = 16.0

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

Comment

2,2′-Diamino-4,4′-bi-1,3-thiazole (DABT) complexes of transition metals have shown their potential application in the field of magnetic materials (Sun *et al.*, 1997). A series of DABT–metal complexes has been prepared in our laboratory, and their crystal structures have been determined (Liu *et al.*, 2001; Liu & Xu, 2004). DABT is structurally similar to 2,2′-bipyridyl, but non-coplanarity of the thiazole rings in DABT has usually been observed in metal complexes (Liu & Xu, 2004). We present here the X-ray structure of the title Ni^{II} complex, (I), to compare with DABT complexes reported previously.



(I)

The molecular structure of (I) is illustrated in Fig. 1 and selected geometric parameters are given in Table 1. The Ni^{II} complex has a distorted octahedral coordination geometry, formed by one DABT, one malonate dianion and two coordinated water molecules. DABT is essentially planar in the complex, the maximum atomic deviation being 0.0405 (9) Å (S2). The DABT mean plane is tilted out of the equatorial coordination plane formed by atoms O1, O3, N1 and N3 with a dihedral angle of 9.87 (5)°, and the Ni atom is 0.2713 (15) Å out of the mean DABT plane.

The malonate dianion is also planar, the maximum atomic deviation being 0.0648 (16) Å (C8). The malonate chelates to the Ni atom through both terminal carboxy groups, and the malonate mean plane is tilted out of the equatorial coordination plane with a dihedral angle of 11.65 (5)°. Thus the

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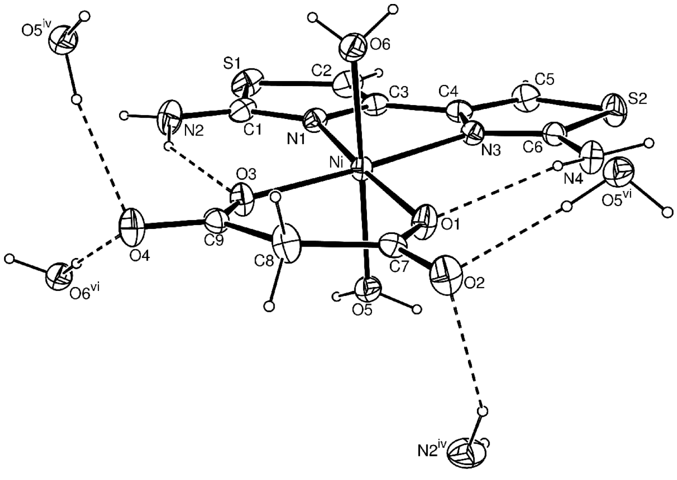

Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. Hydrogen bonds are indicated by dashed lines [symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (iv) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vii) $\frac{1}{2} + x, y, \frac{1}{2}- - z$].

chelate six-membered ring displays an envelope conformation, with the Ni atom in the flap position, displaced 0.2964 (16) Å out of the mean malonate plane. This is very different from the boat conformation found in most metal complexes with a chelating malonate ligand (Calogero *et al.*, 1997; Hay *et al.*, 1997; Ray & Hathaway, 1982; Lin *et al.*, 2003). The C7—C8—C9 bond angle of 123.79 (14)° is significantly larger than corresponding bond angles of 113.3 (2)° found in a Co^{II} complex (Lin *et al.*, 2003) and 114.8 (2)° found in a Cu^{II} complex (Hay *et al.*, 1997), both with a boat chelating conformation for the malonate ligand. Each carboxy group is monodentate in the crystal structure; uncoordinated carboxy O atoms (O2 and O4) are hydrogen bonded to coordinated atoms of neighboring complex molecules, as shown in Fig. 1.

Extensive hydrogen bonding is present in the crystal structure (Table 2). The amino groups of DABT are involved in both intramolecular and intermolecular hydrogen bonding. The coordinated water molecules link with neighboring complexes *via* hydrogen bonding.

Experimental

An aqueous solution (15 ml) of malonic acid (0.10 g, 0.1 mmol) and Na_2CO_3 (0.11 g, 0.1 mmol) was mixed with an aqueous solution (15 ml) of $NiCl_2 \cdot 6H_2O$ (0.24 g, 0.1 mmol) and DABT (0.20 g, 0.1 mmol), The mixture was refluxed for 3 h and filtered. Green crystals were obtained from the filtrate after 4 d.

Crystal data

$[Ni(C_6H_6N_4S_2)(C_3H_2O_4)(H_2O)_2]$
$M_r = 395.06$
Orthorhombic, *Pbca*
$a = 11.0826\ (3)$ Å
$b = 12.1879\ (3)$ Å
$c = 20.7505\ (5)$ Å
$V = 2802.85\ (12)$ Å^3
$Z = 8$
$D_x = 1.872$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 22240 reflections
$\theta = 2.4$–25.5°
$\mu = 1.72$ mm^{-1}
$T = 296\ (2)$ K
Prism, green
0.34 × 0.32 × 0.24 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.57$, $T_{max} = 0.66$
25652 measured reflections

3207 independent reflections
2983 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.4°$
$h = -13 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.08$
3207 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 1.626P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0057 (2)

Table 1
Selected geometric parameters (Å, °).

Ni—O1	1.9997 (11)	O1—C7	1.2487 (19)
Ni—O3	2.0029 (11)	O2—C7	1.2536 (19)
Ni—N3	2.0612 (12)	O3—C9	1.2572 (19)
Ni—N1	2.0818 (13)	O4—C9	1.2523 (19)
Ni—O6	2.1007 (12)	C7—C8	1.520 (2)
Ni—O5	2.1318 (12)	C8—C9	1.524 (2)
O1—Ni—O3	91.50 (5)	O1—C7—C8	122.24 (14)
C7—O1—Ni	129.06 (10)	C7—C8—C9	123.79 (14)
C9—O3—Ni	128.44 (10)	O3—C9—C8	122.13 (14)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$O3	0.86	2.16	2.920 (2)	148
N2—H2$B\cdots$O2^{i}	0.87	2.30	3.081 (2)	150
N4—H4$A\cdots$O1	0.82	2.18	2.8823 (18)	143
N4—H4$B\cdots$N2^{ii}	0.89	2.35	3.208 (2)	161
O5—H5$A\cdots$O2^{iii}	0.86	1.90	2.7541 (18)	175
O5—H5$B\cdots$O4^{iv}	0.88	2.02	2.8832 (18)	167
O6—H6$A\cdots$N4^{v}	0.81	2.11	2.9129 (19)	175
O6—H6$B\cdots$O4^{vi}	0.83	1.93	2.7607 (18)	174

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (iv) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, z$; (vi) $\frac{1}{2} + x, y, \frac{1}{2} - z$.

H atoms on water and amino groups were located in a difference Fourier map and were included in the structure-factor calculation with fixed positional parameters and U_{iso}(H) of 0.05 Å^2. H atoms on carbon were placed in calculated positions, with C—H = 0.93 Å (thiazole) or 0.97 Å (methylene), and included in the final cycles of refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku Corporation, 2002); 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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