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Bis(2,2′-diamino-4,4′-bi-1,3-thiazole-κ^2N,N')-(phthalato-κ^2O,O')nickel(II) 3.5-hydrate

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Key indicators

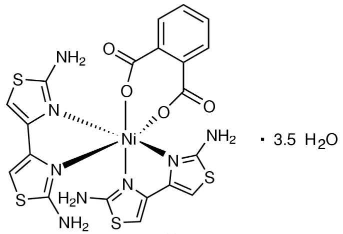
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 87%
Disorder in solvent or counterion
R factor = 0.045
wR factor = 0.112
Data-to-parameter ratio = 16.7

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

The crystal stucture of the title compound, $[Ni(C_8H_4O_4)(C_6H_6N_4S_2)_2]\cdot 3.5H_2O$, consists of a nickel(II) complex and water of crystallization. The complex assumes an octahedral geometry formed by one phthalate dianion and two diaminobithiazole molecules.

Comment

Metal complexes of 2,2′-diamino-4,4′-bi-1,3-thiazole (DABT) have shown potential application in some fields (Waring, 1981; Fisher *et al.*, 1985). As part of a series of investigations of metal complexes of DABT, the title nickel(II) complex, (I), was prepared.



(I)

The molecular structure of (I) is shown in Fig. 1. The complex molecule displays an octahedral coordination geometry formed by two DABT molecules and one phthalate dianion. The phthalate dianion chelates to Ni *via* both terminal carboxyl groups; these are approximately perpendicular to each other, with a dihedral angle of 84.3 (4)°. Each carboxyl

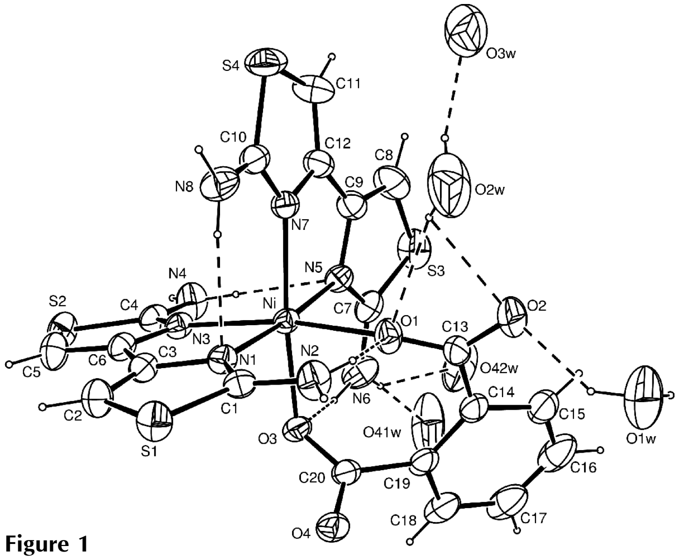


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. Dashed lines indicate the hydrogen bonding.

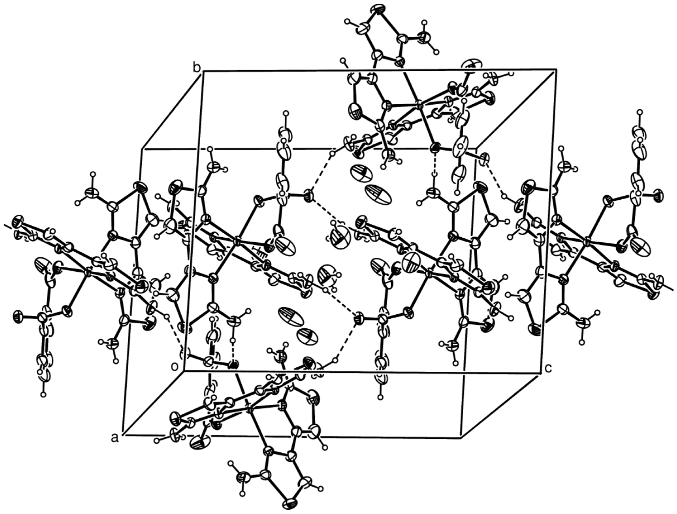


Figure 2
A molecular packing diagram, dashed lines showing the hydrogen bonding between Ni^{II} complex molecules.

group is coordinated in a monodentate fashion to Ni; uncoordinated carboxyl O atoms are hydrogen bonded to neighboring complex or water molecules (Table 2). The Ni—O1 and Ni—O3 bond distances [2.0752 (19) and 2.0895 (19) Å, respectively] are essentially the same, but the Ni—O1—C13 angle of 140.2 (2)° is much larger than the Ni—O3—C20 angle of 119.91 (18) Å.

Within DABT moieties the average C—N bond distance of 1.334 (4) Å between amino groups and thiazole rings suggests the existence of electron delocalization. The bond distances, 1.459 (4) and 1.453 (5) Å for C3—C6 and C9—C12, respectively, correspond to C—C single bonds between sp^2-hybridized C atoms. The dihedral angles between thiazole rings are 7.90 (13) and 9.72 (17)°. These values are comparable to 8.4 and 10.2° found in a cadmium(II) complex of DABT (Liu *et al.*, 2003).

Extensive hydrogen bonding occurs in the crystal structure. All water molecules are involved in hydrogen bonding, as shown in Fig. 1. The amino groups of DABT are hydrogen bonded to adjacent coordinated O or N atoms to stabilize the molecular structure (Fig. 1). Moreover, three amino groups (N2, N4 and N8) link neighboring complex molecules *via* N—H···O hydrogen bonds, thus forming a supramolecular structure, as shown in Fig. 2 and Table 2.

Experimental

The microcrystals of DABT were obtained in the manner reported by Erlenmeyer (1948). An aqueous solution (20 ml) containing DABT (0.20 g, 1 mmol) and $NiCl_2$ (0.13 g, 1 mmol) was mixed with another aqueous solution (10 ml) of phthalic acid (0.17 g, 1 mmol) and NaOH (0.08 g, 2 mmol). The mixture was refluxed for 3 h. The solution was filtered after cooling to room temperature. Green single crystals were obtained from the filtrate after 3 d.

Crystal data

$[Ni(C_8H_4O_4)(C_6H_6N_4S_2)_2]\cdot 3.5H_2O$
$M_r = 682.41$
Monoclinic, $P2_1/c$
$a = 14.5564\ (14)$ Å
$b = 13.5072\ (12)$ Å
$c = 15.7929\ (11)$ Å
$\beta = 115.430\ (12)°$
$V = 2804.3\ (5)$ Å^3
$Z = 4$
$D_x = 1.616$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16667 reflections
$\theta = 2.0$–$24.0°$
$\mu = 1.05$ mm^{-1}
$T = 295\ (2)$ K
Prism, green
$0.34 \times 0.27 \times 0.11$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.698$, $T_{max} = 0.890$
25568 measured reflections
6343 independent reflections
4886 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.4°$
$h = -18 \rightarrow 18$
$k = -15 \rightarrow 17$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.112$
$S = 1.03$
6343 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 2.0505P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Ni—O3	2.0752 (19)	N2—C1	1.326 (4)
Ni—O1	2.0895 (19)	N4—C4	1.334 (4)
Ni—N7	2.106 (2)	N6—C7	1.334 (4)
Ni—N3	2.108 (2)	N8—C10	1.340 (4)
Ni—N5	2.116 (2)	C3—C6	1.459 (4)
Ni—N1	2.122 (2)	C9—C12	1.453 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1	0.86	2.06	2.816 (3)	146
N2—H2B···O4^{i}	0.86	2.12	2.914 (3)	154
N4—H4A···N5	0.86	2.39	3.154 (4)	148
N4—H4B···O4^{ii}	0.86	2.17	2.949 (4)	150
N6—H6A···O3	0.86	2.24	2.966 (4)	142
N6—H6B···O41W	0.86	1.91	2.758 (11)	171
N6—H6B···O42W	0.86	2.43	3.197 (12)	149
N8—H8A···N1	0.86	2.30	3.062 (4)	148
N8—H8B···O3^{iii}	0.86	2.18	2.808 (4)	130
O1W—H11W···O2	0.90	2.02	2.786 (8)	143
O1W—H12W···O42W^{iv}	0.91	2.47	3.005 (11)	118
O1W—H12W···O3W^{v}	0.91	2.43	3.317 (10)	164
O2W—H21W···O1	0.86	2.37	3.183 (5)	157
O2W—H21W···O2	0.86	2.33	2.801 (6)	114
O2W—H22W···O3W	0.90	1.86	2.571 (9)	135

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

The refinement showed that some of the water molecules are disordered in the crystal structure. The site-occupancy factors of atoms O3W, O41W and O42W converged to 0.63 (2), 0.400 (19) and 0.626 (13), respectively, in the isotropic refinement stage. In the final cycles of anisotropic refinement, the occupancy factors of these disordered O atoms were fixed as 0.5, and H atoms bound to them were not located. H atoms of the ordered water molecules (O1W and

O2*W*) were located in a difference Fourier map and were included in the refinement with fixed positional parameters and $U_{\rm iso}$ values of 0.05 Å^2. Other H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and included in the final cycles of refinement as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ of the carrier atoms.

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