

# Crystal structure of aqua-*trans*-bis(dimethyl sulfoxide- $\kappa$ O)(pyridine-2,6-dicarboxylato- $\kappa^3$ O<sup>2</sup>,N,O<sup>6</sup>)nickel(II)

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Received 29 March 2017

Accepted 22 April 2017

Edited by M. Weil, Vienna University of Technology, Austria

**Keywords:** crystal structure; pyridine-2,6-dicarboxylic acid dianion; dimethyl sulfoxide; nickel(II); hydrogen bonding.

**CCDC reference:** 1545417

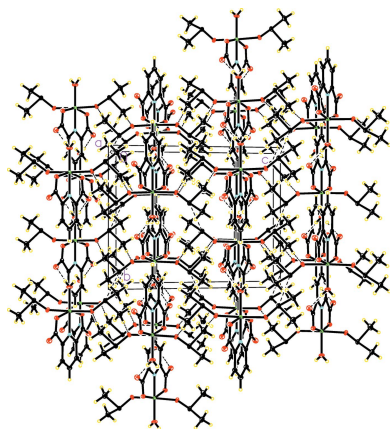
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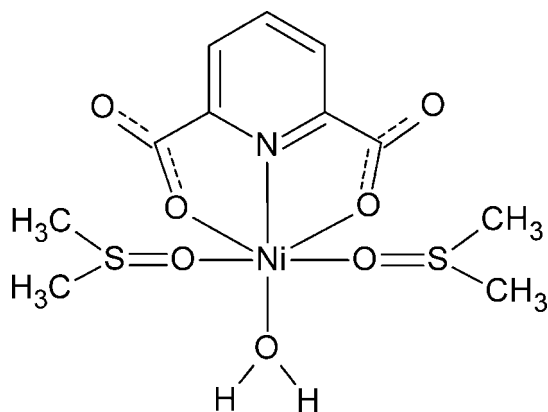
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In the title complex, [Ni(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)(C<sub>2</sub>H<sub>6</sub>OS)<sub>2</sub>(H<sub>2</sub>O)], the Ni<sup>II</sup> cation is situated on a twofold rotation axis and exhibits a distorted octahedral NO<sub>5</sub> coordination environment defined by a tridentate pyridine-2,6-dicarboxylic acid dianion (dpa<sup>2-</sup>), two dimethyl sulfoxide (DMSO) molecules, and a water molecule. In the crystal, the complex molecules are linked by O—H...O and C—H...O hydrogen bonds into a three-dimensional network whereby DMSO molecules from neighboring complexes overlap to form layers parallel to (001), alternating with layers of Ni<sup>II</sup>–dpa<sup>2-</sup> moieties. The title complex is isotopic with its cobalt(II) analogue.

## 1. Chemical context

Crystal engineering plays an important role in the research of molecule-based functional materials by providing an effective approach towards the rational design and preparation of compounds with special structural features (Robin & Fromm, 2006; Cook *et al.*, 2013; Wang *et al.*, 2013). The crystallization of coordination polymers involves both the formation of a local coordination geometry and the propagation and packing of extended polymeric structures in the three-dimensional space. The competition among various types of intermolecular interactions plays a critical role in this process and is strongly influenced by synthetic conditions such as the choice of solvent, temperature, and the molecular features of the starting materials (Li & Du, 2011; Du *et al.*, 2013). Although much has been learned about how the synthetic conditions affect intermolecular interactions and the final crystal structures, the targeted synthesis of a coordination polymer with a particular crystal structure is still a challenge. We recently reported an Ni<sup>II</sup>-containing one-dimensional coordination polymer based on the tridentate 2,6-pyridine dicarboxylic acid dianion (dpa<sup>2-</sup>) and bridging pyrazine molecules that was prepared by using DMSO as the solvent (Liu *et al.*, 2016). The one-dimensional polymeric structure exhibits  $\pi$ – $\pi$  interactions that were not previously observed when water was used as the solvent under the same preparation conditions. In order to explore the bridging effect of substituted pyrazine, we have repeated this preparation using 2-chloropyrazine to replace pyrazine under the same synthetic conditions. We report herein the synthesis and crystal structure of the resulting title compound for which incorporation of 2-chloropyrazine was not observed.





## 2. Structural commentary

The title complex crystallizes in the monoclinic space group  $C2/c$  with half of the molecule in the asymmetric unit, the other half being generated by twofold rotation symmetry. The tridentate 2,6-pyridine dicarboxylic acid dianion coordinates to the  $\text{Ni}^{\text{II}}$  cation in a meridional fashion *via* the pyridine nitrogen atom and two carboxylate oxygen atoms (Fig. 1). The reactant 2-chloropyrazine is not found in the structure of the title complex. Instead, the  $\text{Ni}^{\text{II}}$  cation is further coordinated by two *trans*-positioned DMSO molecules and a water molecule

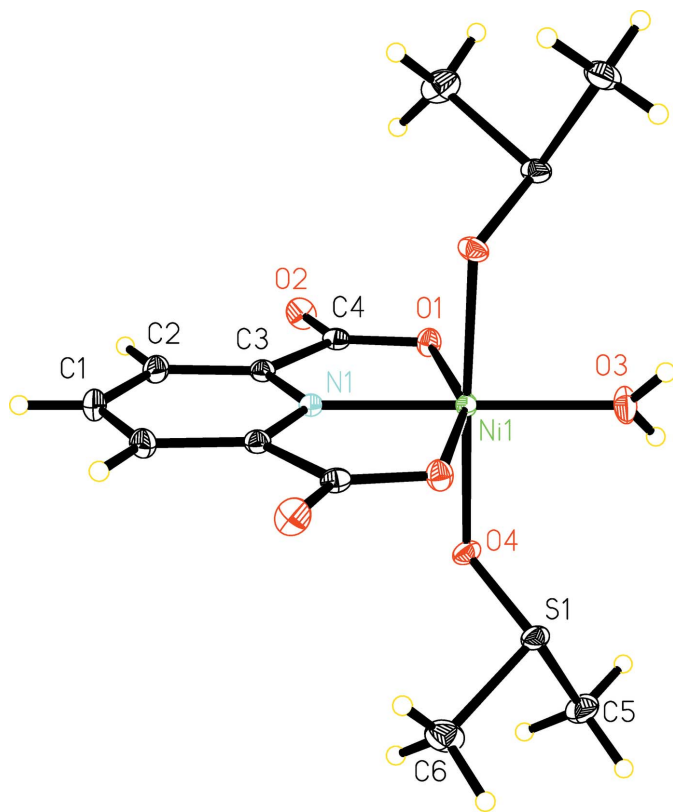


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Unlabeled atoms are related by the symmetry transformation  $-x, y, \frac{1}{2} - z$ .

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3-H3\cdots O2^i$	0.790 (17)	1.867 (17)	2.6555 (10)	176.3 (18)
$C5-H5B\cdots O2^i$	0.98	2.58	3.3650 (14)	137
$C6-H6A\cdots O2^{ii}$	0.98	2.62	3.3504 (13)	132
$C6-H6B\cdots O4^{iii}$	0.98	2.38	3.3302 (14)	162

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

through their oxygen atoms. Water molecules may have been produced as a result of the reaction between 2,6-pyridine dicarboxylic acid and nickel carbonate. The two  $\text{Ni}-\text{O}_{1\text{dpa}}$  bonds have the same length 2.1130 (7)  $\text{\AA}$  and the two  $\text{Ni}-\text{O}_{4\text{DMSO}}$  bonds have the same length [2.0934 (7)  $\text{\AA}$ ]. The  $\text{Ni}-\text{N1}$  bond length is 1.9613 (12)  $\text{\AA}$  and the  $\text{Ni}-\text{O}_{3\text{water}}$  bond length is 2.0040 (11)  $\text{\AA}$ , both being significantly shorter than the other four bonds, resulting in a distorted octahedral  $\text{NO}_5$  coordination environment of the  $\text{Ni}^{\text{II}}$  cation. These bond lengths are very similar to those observed in the pyrazine-bridged one-dimensional structure reported previously (Liu *et al.*, 2016).

## 3. Supramolecular features

In the crystal, the mononuclear complexes are linked *via* an extensive network of  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds where the hydrogen-bond donors are the  $\text{C}-\text{H}$  groups of DMSO molecules and the  $\text{O}-\text{H}$  groups of the coordinating

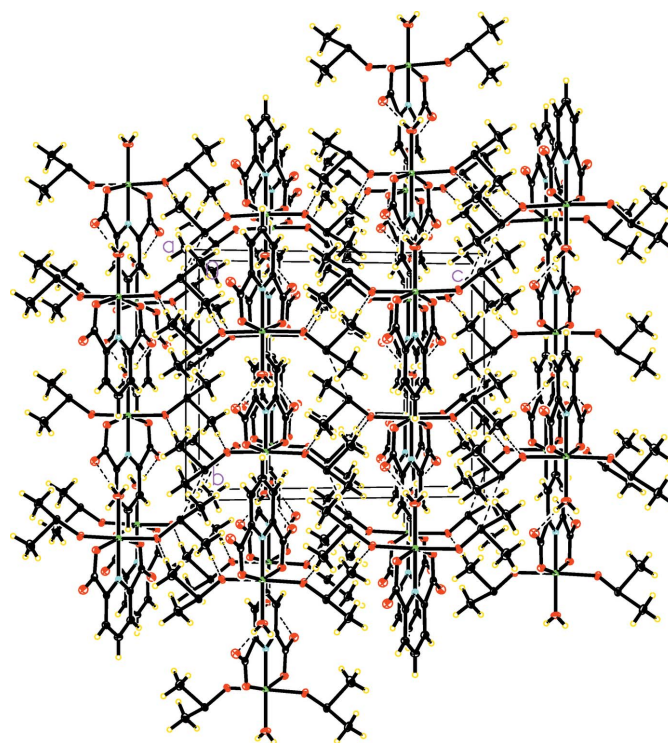


Figure 2

The crystal packing of the title compound, showing hydrogen bonds as dashed lines.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Ni(C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> )(C <sub>2</sub> H <sub>6</sub> OS) <sub>2</sub> (H <sub>2</sub> O)]
<i>M<sub>r</sub></i>	398.08
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.8767 (5), 11.4597 (5), 14.3166 (7)
$\beta$ (°)	104.4577 (7)
<i>V</i> (Å <sup>3</sup> )	1569.09 (13)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.53
Crystal size (mm)	0.46 × 0.17 × 0.11
Data collection	
Diffractometer	Bruker APEXII DUO CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2014)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.678, 0.910
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	18746, 1936, 1907
<i>R<sub>int</sub></i>	0.011
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.666
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.016, 0.043, 1.06
No. of reflections	1936
No. of parameters	108
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.46, -0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *XP* in *SHELXTL-Plus* (Sheldrick, 2008) and *pubCIF* (Westrip, 2010).

water molecules and the hydrogen-bond acceptors are the non-coordinating O2 atoms of the 2,6-pyridine dicarboxylic acid dianion and the O4 atoms of the DMSO molecules (Table 1, Fig. 2). In the crystal packing, layers of the Ni<sup>II</sup>-dpa<sup>2-</sup> complexes alternating with layers of DMSO molecules are formed parallel to (001) (Fig. 2).

#### 4. Database survey

A search of the Cambridge Structural Database (Groom *et al.*, 2016) returned eight structures that are related to the title complex. These structures incorporate some or all of the ligands in the title complex and include mononuclear and binuclear complexes, as well as coordination polymers. One of the structures is *mer*-aqua-bis(dimethylsulfoxide-*O*)(pyridine-2,6-dicarboxylato-*N,O,O'*)cobalt(II) (Felloni *et al.*, 2010) that crystallizes isotypically with the title complex. Therefore bond lengths and bond angles surrounding the Co<sup>II</sup> are very similar to those in the title complex. Another mononuclear complex is aquachlorido(dimethyl sulfoxide-*O*)(pyridine-2,6-dicarboxylato-*N,O,O'*)iron(III) (Rafizadeh *et al.*, 2006). In the crystal, this complex also forms alternating layers parallel to (001) due to the interdigitation of DMSO molecules. Other complexes in the search results involve either coordinating or non-coordinating DMSO molecules and one or more 2,6-pyridine dicarboxylate dianions coordinating to a metal ion.

#### 5. Synthesis and crystallization

Anhydrous NiCO<sub>3</sub> (0.33 mmol, 39.56 mg), 2,6-pyridine dicarboxylic acid (0.33 mmol, 55.71 mg), and 2-chloropyridazine (0.50 mmol, 57.26 mg) were mixed in 10 ml dimethyl sulfoxide under stirring for 30 minutes. The resulting mixture was placed in a stainless steel autoclave. The autoclave was then sealed and heated to 373 K for 24 h and cooled to room temperature at a rate of 0.1 K per minute. The resulting green crystals were collected by filtration (yield 30.0%). Selected IR bands (KBr, cm<sup>-1</sup>): 3134.9 (O–H), 1613.1 (C=O), 1365.8 (C–O), 999.6 (S=O).

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The title complex is located on a twofold rotation axis, thus half of it occupies the asymmetric unit. The coordinating water molecule lies on the symmetry axis which requires one hydrogen atom to be located while the other is related by symmetry. This hydrogen atom was obtained from a difference-Fourier map and was refined freely. The other hydrogen atoms were positioned geometrically (C–H = 0.93/1.00 Å) and allowed to ride with *U*<sub>iso</sub>(H) = 1.2/1.5*U*<sub>eq</sub>(C). Methyl hydrogen atoms were allowed to rotate but not to tip.

#### Acknowledgements

CL wishes to acknowledge the financial support of the Vice President Research Fund, Grenfell Campus, Memorial University of Newfoundland. KAA wishes to acknowledge the National Science Foundation and the University of Florida for funding of the purchase of the X-ray equipment.

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## supporting information

*Acta Cryst.* (2017). E73, 777-779 [https://doi.org/10.1107/S2056989017006090]

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### Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Aqua-*trans*-bis(dimethyl sulfoxide- $\kappa$ O)(pyridine-2,6-dicarboxylato- $\kappa^3$ O<sup>2</sup>,N,O<sup>6</sup>)nickel(II)

#### Crystal data

[Ni(C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub>)(C<sub>2</sub>H<sub>6</sub>OS)<sub>2</sub>(H<sub>2</sub>O)]

$M_r = 398.08$

Monoclinic, *C2/c*

$a = 9.8767$  (5) Å

$b = 11.4597$  (5) Å

$c = 14.3166$  (7) Å

$\beta = 104.4577$  (7)°

$V = 1569.09$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 824$

$D_x = 1.685$  Mg m<sup>-3</sup>

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

Cell parameters from 9953 reflections

$\theta = 2.0$ – $28.0$ °

$\mu = 1.53$  mm<sup>-1</sup>

$T = 100$  K

Block, green

$0.46 \times 0.17 \times 0.11$  mm

#### Data collection

Bruker APEXII DUO CCD  
diffractometer

Radiation source: fine-focus sealed tube

$\phi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2014)

$T_{\min} = 0.678$ ,  $T_{\max} = 0.910$

18746 measured reflections

1936 independent reflections

1907 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.011$

$\theta_{\max} = 28.3$ °,  $\theta_{\min} = 2.8$ °

$h = -13 \rightarrow 13$

$k = -15 \rightarrow 15$

$l = -19 \rightarrow 19$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.016$

$wR(F^2) = 0.043$

$S = 1.06$

1936 reflections

108 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 1.5829P]$

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

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

$\Delta\rho_{\max} = 0.46$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.24$  e Å<sup>-3</sup>

*Special details*

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

**Refinement.** All H atoms were positioned geometrically ( $C-H = 0.93/1.00 \text{ \AA}$ ) and allowed to ride with  $U_{iso}(H) = 1.2/1.5U_{eq}(C)$ . Methyl ones were allowed to rotate around the corresponding  $C-C$ .

The Ni complex is located on a 2-fold rotational axis of symmetry thus half of it occupies the asymmetric unit. The coordinated water molecule lies on the symmetry axis which requires one proton to be located while the other is related by the symmetry. The water proton was obtained from a Difference Fourier map and refined freely.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}^*/U_{eq}$
Ni1	0.0000	0.32387 (2)	0.2500	0.00867 (6)
S1	0.08818 (3)	0.40008 (2)	0.46249 (2)	0.01346 (7)
O1	0.16898 (7)	0.28806 (6)	0.18844 (5)	0.01235 (14)
O2	0.29613 (8)	0.13796 (7)	0.15626 (6)	0.01647 (15)
O3	0.0000	0.49874 (10)	0.2500	0.0186 (2)
H3	0.0626 (17)	0.5376 (15)	0.2789 (12)	0.033 (4)*
O4	0.13764 (8)	0.32772 (6)	0.38736 (5)	0.01257 (14)
N1	0.0000	0.15272 (10)	0.2500	0.0095 (2)
C1	0.0000	-0.08533 (12)	0.2500	0.0151 (3)
H1A	0.0000	-0.1682	0.2500	0.018*
C2	0.10055 (10)	-0.02463 (9)	0.21553 (7)	0.01328 (18)
H2A	0.1691	-0.0650	0.1919	0.016*
C3	0.09697 (10)	0.09684 (8)	0.21703 (7)	0.01026 (17)
C4	0.19693 (10)	0.18040 (9)	0.18444 (7)	0.01114 (18)
C5	0.24415 (12)	0.46192 (10)	0.53687 (8)	0.0204 (2)
H5A	0.2213	0.5058	0.5897	0.031*
H5B	0.2865	0.5145	0.4982	0.031*
H5C	0.3102	0.3994	0.5636	0.031*
C6	0.04879 (12)	0.29765 (11)	0.54609 (8)	0.0213 (2)
H6A	0.0278	0.3397	0.6004	0.032*
H6B	0.1294	0.2463	0.5699	0.032*
H6C	-0.0324	0.2508	0.5138	0.032*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.00926 (9)	0.00735 (9)	0.00927 (9)	0.000	0.00206 (6)	0.000
S1	0.01554 (12)	0.01458 (12)	0.00942 (12)	0.00621 (9)	0.00155 (9)	-0.00145 (8)
O1	0.0122 (3)	0.0109 (3)	0.0147 (3)	-0.0010 (3)	0.0048 (3)	-0.0004 (3)
O2	0.0138 (3)	0.0181 (4)	0.0196 (4)	0.0040 (3)	0.0081 (3)	0.0023 (3)
O3	0.0178 (5)	0.0085 (5)	0.0237 (6)	0.000	-0.0057 (4)	0.000
O4	0.0131 (3)	0.0143 (3)	0.0099 (3)	0.0037 (3)	0.0021 (3)	-0.0030 (2)
N1	0.0102 (5)	0.0094 (5)	0.0083 (5)	0.000	0.0011 (4)	0.000
C1	0.0189 (7)	0.0091 (6)	0.0170 (7)	0.000	0.0038 (5)	0.000
C2	0.0143 (4)	0.0116 (4)	0.0136 (4)	0.0025 (4)	0.0028 (3)	-0.0008 (3)

C3	0.0103 (4)	0.0114 (4)	0.0085 (4)	0.0005 (3)	0.0012 (3)	0.0001 (3)
C4	0.0099 (4)	0.0140 (5)	0.0088 (4)	-0.0002 (3)	0.0009 (3)	0.0006 (3)
C5	0.0233 (5)	0.0204 (5)	0.0137 (5)	0.0012 (4)	-0.0022 (4)	-0.0044 (4)
C6	0.0227 (5)	0.0259 (6)	0.0180 (5)	0.0069 (4)	0.0105 (4)	0.0038 (4)

*Geometric parameters (Å, °)*

Ni1—N1	1.9613 (12)	N1—C3 <sup>i</sup>	1.3327 (11)
Ni1—O3	2.0040 (11)	C1—C2 <sup>i</sup>	1.3994 (12)
Ni1—O4	2.0934 (7)	C1—C2	1.3995 (12)
Ni1—O4 <sup>i</sup>	2.0934 (7)	C1—H1A	0.9500
Ni1—O1 <sup>i</sup>	2.1130 (7)	C2—C3	1.3927 (14)
Ni1—O1	2.1130 (7)	C2—H2A	0.9500
S1—O4	1.5316 (7)	C3—C4	1.5296 (13)
S1—C5	1.7860 (11)	C5—H5A	0.9800
S1—C6	1.7872 (12)	C5—H5B	0.9800
O1—C4	1.2686 (12)	C5—H5C	0.9800
O2—C4	1.2476 (12)	C6—H6A	0.9800
O3—H3	0.790 (17)	C6—H6B	0.9800
N1—C3	1.3326 (11)	C6—H6C	0.9800
N1—Ni1—O3	180.0	C2 <sup>i</sup> —C1—C2	120.38 (13)
N1—Ni1—O4	91.21 (2)	C2 <sup>i</sup> —C1—H1A	119.8
O3—Ni1—O4	88.79 (2)	C2—C1—H1A	119.8
N1—Ni1—O4 <sup>i</sup>	91.21 (2)	C3—C2—C1	117.93 (10)
O3—Ni1—O4 <sup>i</sup>	88.79 (2)	C3—C2—H2A	121.0
O4—Ni1—O4 <sup>i</sup>	177.58 (4)	C1—C2—H2A	121.0
N1—Ni1—O1 <sup>i</sup>	78.80 (2)	N1—C3—C2	120.60 (9)
O3—Ni1—O1 <sup>i</sup>	101.20 (2)	N1—C3—C4	112.51 (9)
O4—Ni1—O1 <sup>i</sup>	90.43 (3)	C2—C3—C4	126.88 (9)
O4 <sup>i</sup> —Ni1—O1 <sup>i</sup>	90.04 (3)	O2—C4—O1	126.23 (9)
N1—Ni1—O1	78.80 (2)	O2—C4—C3	118.26 (9)
O3—Ni1—O1	101.20 (2)	O1—C4—C3	115.51 (9)
O4—Ni1—O1	90.04 (3)	S1—C5—H5A	109.5
O4 <sup>i</sup> —Ni1—O1	90.43 (3)	S1—C5—H5B	109.5
O1 <sup>i</sup> —Ni1—O1	157.60 (4)	H5A—C5—H5B	109.5
O4—S1—C5	104.76 (5)	S1—C5—H5C	109.5
O4—S1—C6	106.00 (5)	H5A—C5—H5C	109.5
C5—S1—C6	99.26 (6)	H5B—C5—H5C	109.5
C4—O1—Ni1	114.28 (6)	S1—C6—H6A	109.5
Ni1—O3—H3	124.3 (13)	S1—C6—H6B	109.5
S1—O4—Ni1	115.15 (4)	H6A—C6—H6B	109.5
C3—N1—C3 <sup>i</sup>	122.56 (12)	S1—C6—H6C	109.5
C3—N1—Ni1	118.72 (6)	H6A—C6—H6C	109.5
C3 <sup>i</sup> —N1—Ni1	118.72 (6)	H6B—C6—H6C	109.5

Symmetry code: (i)  $-x, y, -z+1/2$ .

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3···O2 <sup>ii</sup>	0.790 (17)	1.867 (17)	2.6555 (10)	176.3 (18)
C5—H5B···O2 <sup>ii</sup>	0.98	2.58	3.3650 (14)	137
C6—H6A···O2 <sup>iii</sup>	0.98	2.62	3.3504 (13)	132
C6—H6B···O4 <sup>iv</sup>	0.98	2.38	3.3302 (14)	162

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