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Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.049
 wR factor = 0.111
Data-to-parameter ratio = 17.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tris(1*H*-imidazole- κN^3)(thiodiacetato- $\kappa^3 O, S, O'$)-
nickel(II) monohydrate

The title complex, $[\text{Ni}(\text{C}_4\text{H}_4\text{O}_4\text{S})(\text{C}_3\text{H}_4\text{N}_2)_3]\cdot\text{H}_2\text{O}$, displays a distorted octahedral $\text{NiN}_3\text{O}_2\text{S}$ coordination geometry, formed by three imidazole (imid) ligands and one thiodiacetate dianion. The Ni^{II} atom is displaced from one of the imid planes, and the angle between the corresponding $\text{Ni}-\text{N}$ bond and the imid plane is $21.94(19)^\circ$. This spatial orientation is stabilized by an intermolecular $\text{C}-\text{H}\cdots\pi$ interaction between one imid ligand and the $\text{C}-\text{H}$ bond of an adjacent imid ligand.

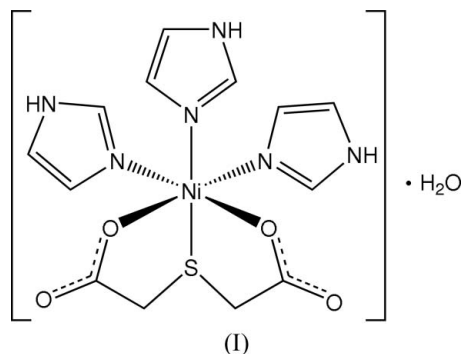
Received 7 July 2005

Accepted 8 July 2005

Online 16 July 2005

Comment

As part of our ongoing investigations of noncovalent interactions, such as aromatic stacking and $\text{C}-\text{H}\cdots\pi$ interactions, the title compound, (I), has been prepared and its X-ray crystal structure is presented here.



The Ni^{II} atom is surrounded by three imidazole (imid) ligands and one thiodiacetate (TDA) dianion, to form a distorted octahedral $\text{NiN}_3\text{O}_2\text{S}$ coordination geometry (Fig. 1). The tridentate TDA chelates to the Ni^{II} atom in a facial configuration, the two five-membered chelate rings being nearly perpendicular to each other with a dihedral angle of $86.18(6)^\circ$. The O1-containing ring is almost planar, the maximum atomic deviation being $0.064(2)$ Å (for C1). The O3-containing ring displays an envelope configuration, with the Ni^{II} atom lying in the flap position, $0.534(5)$ Å out of the mean plane formed by the other four atoms.

The Ni^{II} atom is nearly coplanar with N13-imid and N23-imid, and the angles between each $\text{Ni}-\text{N}$ bond and the corresponding imid plane are $1.19(18)$ and $5.7(2)^\circ$, respectively. It is notable that the angle between the $\text{Ni}-\text{N}33$ bond and N33-imid is large, $21.94(19)^\circ$, and the Ni^{II} atom is displaced from the N33-imid plane by $0.782(6)$ Å. Similar situations were also found in some other reported structures. A search of the Cambridge Structural Database (CSD, Version 5.26, update of May 2005; Allen, 2002) shows 359 first-row metallic complexes with imid ligands, and only three

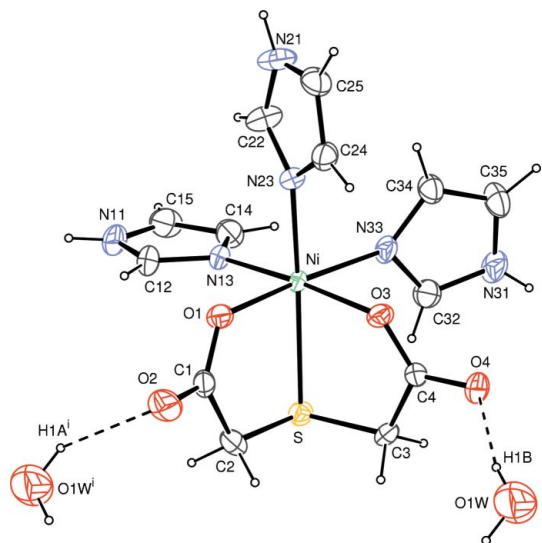


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $1 - x, -y, -z$.]

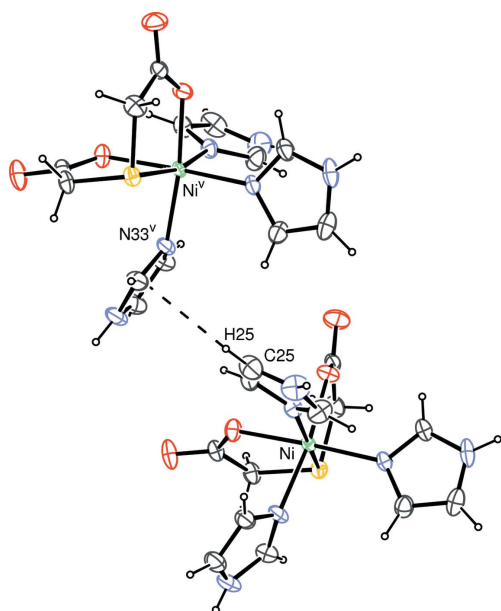


Figure 2
The intermolecular C—H... π interactions (dashed lines) in (I). [Symmetry code: (v) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

structures (Server-Carrio *et al.*, 1996; McFadden *et al.*, 1975; Li *et al.*, 2004) have the corresponding angles mentioned above larger than 20° , the angles being $34.7(3)$, 29.02 and $22.03(11)^\circ$, respectively. In our structure, a C—H... π interaction between C24—H24 and N33-imid (Fig. 2) stabilizes the spatial orientation of the N33-imid ring. The distance between H24 and C_g (the centroid of the N33-ring) is 2.74 \AA , and C24—H24... C_g is 141° .

Neighbouring complexes are connected to each other *via* N—H...O hydrogen bonds and atom H21 is involved in a bifurcated N—H... (O,O) hydrogen bond (angle sum about H21 is 357°) (Fig. 3). Hydrogen-bonding interactions also exist

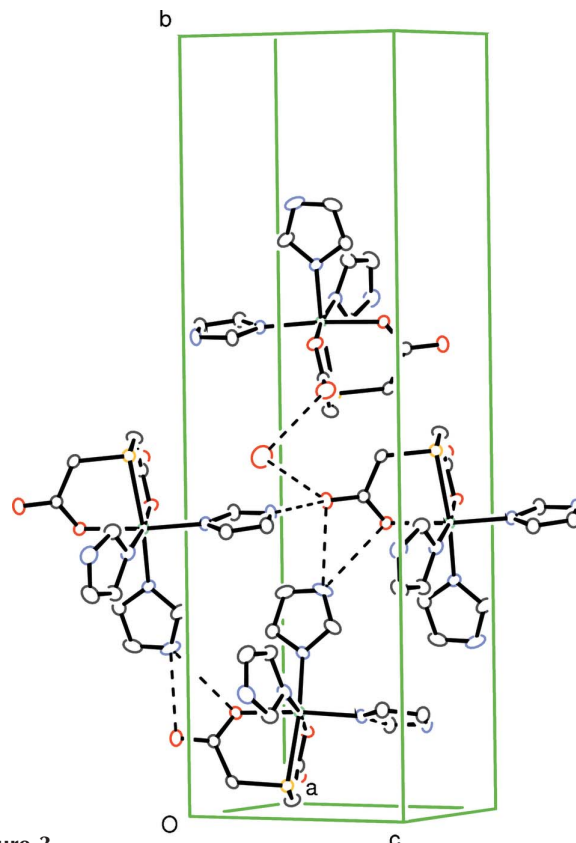


Figure 3
Part of the packing of (I), showing the intermolecular hydrogen bonding (dashed lines). H atoms have been omitted.

between water molecules and uncoordinated O atoms (O2/O4) of TDA (Fig. 1).

Experimental

The starting chemicals were of analytical grade and used as received. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.47 g, 2 mmol) was added to an aqueous solution (5 ml) of Na_2CO_3 (0.21 g, 2 mmol) and H_2TDA (0.30 g, 2 mmol). An ethanol solution (20 ml) containing imid (0.14 g, 2 mmol) was then mixed with the above solution. The mixture was refluxed for 5 h, and filtered after being cooled to room temperature. Green single crystals were obtained after about one week.

Crystal data

$[\text{Ni}(\text{C}_4\text{H}_4\text{O}_4\text{S})(\text{C}_3\text{H}_4\text{N}_2)_3] \cdot \text{H}_2\text{O}$
 $M_r = 429.10$
 Monoclinic, $P2_1/n$
 $a = 8.2351(3) \text{ \AA}$
 $b = 25.3931(8) \text{ \AA}$
 $c = 8.6540(3) \text{ \AA}$
 $\beta = 104.8510(10)^\circ$
 $V = 1749.23(10) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.629 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 13236 reflections
 $\theta = 1.6\text{--}27.5^\circ$
 $\mu = 1.27 \text{ mm}^{-1}$
 $T = 295(3) \text{ K}$
 Platelet, blue
 $0.33 \times 0.31 \times 0.03 \text{ mm}$

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.662$, $T_{\max} = 0.965$
 16127 measured reflections

4014 independent reflections
 3487 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\max} = 27.5^\circ$
 $h = -10 \rightarrow 10$
 $k = -32 \rightarrow 32$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.111$
 $S = 1.18$
 4014 reflections
 235 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 2.1571P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.66 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Ni—O1	2.044 (2)	Ni—N23	2.059 (3)
Ni—O3	2.096 (2)	Ni—N33	2.089 (3)
Ni—N13	2.067 (3)	Ni—S	2.4748 (8)
O1—Ni—O3	88.05 (10)	O3—Ni—S	81.26 (6)
O1—Ni—N13	92.58 (10)	N13—Ni—N23	93.83 (10)
O1—Ni—N23	87.70 (10)	N13—Ni—N33	94.89 (11)
O1—Ni—N33	172.54 (11)	N13—Ni—S	93.79 (7)
O1—Ni—S	82.30 (7)	N23—Ni—N33	91.78 (11)
O3—Ni—N13	174.88 (10)	N23—Ni—S	167.68 (8)
O3—Ni—N23	91.26 (10)	N33—Ni—S	97.19 (8)
O3—Ni—N33	84.52 (11)		

Table 2
 Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1A \cdots O2 ⁱ	0.85	2.37	3.056 (5)	138
O1W—H1B \cdots O4	0.85	2.01	2.839 (5)	165
N11—H11 \cdots O4 ⁱⁱ	0.86	2.07	2.845 (5)	149
N21—H21 \cdots O3 ⁱⁱⁱ	0.86	2.21	3.048 (4)	165
N21—H21 \cdots O4 ⁱⁱⁱ	0.86	2.29	2.950 (4)	134
N31—H31 \cdots O1 ^{iv}	0.86	1.90	2.730 (4)	163

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

The H atoms of water molecules were located in a difference Fourier map and refined as riding in their as-found relative positions, with a fixed U_{iso} value of 0.08 \AA^2 . Other H atoms were placed in calculated positions, with C—H = 0.97 (methylene) or 0.93 \AA (aromatic) and N—H = 0.86 \AA , and were included in the final cycles of refinement in the riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the National Natural Science Foundation of China (grant No. 20443003).

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