

Tetraaquabis(pyridine-3-sulfonato- κ N)-nickel(II)

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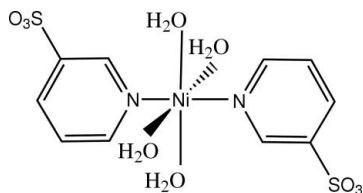
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 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.024; wR factor = 0.065; data-to-parameter ratio = 13.3.

In the molecule of the title compound, $[\text{Ni}(\text{C}_5\text{H}_4\text{NO}_3\text{S})_2(\text{H}_2\text{O})_4]$, the Ni^{II} cation is located on an inversion center and is coordinated by four water molecules and two pyridine-3-sulfonato anions with an NiN_2O_4 distorted octahedral geometry. The face-to-face separation of 3.561 (5) Å between parallel pyridine rings indicates the existence of weak π - π stacking between the pyridine rings. The structure also contains intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding.

Related literature

For general background, see: Deisenhofer & Michel (1989); Su & Xu (2004); Liu *et al.* (2004); Li *et al.* (2005). For a related structure, see: Walsh & Hathaway (1980). For related literature, see: Cotton & Wilkinson (1972).



Experimental

Crystal data

 $[\text{Ni}(\text{C}_5\text{H}_4\text{NO}_3\text{S})_2(\text{H}_2\text{O})_4]$
 $M_r = 447.08$

 Monoclinic, $P2_1/n$
 $a = 7.5399$ (8) Å

 $b = 12.6939$ (15) Å

 $c = 8.7810$ (8) Å

 $\beta = 97.419$ (12)°

 $V = 833.40$ (15) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 1.47$ mm⁻¹
 $T = 295$ (2) K

 $0.32 \times 0.22 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer

Absorption correction: multi-scan

 (*ABSCOR*; Higashi, 1995)

 $T_{\text{min}} = 0.660$, $T_{\text{max}} = 0.745$

 8877 measured reflections
 1524 independent reflections

 1449 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.065$
 $S = 1.06$

1524 reflections

115 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³
Table 1

Selected bond lengths (Å).

Ni—O1	2.0828 (14)	Ni—N1	2.1026 (16)
Ni—O2	2.0739 (14)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O3 ⁱ	0.81	2.39	3.162 (3)	158
O1—H1A \cdots O4 ⁱ	0.81	2.44	3.119 (2)	142
O1—H1B \cdots O4 ⁱⁱ	0.89	1.83	2.722 (2)	177
O2—H2A \cdots O3 ⁱⁱⁱ	0.84	1.97	2.787 (2)	163
O2—H2B \cdots O5 ^{iv}	0.86	1.89	2.748 (2)	174
C1—H1 \cdots O4 ⁱ	0.93	2.34	3.212 (3)	155

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

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.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2227).

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supplementary materials

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Tetraaquabis(pyridine-3-sulfonato- κ N)nickel(II)

B.-Y. Zhang, J.-J. Nie and D.-J. Xu

Comment

As π - π stacking between aromatic rings plays an important role in electron transfer process in some biological system (Deisenhofer & Michel, 1989), π - π stacking has attracted our much attention in past years (Su & Xu, 2004; Liu *et al.*, 2004; Li *et al.*, 2005). In order to investigate the influence of substituents on aromatic stacking, the title pyridine-sulfate complex has recently prepared and its crystal structure is reported here.

The molecular structure of the title compound is shown in Fig. 1. The Ni^{II} cation is located in an inversion center and coordinated by four water molecules and two pyridine-3-sulfonate anions with a NiN₂O₄ distorted octahedral geometry (Table 1), similar to the analogue of Zn^{II} (Walsh & Hathaway, 1980). Partially overlapped arrangement is observed between parallel pyridine rings (Fig. 2). The face-to-face separation of 3.561 (5) Å between parallel pyridine rings is shorter than the van der Waals thickness of an aromatic ring (3.70 Å; Cotton & Wilkinson, 1972), and indicates the existence of weak π - π stacking between the pyridine rings.

The intermolecular O—H \cdots O hydrogen bonding and weak C—H \cdots O hydrogen bonding (Table 2) help to stabilize the crystal structure.

Experimental

Pyridine-3-sulfonic acid (0.159 g, 1 mmol), Na₂CO₃ (0.053 g, 0.5 mmol), NiCl₂·6H₂O (0.238 g, 1 mmol) were dissolved in a mixture solution of water (8 ml) and ethanol (2 ml). The solution was placed in a 15 ml Teflon-lined stainless steel autoclave under autogenous pressure at 398 K for 75 h and filtered after cooling to room temperature. The blue single crystals of the title compound were obtained from the filtrate after 3 months.

Refinement

Water H atoms were located in a difference Fourier map and refined as riding in as-found relative positions with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Aromatic H atoms were placed in calculated positions with C—H = 0.93 Å and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

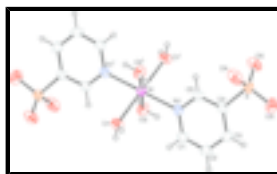


Fig. 1. The molecular structure of the title compound with 40% probability displacement (arbitrary spheres for H atoms) [symmetry codes: (i)1 - x, 1 - y, 1 - z].

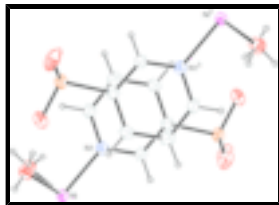


Fig. 2. A diagram showing π - π stacking between pyridine rings [symmetry code: (ii) $1 - x, 1 - y, -z$].

Tetraaquabis(pyridine-3-sulfonato- κ N)nickel(II)

Crystal data

$[\text{Ni}(\text{C}_5\text{H}_4\text{NO}_3\text{S})_2(\text{H}_2\text{O})_4]$

$M_r = 447.08$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 7.5399\ (8)\ \text{\AA}$

$b = 12.6939\ (15)\ \text{\AA}$

$c = 8.7810\ (8)\ \text{\AA}$

$\beta = 97.419\ (12)^\circ$

$V = 833.40\ (15)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 460$

$D_x = 1.782\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5256 reflections

$\theta = 2.8\text{--}24.0^\circ$

$\mu = 1.47\ \text{mm}^{-1}$

$T = 295\ (2)\ \text{K}$

Prism, blue

$0.32 \times 0.22 \times 0.20\ \text{mm}$

Data collection

Rigaku R-Axis RAPID IP
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $10.0\ \text{pixels mm}^{-1}$

$T = 295\ (2)\ \text{K}$

ω scans

Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)

$T_{\min} = 0.660, T_{\max} = 0.745$

8877 measured reflections

1524 independent reflections

1449 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 25.4^\circ$

$\theta_{\min} = 2.8^\circ$

$h = -9 \rightarrow 9$

$k = -15 \rightarrow 15$

$l = -9 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.065$

$S = 1.06$

1524 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 0.5265P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.29\ \text{e \AA}^{-3}$

115 parameters

$$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni	0.5000	0.5000	0.5000	0.02883 (13)
S	0.45204 (7)	0.75905 (4)	-0.03581 (6)	0.03407 (15)
N1	0.5850 (2)	0.54221 (13)	0.28948 (18)	0.0307 (3)
O1	0.76142 (19)	0.48676 (11)	0.60868 (18)	0.0388 (3)
H1B	0.8326	0.5397	0.5900	0.058*
H1A	0.8182	0.4333	0.5998	0.058*
O2	0.50231 (19)	0.34035 (11)	0.45010 (17)	0.0411 (3)
H2A	0.5076	0.3156	0.3615	0.062*
H2B	0.4194	0.3021	0.4815	0.062*
O3	0.5370 (3)	0.76975 (16)	-0.1732 (2)	0.0687 (6)
O4	0.4828 (2)	0.85025 (12)	0.0624 (2)	0.0554 (5)
O5	0.2658 (2)	0.73019 (12)	-0.06337 (19)	0.0481 (4)
C1	0.7217 (3)	0.49242 (15)	0.2368 (3)	0.0370 (5)
H1	0.7768	0.4372	0.2943	0.044*
C2	0.7839 (3)	0.51907 (18)	0.1020 (3)	0.0452 (5)
H2	0.8783	0.4819	0.0693	0.054*
C3	0.7053 (3)	0.60162 (17)	0.0150 (3)	0.0405 (5)
H3	0.7461	0.6218	-0.0762	0.049*
C4	0.5641 (2)	0.65298 (14)	0.0684 (2)	0.0298 (4)
C5	0.5074 (3)	0.62143 (15)	0.2044 (2)	0.0320 (4)
H5	0.4116	0.6565	0.2384	0.038*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.0309 (2)	0.0273 (2)	0.0284 (2)	0.00105 (13)	0.00426 (14)	0.00418 (13)
S	0.0419 (3)	0.0278 (3)	0.0317 (3)	0.0027 (2)	0.0018 (2)	0.00399 (19)
N1	0.0329 (8)	0.0290 (8)	0.0302 (8)	0.0016 (7)	0.0037 (6)	0.0034 (7)
O1	0.0336 (7)	0.0355 (8)	0.0467 (9)	0.0018 (6)	0.0031 (6)	0.0056 (6)

supplementary materials

O2	0.0512 (9)	0.0328 (8)	0.0409 (8)	-0.0017 (6)	0.0122 (7)	-0.0002 (6)
O3	0.0861 (14)	0.0758 (13)	0.0491 (11)	0.0261 (11)	0.0269 (10)	0.0305 (9)
O4	0.0591 (10)	0.0297 (8)	0.0707 (11)	0.0048 (7)	-0.0174 (8)	-0.0095 (8)
O5	0.0441 (9)	0.0358 (8)	0.0600 (10)	0.0039 (7)	-0.0103 (7)	-0.0022 (7)
C1	0.0360 (11)	0.0328 (11)	0.0417 (12)	0.0064 (8)	0.0034 (9)	0.0061 (8)
C2	0.0417 (12)	0.0431 (12)	0.0542 (14)	0.0126 (10)	0.0188 (10)	0.0065 (10)
C3	0.0455 (12)	0.0393 (11)	0.0395 (12)	0.0036 (9)	0.0154 (9)	0.0055 (9)
C4	0.0337 (9)	0.0255 (9)	0.0295 (10)	-0.0002 (7)	0.0016 (8)	0.0005 (7)
C5	0.0333 (9)	0.0314 (10)	0.0313 (10)	0.0041 (8)	0.0047 (8)	0.0004 (8)

Geometric parameters (\AA , $^\circ$)

Ni—O1 ⁱ	2.0828 (14)	O1—H1B	0.8886
Ni—O1	2.0828 (14)	O1—H1A	0.8115
Ni—O2 ⁱ	2.0739 (14)	O2—H2A	0.8450
Ni—O2	2.0739 (14)	O2—H2B	0.8642
Ni—N1 ⁱ	2.1026 (16)	C1—C2	1.370 (3)
Ni—N1	2.1026 (16)	C1—H1	0.9300
S—O5	1.4412 (16)	C2—C3	1.384 (3)
S—O3	1.4438 (18)	C2—H2	0.9300
S—O4	1.4445 (16)	C3—C4	1.381 (3)
S—C4	1.7788 (19)	C3—H3	0.9300
N1—C1	1.341 (3)	C4—C5	1.379 (3)
N1—C5	1.341 (2)	C5—H5	0.9300
O2 ⁱ —Ni—O2	180.0	C5—N1—Ni	121.36 (13)
O2 ⁱ —Ni—O1 ⁱ	89.12 (6)	Ni—O1—H1B	114.4
O2—Ni—O1 ⁱ	90.88 (6)	Ni—O1—H1A	120.2
O2 ⁱ —Ni—O1	90.88 (6)	H1B—O1—H1A	106.0
O2—Ni—O1	89.12 (6)	Ni—O2—H2A	124.1
O1 ⁱ —Ni—O1	180.0	Ni—O2—H2B	117.1
O2 ⁱ —Ni—N1 ⁱ	92.95 (6)	H2A—O2—H2B	101.9
O2—Ni—N1 ⁱ	87.05 (6)	N1—C1—C2	123.07 (19)
O1 ⁱ —Ni—N1 ⁱ	92.61 (6)	N1—C1—H1	118.5
O1—Ni—N1 ⁱ	87.39 (6)	C2—C1—H1	118.5
O2 ⁱ —Ni—N1	87.05 (6)	C1—C2—C3	119.6 (2)
O2—Ni—N1	92.95 (6)	C1—C2—H2	120.2
O1 ⁱ —Ni—N1	87.39 (6)	C3—C2—H2	120.2
O1—Ni—N1	92.61 (6)	C4—C3—C2	117.6 (2)
N1 ⁱ —Ni—N1	180.0	C4—C3—H3	121.2
O5—S—O3	114.30 (12)	C2—C3—H3	121.2
O5—S—O4	112.45 (10)	C5—C4—C3	119.71 (18)
O3—S—O4	111.67 (12)	C5—C4—S	119.06 (14)
O5—S—C4	106.36 (9)	C3—C4—S	121.23 (15)
O3—S—C4	105.58 (10)	N1—C5—C4	122.60 (18)
O4—S—C4	105.69 (9)	N1—C5—H5	118.7
C1—N1—C5	117.40 (17)	C4—C5—H5	118.7

C1—N1—Ni 121.22 (13)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1A \cdots O3 ⁱⁱ	0.81	2.39	3.162 (3)	158
O1—H1A \cdots O4 ⁱⁱ	0.81	2.44	3.119 (2)	142
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Symmetry codes: (ii) $-x+3/2, y-1/2, -z+1/2$; (iii) $x+1/2, -y+3/2, z+1/2$; (iv) $-x+1, -y+1, -z$; (v) $-x+1/2, y-1/2, -z+1/2$.

Fig. 1

