

catena-Poly[[diaquanickel(II)]-bis(μ -pyridine-4-sulfinato)- κ^2 N,O; κ^2 O,N]

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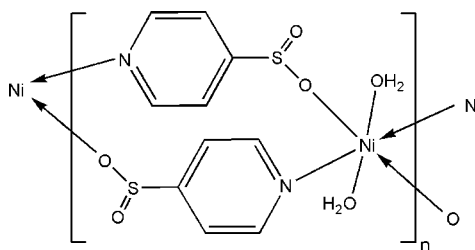
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.031; wR factor = 0.080; data-to-parameter ratio = 12.2.

In the title coordination polymer, $[\text{Ni}(\text{C}_5\text{H}_4\text{NO}_2\text{S})_2(\text{H}_2\text{O})_2]_n$, the Ni^{II} ion is located on an inversion centre and is octahedrally coordinated by two N and two O atoms of four symmetry-related and deprotonated pyridine-4-sulfinato (ps) ligands together with two water molecules in axial positions. The ps^- anions, acting as μ_2 -bridging ligands, link neighbouring Ni^{II} ions into a chain structure along the c axis. These polymeric chains are extended into a three-dimensional framework *via* intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with participation of the water molecules.

Related literature

For metal complexes derived from pyridine-4-sulfonic acid, see: Lü *et al.* (2007); Leslie & George (2005a,b).



Experimental

Crystal data

 $[\text{Ni}(\text{C}_5\text{H}_4\text{NO}_2\text{S})_2(\text{H}_2\text{O})_2]$
 $M_r = 379.05$

 Triclinic, $P\bar{1}$
 $a = 6.403$ (5) Å

 $b = 7.309$ (5) Å

 $c = 7.602$ (5) Å

 $\alpha = 96.784$ (8)°

 $\beta = 95.140$ (8)°

 $\gamma = 107.709$ (8)°

 $V = 333.6$ (4) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 1.80$ mm⁻¹
 $T = 296$ K

 $0.25 \times 0.17 \times 0.14$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

 $T_{\text{min}} = 0.662$, $T_{\text{max}} = 0.787$

2417 measured reflections

1180 independent reflections

 1043 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.080$
 $S = 1.00$

1180 reflections

97 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.68$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³
Table 1

Selected geometric parameters (Å, °).

Ni1—Ni ¹	2.008 (2)	Ni1—O1	2.362 (2)
Ni1—O3	2.026 (2)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1W \cdots O2 ^{iv}	0.84	2.00	2.826 (3)	168
O1—H2W \cdots O2 ^v	0.84	2.00	2.827 (3)	169

 Symmetry codes: (iv) $x, y - 1, z$; (v) $-x, -y, -z + 2$.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2818).

References

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supplementary materials

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catena-Poly[[diaquanickel(II)]-bis(μ -pyridine-4-sulfonato)- $\kappa^2 N, O; \kappa^2 O, N$]

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Comment

It is well known that sulfinic acid is not stable compared with sulfonic acid, so it is much difficult to obtain complexes of sulfinic acid as they are easy to be oxidized. In the previous literatures, several metal complexes derived from pyridine-4-sulfonic acid have been reported (Leslie & George, 2005a,b; Lü *et al.*, 2007), whereas the complexes of pyridine-4-sulfinic acid has been not seen so far. Here we describe a nickel(II) complex from pyridine-4-sulfinic acid, (I), (Fig. 1).

The Ni^{II} ion locates on a centre of symmetry and is in a distorted octahedral geometry with two water ligands in axial *trans* positions and two N and two O atoms of four symmetry-related ps⁻ ligands in equatorial plane (Table 1). Each ps⁻ ligand connects two Ni^{II} ions and thus forms one-dimensional chain structure along *c* axis (Fig.2), with adjacent Ni...Ni separation distance of 7.602 (3) Å.

Water molecules take part in hydrogen bonds as double donor, and S=O of ps⁻ ligands acts only as a single acceptor (Table 2, Fig.3). Hydrogen bonds interactions stabilizes and extends chain structure of (I) into a three-dimensional network.

Experimental

A solution of NiCl₂·6H₂O (1 mmol, 0.238 g) in anhydrous ethanol (10 ml) was injected dropwise into a solution of Hps (2 mol, 0.286 g) in methanol (15 ml) under argon. The resulting mixture was stirred at 343 K for 4 h, then cooled to room temperature. After filtration, the filtrate was left to stand at room temperature for slow evaporation. Green block-shaped crystals suitable for X-ray diffraction were obtained in a yield of 17%. Analysis, found: C 31.58, H 3.11, N 7.45, S 16.93%; C₁₀H₁₂N₂NiO₆S₂ requires: C 31.66, H 3.17, N 7.39, S 16.88%.

Refinement

H atoms bonded to C were positioned geometrically with C—H distance of 0.93 Å, and treated as riding atoms, with $U_{iso}(H)=1.2U_{eq}(C)$. The O—H hydrogen atom was located in a difference Fourier map and refined isotropically.

Figures

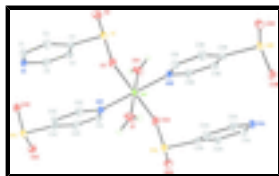


Fig. 1. The coordination environment of Ni^{II} ion in (I). Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (A) (1 - x, -y, 2 - z); (B) (x, y, 1 + z); (C) (1 - x, -y, 1 - z).

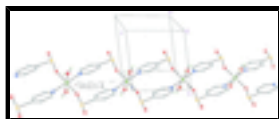


Fig. 2. The chain structure of (I) along c axis. H atoms on C atoms have been omitted.

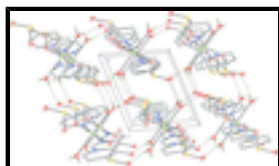


Fig. 3. Packing diagram for (1), showing hydrogen bonds as dashed lines in ab plane. H atoms on C have been deleted.

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Crystal data

[Ni(C₅H₄NO₂S)₂(H₂O)₂]

$M_r = 379.05$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 6.403$ (5) Å

$b = 7.309$ (5) Å

$c = 7.602$ (5) Å

$\alpha = 96.784$ (8)°

$\beta = 95.140$ (8)°

$\gamma = 107.709$ (8)°

$V = 333.6$ (4) Å³

$Z = 1$

$F_{000} = 194$

$D_x = 1.887$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1414 reflections

$\theta = 2.7$ – 27.9°

$\mu = 1.80$ mm⁻¹

$T = 296$ K

Block, green

$0.25 \times 0.17 \times 0.14$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.662$, $T_{\max} = 0.787$

2417 measured reflections

1180 independent reflections

1043 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 25.5^\circ$

$\theta_{\min} = 3.0^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.080$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2]$

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

$S = 1.00$	$(\Delta/\sigma)_{\max} < 0.001$
1180 reflections	$\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$
97 parameters	$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$
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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.0000	1.0000	0.02196 (18)
S1	0.37032 (11)	0.32818 (9)	0.81172 (8)	0.0282 (2)
O1	0.1697 (3)	-0.2599 (3)	0.9900 (3)	0.0432 (5)
H1W	0.1594	-0.3595	0.9190	0.065*
H2W	0.0660	-0.2844	1.0522	0.065*
O2	0.1653 (3)	0.3862 (3)	0.7920 (3)	0.0374 (5)
O3	0.3059 (3)	0.1287 (3)	0.8709 (2)	0.0330 (4)
N1	0.4591 (3)	0.1289 (3)	0.2369 (3)	0.0257 (5)
C1	0.2579 (4)	0.1289 (4)	0.2770 (4)	0.0306 (6)
H1	0.1377	0.0841	0.1873	0.037*
C2	0.2257 (5)	0.1933 (4)	0.4472 (4)	0.0320 (6)
H2	0.0857	0.1920	0.4721	0.038*
C3	0.4053 (4)	0.2601 (3)	0.5805 (3)	0.0250 (5)
C4	0.6131 (4)	0.2690 (4)	0.5387 (3)	0.0271 (6)
H4	0.7370	0.3191	0.6247	0.033*
C5	0.6316 (4)	0.2014 (4)	0.3656 (4)	0.0304 (6)
H5	0.7713	0.2066	0.3369	0.036*

Atomic displacement parameters (\AA^2)

U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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supplementary materials

Ni1	0.0291 (3)	0.0292 (3)	0.0131 (2)	0.0168 (2)	0.00585 (17)	0.00249 (17)
S1	0.0353 (4)	0.0309 (4)	0.0215 (4)	0.0151 (3)	0.0082 (3)	0.0004 (3)
O1	0.0457 (12)	0.0320 (11)	0.0528 (13)	0.0108 (9)	0.0236 (10)	0.0015 (9)
O2	0.0473 (12)	0.0441 (11)	0.0339 (11)	0.0299 (10)	0.0164 (9)	0.0075 (9)
O3	0.0414 (11)	0.0401 (10)	0.0251 (9)	0.0212 (9)	0.0098 (8)	0.0081 (8)
N1	0.0288 (11)	0.0309 (11)	0.0210 (11)	0.0141 (9)	0.0055 (8)	0.0047 (9)
C1	0.0284 (13)	0.0412 (15)	0.0254 (14)	0.0162 (11)	0.0033 (11)	0.0040 (11)
C2	0.0277 (13)	0.0435 (15)	0.0299 (15)	0.0176 (12)	0.0089 (11)	0.0047 (12)
C3	0.0328 (13)	0.0246 (12)	0.0217 (13)	0.0134 (10)	0.0079 (10)	0.0047 (10)
C4	0.0271 (13)	0.0327 (13)	0.0217 (13)	0.0106 (11)	0.0036 (10)	0.0015 (10)
C5	0.0304 (14)	0.0377 (15)	0.0275 (15)	0.0160 (12)	0.0084 (11)	0.0053 (11)

Geometric parameters (Å, °)

Ni1—Ni ⁱ	2.008 (2)	N1—C5	1.336 (4)
Ni1—Ni ⁱⁱ	2.008 (2)	N1—C1	1.350 (3)
Ni1—O3 ⁱⁱⁱ	2.026 (2)	N1—Ni ^{iv}	2.008 (2)
Ni1—O3	2.026 (2)	C1—C2	1.379 (4)
Ni1—O1 ⁱⁱⁱ	2.362 (2)	C1—H1	0.9300
Ni1—O1	2.362 (2)	C2—C3	1.386 (4)
S1—O2	1.498 (2)	C2—H2	0.9300
S1—O3	1.523 (2)	C3—C4	1.380 (4)
S1—C3	1.821 (3)	C4—C5	1.378 (4)
O1—H1W	0.8350	C4—H4	0.9300
O1—H2W	0.8371	C5—H5	0.9300
N1 ⁱ —Ni1—Ni ⁱⁱⁱ	180.000 (1)	H1W—O1—H2W	109.3
N1 ⁱ —Ni1—O3 ⁱⁱⁱ	90.55 (9)	S1—O3—Ni1	128.93 (12)
N1 ⁱⁱ —Ni1—O3 ⁱⁱⁱ	89.45 (9)	C5—N1—C1	118.2 (2)
N1 ⁱ —Ni1—O3	89.45 (9)	C5—N1—Ni ^{iv}	119.50 (18)
N1 ⁱⁱ —Ni1—O3	90.55 (9)	C1—N1—Ni ^{iv}	121.99 (18)
O3 ⁱⁱⁱ —Ni1—O3	180.000 (1)	N1—C1—C2	121.9 (2)
N1 ⁱ —Ni1—O1 ⁱⁱⁱ	92.01 (8)	N1—C1—H1	119.1
N1 ⁱⁱ —Ni1—O1 ⁱⁱⁱ	87.99 (8)	C2—C1—H1	119.1
O3 ⁱⁱⁱ —Ni1—O1 ⁱⁱⁱ	85.24 (9)	C1—C2—C3	118.9 (2)
O3—Ni1—O1 ⁱⁱⁱ	94.76 (9)	C1—C2—H2	120.5
N1 ⁱ —Ni1—O1	87.99 (8)	C3—C2—H2	120.5
N1 ⁱⁱ —Ni1—O1	92.01 (8)	C4—C3—C2	119.5 (2)
O3 ⁱⁱⁱ —Ni1—O1	94.76 (9)	C4—C3—S1	119.35 (19)
O3—Ni1—O1	85.24 (9)	C2—C3—S1	121.1 (2)
O1 ⁱⁱⁱ —Ni1—O1	180.0	C3—C4—C5	118.0 (2)
O2—S1—O3	107.19 (12)	C3—C4—H4	121.0
O2—S1—C3	102.55 (12)	C5—C4—H4	121.0
O3—S1—C3	99.77 (11)	N1—C5—C4	123.3 (2)
Ni1—O1—H1W	114.8	N1—C5—H5	118.3
Ni1—O1—H2W	135.0	C4—C5—H5	118.3

O2—S1—O3—Ni1	-157.49 (13)	C1—C2—C3—S1	-174.8 (2)
C3—S1—O3—Ni1	96.00 (15)	O2—S1—C3—C4	155.44 (19)
N1 ⁱ —Ni1—O3—S1	-93.25 (15)	O3—S1—C3—C4	-94.3 (2)
N1 ⁱⁱ —Ni1—O3—S1	86.75 (15)	O2—S1—C3—C2	-26.8 (2)
O1 ⁱⁱⁱ —Ni1—O3—S1	-1.28 (15)	O3—S1—C3—C2	83.4 (2)
O1—Ni1—O3—S1	178.72 (15)	C2—C3—C4—C5	-3.1 (4)
C5—N1—C1—C2	-2.8 (4)	S1—C3—C4—C5	174.71 (19)
Ni1 ^{iv} —N1—C1—C2	170.9 (2)	C1—N1—C5—C4	2.7 (4)
N1—C1—C2—C3	0.1 (4)	Ni1 ^{iv} —N1—C5—C4	-171.20 (19)
C1—C2—C3—C4	2.9 (4)	C3—C4—C5—N1	0.3 (4)

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

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—H1W \cdots O2 ^v	0.84	2.00	2.826 (3)	168
O1—H2W \cdots O2 ^{vi}	0.84	2.00	2.827 (3)	169

Symmetry codes: (v) $x, y-1, z$; (vi) $-x, -y, -z+2$.

Fig. 1

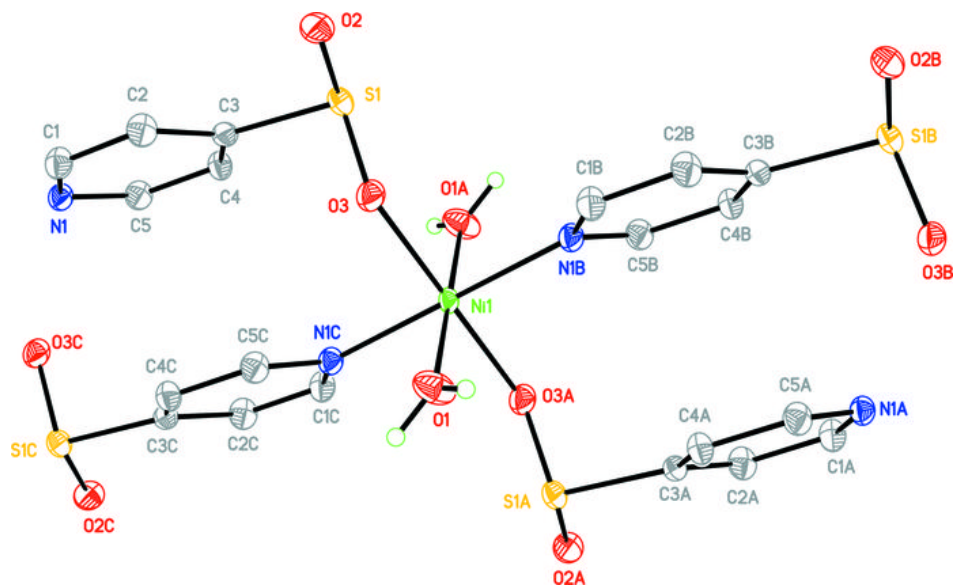


Fig. 2

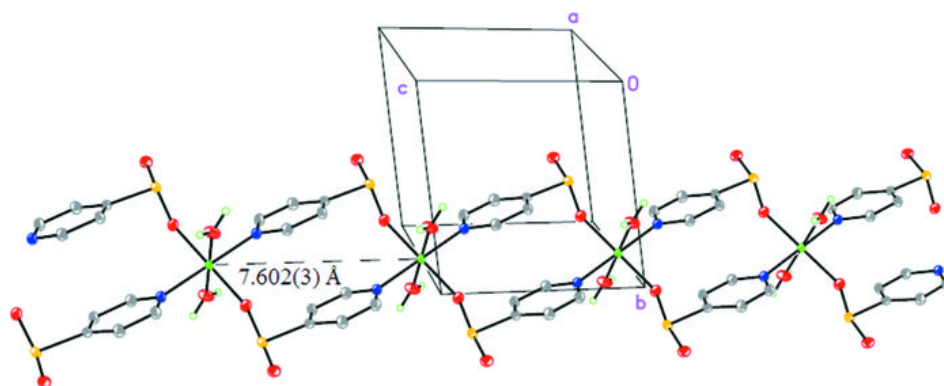


Fig. 3

