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[2,6-Bis(1*H*-benzimidazol-2-yl-κN^3)pyridine-κN](dimethylformamide-κO)(thiosulfato-$\kappa^2 O,S$)nickel(II) monohydrate

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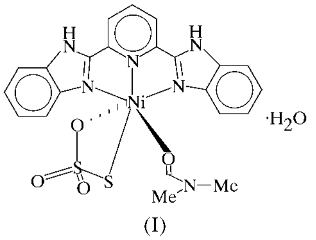
The structure of the title compound, [Ni(ths)(bbip)(dmf)]·H_2O [ths is thiosulfate, S_2O_3; bbip is 2,6-bis(1*H*-benzimidazol-2-yl)pyridine, $C_{21}H_{13}N_5$; and dmf is dimethylformamide, C_3H_7NO], is monomeric, with the nickel ion octahedrally surrounded by an *N*,*N*′,*N*″-tridentate bbip molecule, an *S*,*O*-bidentate ths molecule and an *O*-monodentate dmf molecule. The H atoms of the hydration water molecule and the amino groups of bbip are involved in hydrogen bonding and determine a spatial organization of broad layers parallel to (001), which are connected by weak interactions.

Comment

The coordination properties of the thiosulfate group have been extensively studied by our group in connection with their relevance in the discussion of $d\pi$–$p\pi$ bonding in sulfur oxo-anions. The anion is a versatile ligand, since it contains atoms classified as both soft and hard bases (Pearson, 1973). This situation produces a variety of coordination modes, especially when the metal ion is intermediate between classes *a* and *b* in the aforementioned classification. One factor that seems to influence the manner in which the ligand coordinates is the geometry of the organic ligands present in the complex. In this context, we have found the reaction between Ni^{2+} and $S_2O_3^{2-}$, in the presence of polynitrogenated bases, to be a very prolific one, with a variety of compounds of varied characteristics being generated (Freire *et al.*, 1999; Freire, Baggio, Mombru & Baggio, 2000; Freire, Baggio, Mariezcurrena & Baggio, 2000; Freire, Baggio, Suescun & Baggio, 2000), including products that are the result of redox processes (Freire, Baggio & Baggio, 2001). In this paper, we report an X-ray structural study of the title compound, (I).



(I)

The structure of (I) is monomeric, with the nickel ion surrounded by three different ligands, *viz*. a tridentate bis(benzimidazolyl)pyridine molecule (bbip), a bidentate thiosulfate molecule (ths) and a monodentate dimethylformamide molecule (dmf) (Fig. 1). The result is a highly distorted octahedral environment for the cation, with adjacent coordination sites subtending angles as narrow as 76.78 (10)° (expected 90°) and opposite centers 153.71 (11)° apart (expected 180°).

The bbip ligand does not depart from the geometry it usually adopts when complexed to a cation; the unprotonated imidazolyl N atoms are *cis* to the pyridyl N atom, thus defining the tridentate bite. Because of the restraints imposed by this chelate character, the three coordinated N atoms in the ligand are constrained not to be equidistant from the cation, the central Ni—N2 bond [2.054 (3) Å] being shorter than the other two bonds [2.107 (3) and 2.124 (3) Å]. In addition, the stress arising from coordination tends to distort the molecule into a concave shape, the lateral wings being bent with respect to the central ring by 6.1 (1) and 6.8 (1)°, respectively.

The ths anion binds through the common *S*,*O*-chelate mode; a search in the November 2002 release of the Cambridge Structural Database (CSD; Allen, 2002) showed 11 such coordinations of the anion out of the 49 entries in which it appears bound to a metal. In the present structure, atom S1 occupies the remaining equatorial site, in the plane defined by bbip and opposite the central (and shortest) Ni—N2 bond. This behavior appears to be common in these types of compounds, as it has also been observed in [Ni(tpy)(ths)]·H_2O (tpy is terpyridine; Freire, Baggio, Goeta & Baggio, 2001),

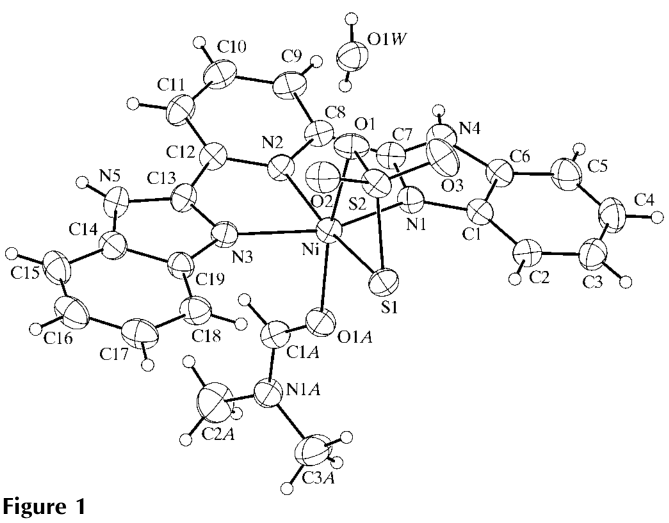


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 40% probability level.

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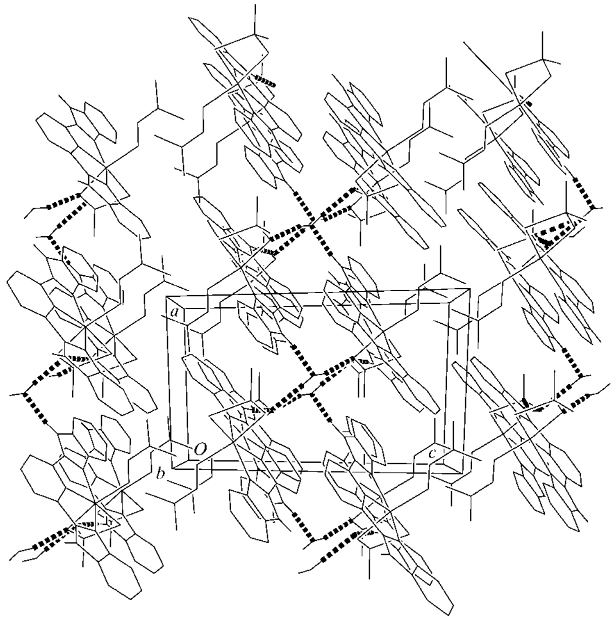

Figure 2
The crystal packing in (I), viewed along *b*. Hydrogen bonds are represented by heavy broken lines, and H atoms bonded to C atoms have been omitted for clarity.

which is the only other reported ths complex with a tridentate base.

The structure of the ths anion displays a variety of S—O bond lengths, which are inversely related to the degree of compromise in coordination of the corresponding O atoms. Thus, atom O1, which bonds directly to nickel and is also involved in a medium-strength hydrogen bond, forms the longest (*i.e.* weakest) bond [S2—O1 = 1.494 (2) Å]. The intermediate bond length involves atom O2, which only takes part in hydrogen bonding [S2—O2 = 1.473 (2) Å]. Finally, atom O3 (which is not involved in any other interaction) provides the shortest (*i.e.* strongest) bond [S2—O3 = 1.441 (2) Å]. This effect is accompanied by a reduction of the corresponding S—S—O angle, which is directly related to the S—O bond enlargement (Table 1). This behavior has been observed previously in a variety of sulfur oxoanions (Freire, Baggio, Mombru & Baggio, 2000; Freire, Baggio, Mariezcurrena & Baggio, 2000; Harvey *et al.*, 2001, 2002).

A monodentate dmf molecule completes the coordination around the Ni atom. The ligand geometry is unexceptional, and although a wide range of C—N and C═O bond-length values are reported in the literature, those in (I) [1.312 (4) and 1.236 (4) Å] are close to the mean values obtained from *ca* 950 cases found in the CSD, *viz*. 1.32 (5) and 1.23 (6) Å, respectively.

The water molecule and imidazolyl H atoms participate in strong hydrogen-bonding interactions (Table 2). The water molecule, acting as a donor, links two centrosymmetrically related molecules, thus forming a closed loop centered at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. These groups, in turn, interact with their homologous groups in neighboring cells through the remaining hydrogen bonds, mediated by the imidazolyl H atoms. The result is the build up of broad two-dimensional structures along *c*, parallel to (001) and one unit cell wide (Fig. 2). Sheets interact with each other in this direction through weaker C—H···O contacts and van der Waals forces. The packing is such as to drive the aromatic groups away from each other, thus preventing any kind of π–π interaction between them.

Experimental

The title compound, (I), was obtained by slow diffusion of two unperturbed solutions. The lower solution was an aqueous solution of nickel nitrate and sodium thiosulfate, while the upper solution was a dmf solution of bbip, the main three components being in a 1:3:1 molar ratio. Crystal growth took place at the interface of the two solutions, producing green prisms of (I) suitable for X-ray diffraction.

Crystal data

$[Ni(S_2O_3)(C_{21}H_{13}N_5)(C_3H_7NO)]\cdot H_2O$
$M_r = 573.29$
Triclinic, $P\overline{1}$
$a = 9.3815$ (8) Å
$b = 9.4096$ (8) Å
$c = 15.1968$ (13) Å
$\alpha = 72.124$ (2)°
$\beta = 83.169$ (2)°
$\gamma = 67.423$ (2)°
$V = 1178.91$ (17) Å^3
$Z = 2$
$D_x = 1.615$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 78 reflections
$\theta = 4.1$–23.3°
$\mu = 1.05$ mm^{-1}
$T = 293$ (2) K
Prism, green
0.35 × 0.25 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: refined from ΔF (*SADABS* in *SAINT-NT*; Bruker, 2000)
$T_{\min} = 0.73$, $T_{\max} = 0.81$
5399 measured reflections
4505 independent reflections
3230 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 26.0$°
$h = -5 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.109$
$S = 0.87$
4505 reflections
335 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N2	2.054 (3)	Ni—S1	2.4037 (10)
Ni—O1*A*	2.080 (2)	S1—S2	2.0137 (12)
Ni—N3	2.107 (3)	S2—O3	1.441 (2)
Ni—N1	2.124 (3)	S2—O2	1.473 (2)
Ni—O1	2.142 (2)	S2—O1	1.494 (2)
N2—Ni—O1*A*	97.71 (10)	O1*A*—Ni—S1	94.58 (7)
N2—Ni—N3	77.01 (10)	N3—Ni—S1	100.47 (8)
O1*A*—Ni—N3	91.86 (10)	N1—Ni—S1	105.58 (8)
N2—Ni—N1	76.78 (10)	O1—Ni—S1	74.48 (7)
O1*A*—Ni—N1	89.61 (10)	O3—S2—O2	111.37 (15)
N3—Ni—N1	153.71 (11)	O3—S2—O1	112.01 (15)
N2—Ni—O1	93.34 (9)	O2—S2—O1	108.68 (14)
O1*A*—Ni—O1	168.70 (9)	O3—S2—S1	111.21 (12)
N3—Ni—O1	92.91 (9)	O2—S2—S1	110.54 (10)
N1—Ni—O1	90.65 (9)	O1—S2—S1	102.70 (10)
N2—Ni—S1	167.51 (8)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WA\cdots$O2	0.88 (3)	2.01 (3)	2.877 (3)	168 (3)
O1W—H1$WB\cdots$O1$^{\rm i}$	0.89 (3)	1.90 (3)	2.752 (3)	162 (3)
N4—H4$A\cdots$O2$^{\rm ii}$	0.894 (6)	1.882 (7)	2.773 (4)	174.0 (10)
N5—H5$A\cdots$O1$W^{\rm iii}$	0.893 (18)	1.813 (17)	2.700 (4)	172.9 (11)

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

H atoms attached to C atoms were added at their expected positions and refined as riding. Methyl H atoms were additionally allowed to rotate. Water H atoms and those on the protonated N atoms in the bbip ligands were found in the final difference Fourier map and refined with restrained N—H [0.893 (18) and 0.894 (6) Å], O—H [0.88 (3) and 0.89 (3) Å] and H$\cdots$H (0.66 × O—H) distances.

Data collection: *SMART–NT* (Bruker, 2001); cell refinement: *SMART–NT*; data reduction: *SAINT–NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1117). Services for accessing these data are described at the back of the journal.

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