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Tetraaquabis[2-(4-pyridylsulfanyl)-acetato- κ N]nickel(II)

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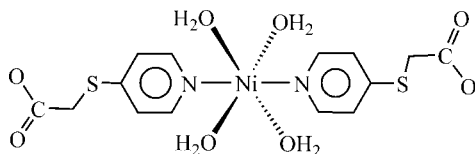
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.022; wR factor = 0.061; data-to-parameter ratio = 13.0.

In the centrosymmetric title complex, $[\text{Ni}(\text{C}_7\text{H}_6\text{NO}_2\text{S})_2(\text{H}_2\text{O})_4]$, the Ni^{II} atom, located on a centre of inversion, is coordinated by two N atoms from two 2-(4-pyridylsulfanyl)-acetate ligands and four water O atoms in an octahedral geometry. In the crystal, intermolecular O—H...O hydrogen bonds between the coordinated water molecules and the carboxylate group of the anionic 2-(4-pyridylsulfanyl)acetate ligands link these discrete mononuclear units into a three-dimensional network.

Related literature

For structures and applications of metal complexes with polycarboxylate-based pyridine ligands, see: Zhao *et al.* (2010); Wang *et al.* (2007). For metal complexes with 2-(4-pyridylsulfanyl)acetate ligands, see: Kondo *et al.* (2002); Zhang *et al.* (2004); Qin *et al.* (2004).



Experimental

Crystal data

$[\text{Ni}(\text{C}_7\text{H}_6\text{NO}_2\text{S})_2(\text{H}_2\text{O})_4]$	$\alpha = 92.713$ (1)°
$M_r = 467.15$	$\beta = 103.440$ (1)°
Triclinic, $P\bar{1}$	$\gamma = 115.120$ (1)°
$a = 6.3577$ (4) Å	$V = 456.75$ (5) Å ³
$b = 7.0330$ (5) Å	$Z = 1$
$c = 11.7624$ (8) Å	Mo $K\alpha$ radiation

 $\mu = 1.34$ mm⁻¹
 $T = 296$ K

 $0.22 \times 0.20 \times 0.14$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	2358 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	1610 independent reflections
$T_{\text{min}} = 0.758$, $T_{\text{max}} = 0.835$	1525 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.008$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	124 parameters
$wR(F^2) = 0.061$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.22$ e Å ⁻³
1610 reflections	$\Delta\rho_{\text{min}} = -0.28$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3A}\cdots\text{O2}^{\text{I}}$	0.85	2.13	2.951 (2)	161
$\text{O3}-\text{H3B}\cdots\text{O1}^{\text{ii}}$	0.85	1.92	2.7265 (18)	158
$\text{O4}-\text{H4A}\cdots\text{O1}^{\text{iii}}$	0.85	1.83	2.6697 (18)	168
$\text{O4}-\text{H4B}\cdots\text{O2}^{\text{iv}}$	0.85	2.01	2.855 (2)	172

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

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2001); 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) and DIAMOND (Brandenburg & Berndt, 1999); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5549).

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supporting information

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Tetraaquabis[2-(4-pyridylsulfanyl)acetato- κ N]nickel(II)

Jing-Yi Wang, Xiu-Guang Wang and Xiao-Jun Zhao

S1. Comment

Recently, functional metal complexes with polycarboxylate-based pyridine ligands have gained more and more interest due to their intriguing structures and potential applications in magnetism (Zhao *et al.* 2010), and luminescence (Wang *et al.* 2007). Acting as one of flexible multifunctional building blocks, 2-(4-pyridylsulfanyl)acetic acid with three potential metal binding sites and various flexible connection modes (Kondo *et al.*, 2002; Zhang *et al.*, 2004; Qin *et al.*, 2004) has been extensively used to construct novel metal complexes with discrete mononuclear structure or polymeric coordination framework with variable dimensionality. Herein, as the continuing investigations on the coordination chemistry of the ligand, we report the crystal structure of a tetraaquonickel(II) complex with deprotonated 2-(4-pyridylsulfanyl)acetate ligand, (I).

The molecular structure of the title mononuclear complex is show Fig.1 and selected bond lengths and angles are listed in Table 1. The Ni^{II} atom in the mononuclear structure of I lies on an inversion centre and is in a octahedral coordination environment involving two pyridyl N atoms from two different 2-(4-pyridylsulfanyl)acetate ligand and four O donors from four water molecules. In the crystal structure, four intermolecular O—H \cdots O hydrogen bonds between the coordinated water molecules and the carboxylate group of 2-(4-pyridylsulfanyl)acetate ligand link adjacent mononuclear structures into a three-dimensional supramolecular network (Fig.2 and Table 2).

S2. Experimental

A methanol solution of 2-(4-pyridylsulfanyl)acetic acid (25.3 mg, 0.1 mmol) was carefully layered onto a buffer layer of ethyl acetate (2.0 ml) in a straight glass tube, meanwhile the pH value of the top layer was carefully adjusted to 7.0 by slow addition of triethylamine. Below which an aqueous solution containing NiCl₂·6H₂O (23.7 mg, 0.1 mmol) was placed. The test tube was left in air under room temperature. Blue block-shaped crystals were harvested within three weeks. Yield: 50% based on 2-(4-pyridylsulfanyl)acetic acid. Anal. Calcd. for C₁₄H₂₀N₂NiO₈S₂: C, 36.00; H, 4.32; N, 6.00%. Found: C, 35.98; H, 4.34; N, 6.03%.

S3. Refinement

H atoms were located in a difference map, but refined using a riding model with C_{aromatic}-H = 0.93Å, C_{methylene}-H = 0.97Å or O-H = 0.85Å. U(H) was set to 1.2 U_{eq}(C) or 1.5 U_{eq}(O).

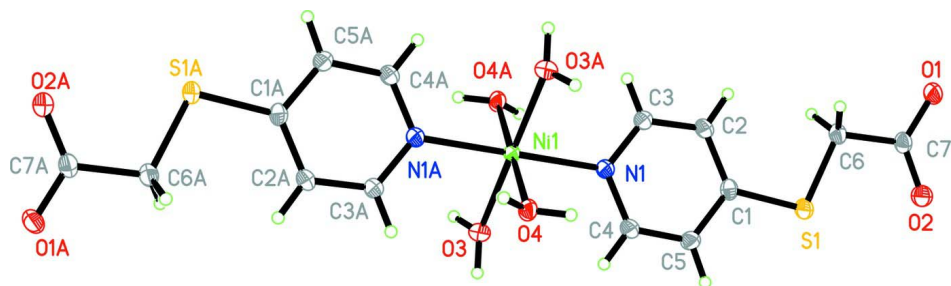


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (A) $-x, -y, -z$.]

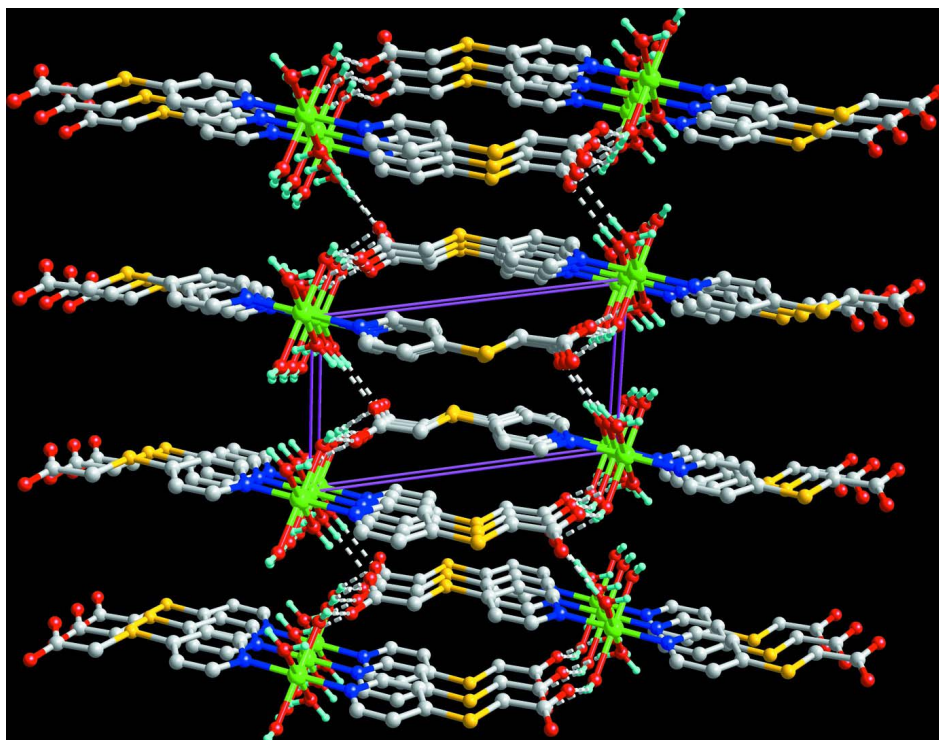


Figure 2

Crystal packing of the title compound, showing O—H...O hydrogen bonds as dashed lines. Only H atoms involved in hydrogen bonds have been included.

Tetraaquabis[2-(4-pyridylsulfanyl)acetato- κ N]nickel(II)

Crystal data

$[\text{Ni}(\text{C}_7\text{H}_6\text{NO}_2\text{S})_2(\text{H}_2\text{O})_4]$

$M_r = 467.15$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 6.3577$ (4) Å

$b = 7.0330$ (5) Å

$c = 11.7624$ (8) Å

$\alpha = 92.713$ (1)°

$\beta = 103.440$ (1)°

$\gamma = 115.120$ (1)°

$V = 456.75$ (5) Å³

$Z = 1$

$F(000) = 242$

$D_x = 1.698$ Mg m⁻³

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

Cell parameters from 2208 reflections

$\theta = 3.2\text{--}27.8^\circ$

$\mu = 1.34$ mm⁻¹

$T = 296$ K $0.22 \times 0.20 \times 0.14$ mm
 Block, blue

Data collection

Bruker APEXII CCD area-detector diffractometer Radiation source: fine-focus sealed tube Graphite monochromator φ and ω scans Absorption correction: multi-scan (SADABS; Bruker, 2001) $T_{\min} = 0.758$, $T_{\max} = 0.835$	2358 measured reflections 1610 independent reflections 1525 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.008$ $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 1.8^\circ$ $h = -7 \rightarrow 7$ $k = -5 \rightarrow 8$ $l = -13 \rightarrow 13$
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Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.022$ $wR(F^2) = 0.061$ $S = 1.05$ 1610 reflections 124 parameters 0 restraints Primary atom site location: structure-invariant direct methods	Secondary atom site location: difference Fourier map Hydrogen site location: inferred from neighbouring sites H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.2312P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.28 \text{ e } \text{\AA}^{-3}$
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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	0.0000	0.0000	0.0000	0.02365 (11)
S1	0.72786 (9)	0.33945 (8)	0.54727 (4)	0.03489 (14)
O1	0.5787 (3)	0.2690 (3)	0.84929 (12)	0.0430 (4)
O2	0.9194 (3)	0.4387 (2)	0.79704 (12)	0.0423 (4)
O3	0.2259 (2)	0.2716 (2)	-0.05684 (11)	0.0347 (3)
H3A	0.1377	0.3317	-0.0833	0.052*
H3B	0.3544	0.3065	-0.0783	0.052*
O4	0.1770 (2)	-0.1742 (2)	-0.03636 (11)	0.0302 (3)
H4A	0.2585	-0.1876	0.0284	0.045*
H4B	0.0891	-0.2861	-0.0878	0.045*
N1	0.2203 (3)	0.1150 (2)	0.17292 (13)	0.0275 (3)
C1	0.5198 (3)	0.2521 (3)	0.40628 (15)	0.0268 (4)
C2	0.2691 (3)	0.1584 (3)	0.38241 (16)	0.0307 (4)
H2	0.1970	0.1401	0.4440	0.037*

C3	0.1292 (3)	0.0933 (3)	0.26627 (16)	0.0315 (4)
H3	-0.0381	0.0307	0.2517	0.038*
C4	0.4625 (3)	0.2085 (3)	0.19676 (16)	0.0313 (4)
H4	0.5298	0.2269	0.1334	0.038*
C5	0.6160 (3)	0.2784 (3)	0.30962 (16)	0.0312 (4)
H5	0.7827	0.3427	0.3216	0.037*
C6	0.5391 (3)	0.2753 (3)	0.64667 (15)	0.0301 (4)
H6A	0.4421	0.3520	0.6348	0.036*
H6B	0.4304	0.1240	0.6296	0.036*
C7	0.6951 (3)	0.3354 (3)	0.77521 (16)	0.0306 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02087 (17)	0.03278 (19)	0.01705 (17)	0.01169 (14)	0.00582 (12)	0.00240 (12)
S1	0.0305 (3)	0.0442 (3)	0.0201 (2)	0.0099 (2)	0.00367 (18)	0.0011 (2)
O1	0.0413 (8)	0.0722 (10)	0.0279 (7)	0.0330 (8)	0.0153 (6)	0.0169 (7)
O2	0.0346 (8)	0.0547 (9)	0.0266 (7)	0.0118 (7)	0.0058 (6)	0.0018 (6)
O3	0.0292 (7)	0.0405 (7)	0.0353 (7)	0.0138 (6)	0.0139 (6)	0.0101 (6)
O4	0.0297 (6)	0.0415 (7)	0.0210 (6)	0.0189 (6)	0.0049 (5)	0.0013 (5)
N1	0.0264 (8)	0.0353 (8)	0.0218 (7)	0.0146 (7)	0.0075 (6)	0.0035 (6)
C1	0.0321 (9)	0.0247 (8)	0.0219 (9)	0.0131 (7)	0.0044 (7)	0.0015 (7)
C2	0.0327 (10)	0.0376 (10)	0.0221 (9)	0.0146 (8)	0.0104 (7)	0.0042 (8)
C3	0.0272 (9)	0.0424 (11)	0.0244 (9)	0.0147 (8)	0.0081 (8)	0.0039 (8)
C4	0.0304 (10)	0.0406 (10)	0.0228 (9)	0.0146 (8)	0.0103 (7)	0.0028 (8)
C5	0.0254 (9)	0.0374 (10)	0.0270 (9)	0.0115 (8)	0.0066 (7)	0.0011 (8)
C6	0.0337 (10)	0.0320 (9)	0.0237 (9)	0.0143 (8)	0.0070 (8)	0.0055 (7)
C7	0.0361 (10)	0.0358 (10)	0.0233 (9)	0.0198 (9)	0.0073 (8)	0.0041 (7)

Geometric parameters (Å, °)

Ni1—O4	2.0727 (12)	N1—C3	1.342 (2)
Ni1—O4 ⁱ	2.0727 (12)	N1—C4	1.344 (2)
Ni1—N1	2.0762 (15)	C1—C2	1.392 (3)
Ni1—N1 ⁱ	2.0762 (15)	C1—C5	1.396 (3)
Ni1—O3 ⁱ	2.0967 (13)	C2—C3	1.377 (3)
Ni1—O3	2.0967 (13)	C2—H2	0.9300
S1—C1	1.7524 (18)	C3—H3	0.9300
S1—C6	1.8035 (19)	C4—C5	1.373 (3)
O1—C7	1.253 (2)	C4—H4	0.9300
O2—C7	1.249 (2)	C5—H5	0.9300
O3—H3A	0.8501	C6—C7	1.528 (3)
O3—H3B	0.8503	C6—H6A	0.9700
O4—H4A	0.8501	C6—H6B	0.9700
O4—H4B	0.8501		
O4—Ni1—O4 ⁱ	179.999 (1)	C2—C1—C5	117.45 (16)
O4—Ni1—N1	92.68 (5)	C2—C1—S1	125.97 (14)

O4 ⁱ —Ni1—N1	87.32 (5)	C5—C1—S1	116.57 (14)
O4—Ni1—N1 ⁱ	87.32 (5)	C3—C2—C1	119.08 (17)
O4 ⁱ —Ni1—N1 ⁱ	92.68 (5)	C3—C2—H2	120.5
N1—Ni1—N1 ⁱ	180.0	C1—C2—H2	120.5
O4—Ni1—O3 ⁱ	86.23 (5)	N1—C3—C2	123.81 (17)
O4 ⁱ —Ni1—O3 ⁱ	93.77 (5)	N1—C3—H3	118.1
N1—Ni1—O3 ⁱ	89.32 (5)	C2—C3—H3	118.1
N1 ⁱ —Ni1—O3 ⁱ	90.69 (5)	N1—C4—C5	123.50 (17)
O4—Ni1—O3	93.77 (5)	N1—C4—H4	118.3
O4 ⁱ —Ni1—O3	86.23 (5)	C5—C4—H4	118.3
N1—Ni1—O3	90.69 (5)	C4—C5—C1	119.45 (17)
N1 ⁱ —Ni1—O3	89.31 (5)	C4—C5—H5	120.3
O3 ⁱ —Ni1—O3	180.0	C1—C5—H5	120.3
C1—S1—C6	103.65 (9)	C7—C6—S1	110.25 (13)
Ni1—O3—H3A	105.2	C7—C6—H6A	109.6
Ni1—O3—H3B	134.1	S1—C6—H6A	109.6
H3A—O3—H3B	117.1	C7—C6—H6B	109.6
Ni1—O4—H4A	109.3	S1—C6—H6B	109.6
Ni1—O4—H4B	114.5	H6A—C6—H6B	108.1
H4A—O4—H4B	117.0	O2—C7—O1	126.41 (18)
C3—N1—C4	116.70 (16)	O2—C7—C6	119.17 (17)
C3—N1—Ni1	122.04 (12)	O1—C7—C6	114.39 (17)
C4—N1—Ni1	121.22 (12)		
O4—Ni1—N1—C3	-125.81 (15)	C4—N1—C3—C2	-0.8 (3)
O4 ⁱ —Ni1—N1—C3	54.19 (15)	Ni1—N1—C3—C2	176.86 (15)
O3 ⁱ —Ni1—N1—C3	-39.62 (15)	C1—C2—C3—N1	-0.1 (3)
O3—Ni1—N1—C3	140.38 (15)	C3—N1—C4—C5	0.8 (3)
O4—Ni1—N1—C4	51.79 (15)	Ni1—N1—C4—C5	-176.94 (14)
O4 ⁱ —Ni1—N1—C4	-128.21 (15)	N1—C4—C5—C1	0.2 (3)
O3 ⁱ —Ni1—N1—C4	137.98 (15)	C2—C1—C5—C4	-1.2 (3)
O3—Ni1—N1—C4	-42.02 (15)	S1—C1—C5—C4	178.42 (14)
C6—S1—C1—C2	0.69 (19)	C1—S1—C6—C7	178.07 (12)
C6—S1—C1—C5	-178.92 (14)	S1—C6—C7—O2	8.2 (2)
C5—C1—C2—C3	1.2 (3)	S1—C6—C7—O1	-170.33 (14)
S1—C1—C2—C3	-178.44 (14)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A \cdots O2 ⁱⁱ	0.85	2.13	2.951 (2)	161
O3—H3B \cdots O1 ⁱⁱⁱ	0.85	1.92	2.7265 (18)	158
O4—H4A \cdots O1 ^{iv}	0.85	1.83	2.6697 (18)	168
O4—H4B \cdots O2 ^v	0.85	2.01	2.855 (2)	172

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