



# Crystal structure of *catena*-poly[[*(dimethyl sulfoxide-κO)(pyridine-2,6-dicarboxylato-κ<sup>3</sup>O,N,O')*nickel(II)]-*μ*-pyrazine-κ<sup>2</sup>N:N']

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**Keywords:** crystal structure; one-dimensional Ni<sup>II</sup> coordination polymer; pyridine-2,6-dicarboxylic acid; pyrazine;  $\pi$ - $\pi$  stacking; C—H... $\pi$  interaction; hydrogen bonding.

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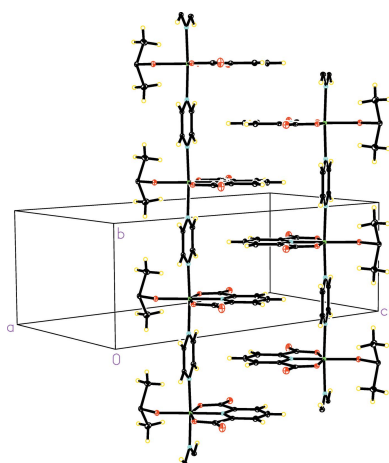
**Supporting information:** this article has supporting information at journals.iucr.org/e

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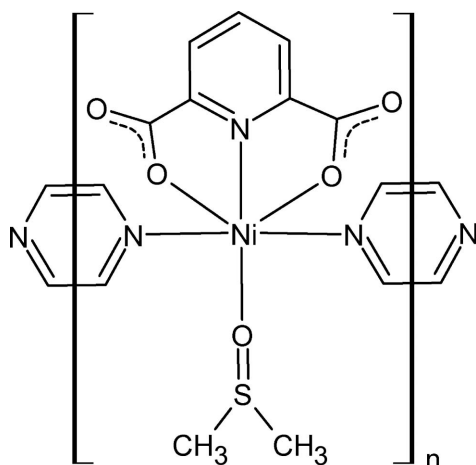
The title coordination polymer, [Ni(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)(C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>6</sub>OS)]<sub>n</sub>, consists of [010] chains composed of Ni<sup>II</sup> ions linked by bis-monodentate-bridging pyrazine molecules. Each of the two crystallographically distinct Ni<sup>II</sup> ions is located on a mirror plane and is additionally coordinated by a dimethyl sulfoxide (DMSO) ligand through the oxygen atom and by a tridentate 2,6-pyridine-dicarboxylic acid dianion through one of each of the carboxylate oxygen atoms and the pyridine nitrogen atom, leading to a distorted octahedral coordination environment. The title structure exhibits an interesting complementarity between coordinative bonding and  $\pi$ - $\pi$  stacking where the Ni—Ni distance of 7.0296 (4) Å across bridging pyrazine ligands allows the pyridine moieties on two adjacent chains to interdigitate at halfway of the Ni—Ni distance, resulting in  $\pi$ - $\pi$  stacking between pyridine moieties with a centroid-to-plane distance of 3.5148 (2) Å. The double-chain thus formed also exhibits C—H... $\pi$  interactions between pyridine C—H groups on one chain and pyrazine molecules on the other chain. As a result, the interior of the double-chain structure is dominated by  $\pi$ - $\pi$  stacking and C—H... $\pi$  interactions, while the space between the double-chains is occupied by a C—H...O hydrogen-bonding network involving DMSO ligands and carboxylate groups located on the exterior of the double-chains. This separation of dissimilar interactions in the interior and exterior of the double-chains further stabilizes the crystal structure.

## 1. Chemical context

In general,  $\pi$ - $\pi$  interactions are considered important mechanisms for molecular recognition and may function as structure-directing factors in the design and preparation of coordination polymers. However,  $\pi$ - $\pi$  interactions are not always observed in the final coordination polymer simply by using starting materials containing aromatic moieties. During our investigation of the rational design and synthesis of coordination polymers, we have previously reported a dinuclear Ni<sup>II</sup> complex obtained by reacting 2,6-pyridine dicarboxylic acid and nickel carbonate using water as solvent (Liu *et al.*, 2011). The intermolecular force between the dinuclear complexes is dominated by hydrogen bonding. We recently repeated the synthesis of this compound using dimethyl sulfoxide (DMSO) as solvent under solvothermal conditions and obtained the title compound. We herein report its synthesis and structure which exhibits both  $\pi$ - $\pi$  stacking and C—H... $\pi$  interactions involving two different aromatic molecules, *viz.* pyridine and pyrazine.

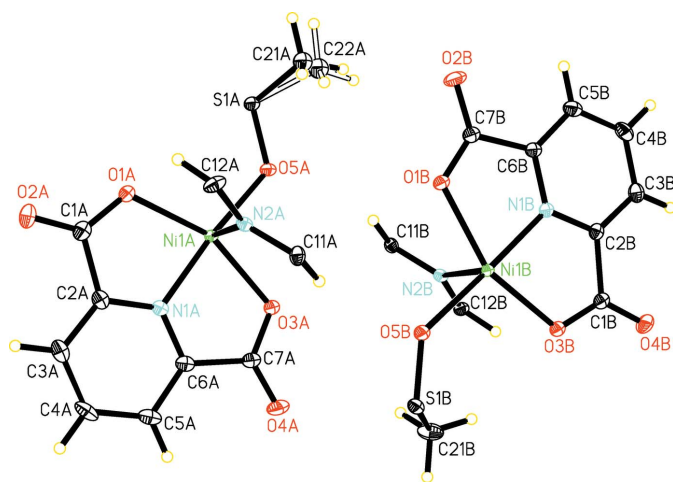


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## 2. Structural commentary

The asymmetric unit contains two half  $\text{Ni}^{\text{II}}$  complexes with mirror symmetry (denoted *A* and *B*), where each of the  $\text{Ni}^{\text{II}}$  atoms is coordinated by a 2,6-pyridine-dicarboxylic acid dianion, a pyrazine molecule, and a DMSO ligand (Fig. 1). The tridentate 2,6-pyridine-dicarboxylate anion coordinates to  $\text{Ni}^{\text{II}}$  in a meridional fashion *via* the pyridine nitrogen atom and two carboxylate oxygen atoms; the DMSO molecule coordinates to  $\text{Ni}^{\text{II}}$  through its oxygen atom and the pyrazine ligands through their N atoms. Thus each  $\text{Ni}^{\text{II}}$  is in an  $\text{N}_3\text{O}_3$  coordination environment. Individual  $\text{Ni}^{\text{II}}$  complexes are linked along the axial positions by bis-monodentate bridging pyrazine molecules to form a linear chain parallel to [010] and propagated through mirror symmetry elements passing through the  $\text{Ni}^{\text{II}}$  atoms, the anions, and bisecting both the pyrazine ligands and the DMSO molecules along the  $\text{S}=\text{O}$  bonds. In the chains, the Ni–Ni distance across bridging pyrazine is 7.0296 (4) Å, *i.e.* the length of the *b* axis.



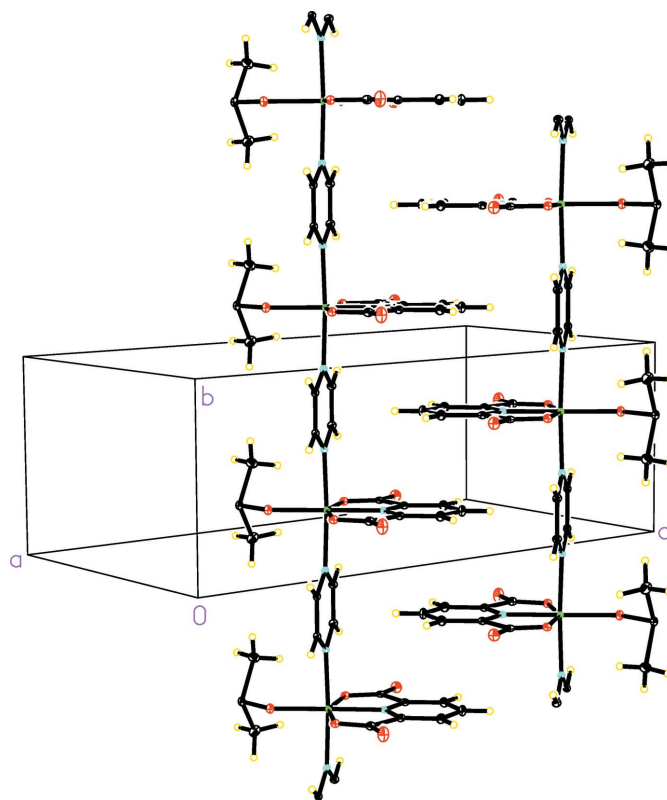
**Figure 1**

A view of the asymmetric unit of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. All disordered components are shown.

## 3. Supramolecular features

In the crystal, two  $\text{Ni}^{\text{II}}$  chains form a double-chain structure *via*  $\pi$ – $\pi$  stacking between their pyridine moieties (Fig. 2). Two stacked pyridine rings in the double-chain structure are separated by a centroid-to-plane distance of 3.5148 (2) Å. This separation distance is half of the Ni–Ni distance, indicating that the formation of  $\pi$ – $\pi$  stacking in the double-chain structure may have been promoted by coordinative bonding distances across bridging pyrazine ligands. A search in the literature returned only a few other examples of coordination polymers exhibiting similar structural features (Zheng *et al.*, 2000; Nawrot *et al.*, 2015). Within the double-chain, two  $\pi$ – $\pi$  stacked pyridine moieties are also parallel-shifted by 1.50422 (8) Å, consistent with values obtained from computational studies (Huber *et al.*, 2014). Although  $\pi$ – $\pi$  stacking interactions are prevalent among systems composed of discrete aromatic molecules, it is not always observed in coordination polymers synthesized from aromatic starting materials. The title structure thus provides an interesting example for further investigation on the interplay between coordinative bonding and  $\pi$ – $\pi$  stacking as a potential strategy for incorporating  $\pi$ – $\pi$  stacking in the design and synthesis of coordination polymers.

Accompanying the  $\pi$ – $\pi$  stacking interaction described above, there is also a T-shaped  $\text{C}–\text{H}\cdots\pi$  interaction between the pyridine C4–H4 group and the bridging pyrazine molecule (Tiekink & Zuckerman-Schpector, 2012), contributing additional stability to the double-chain structure. The



**Figure 2**

A view of the double-chain structure of the title compound running parallel to [010].

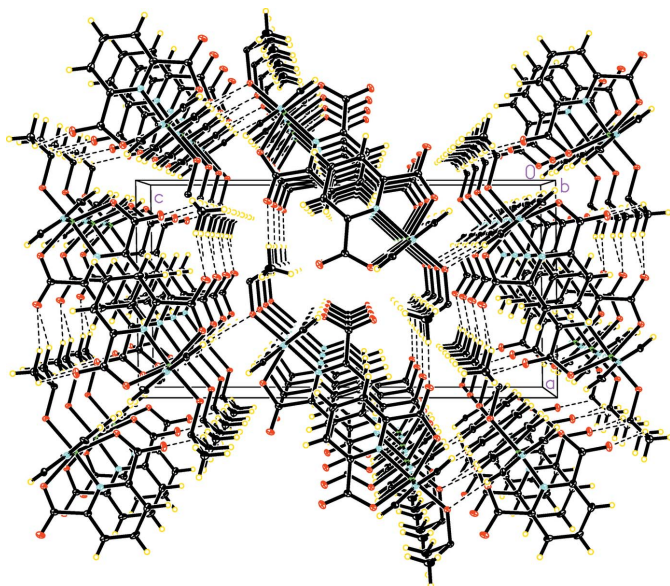
**Table 1**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11B—H11B $\cdots$ O1B	0.95	2.50	3.0442 (13)	117
C11B—H11B $\cdots$ O5A	0.95	2.66	3.2871 (18)	124
C11A—H11A $\cdots$ O3A	0.95	2.42	3.0252 (14)	121
C11A—H11A $\cdots$ O5B	0.95	2.43	3.0462 (17)	122
C12B—H12B $\cdots$ O3B	0.95	2.37	2.9978 (13)	123
C12A—H12A $\cdots$ O1A	0.95	2.45	3.0221 (14)	119
C12A—H12A $\cdots$ O1A <sup>i</sup>	0.95	2.61	3.2230 (18)	122
C21B—H21A $\cdots$ O2B <sup>ii</sup>	0.98	2.49	3.3321 (19)	144
C21A—H21D $\cdots$ O4A <sup>iii</sup>	0.98	2.47	3.277 (4)	139
C21A—H21E $\cdots$ O2A <sup>i</sup>	0.98	2.27	2.959 (9)	126
C21A—H21E $\cdots$ O2A <sup>iv</sup>	0.98	2.50	3.246 (9)	132
C22A—H22A $\cdots$ O4A <sup>iii</sup>	0.98	2.57	3.377 (4)	140

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

concurrency of both parallel  $\pi$ - $\pi$  stacking and T-shaped C—H $\cdots$  $\pi$  interactions in crystal structures is known in the literature, but primarily among systems of discrete aromatic molecules (Tiekink & Zuckerman-Schpector, 2012). We are aware of only one other example of a coordination polymer exhibiting this feature (Felloni *et al.*, 2010). In the C—H $\cdots$  $\pi$  configuration of the title structure, the centroid-to-centroid distance between pyridine and pyrazine is 4.8389 (2) Å, which includes the pyridine C4—H4 bond length of 0.95 Å and a distance of 2.53310 (12) Å from the pyridine H4 atom to the centroid of the pyrazine ring. Although the title structure is a coordination polymer, these distances are in good agreement with results of computational studies performed on discrete aromatic molecules (Mishra & Sathyamurthy, 2005; Hohenstein & Sherrill, 2009; Huber *et al.*, 2014).

In contrast to the  $\pi$ - $\pi$  stacking and C—H $\cdots$  $\pi$  interactions forming the interior of the double-chains, the exterior of the double-chains is mainly occupied by polar DMSO molecules



**Figure 3**  
Crystal packing of the title compound, showing hydrogen-bonding interactions 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>4</sub> H <sub>4</sub> N <sub>2</sub> )(C <sub>2</sub> H <sub>6</sub> OS)]
$M_r$	382.03
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	100
$a, b, c$ (Å)	10.5631 (7), 7.0296 (4), 20.3710 (13)
$\beta$ (°)	90.6447 (11)
$V$ (Å <sup>3</sup> )	1512.54 (16)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.45
Crystal size (mm)	0.37 × 0.15 × 0.05
Data collection	
Diffractometer	Bruker APEXII DUO CCD
Absorption correction	Analytical based on measured indexed crystal faces; <i>XPREP</i> (Bruker, 2014)
$T_{min}, T_{max}$	0.730, 0.965
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	56634, 3756, 3549
$R_{int}$	0.026
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.020, 0.055, 1.07
No. of reflections	3756
No. of parameters	256
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.43, -0.31

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *XP* (Bruker, 2014) and *publCIF* (Westrip, 2010).

and carboxylate groups. As a result, a network of C—H $\cdots$ O hydrogen bonds exists in the space between the double-chains (Fig. 3), linking double-chains to form a three dimensional network. Double-chains of molecule *B* are linked by C21B—H21A $\cdots$ O2B<sup>ii</sup> to form sheets parallel to (001). Double-chains of molecule *A* are linked by C21A—H21E $\cdots$ O2A<sup>i/iv</sup>, C12A—H12A $\cdots$ O1A<sup>i</sup>, C21A—H21D $\cdots$ O4A<sup>iii</sup>, and C22A—H22D $\cdots$ O4A<sup>iii</sup> hydrogen bonds to form sheets extending along the same direction. Thus, alternating sheets with an *ABAB* pattern can be observed. Two neighboring sheets are connected *via* C11A—H11A $\cdots$ O5B and C11B—H11B $\cdots$ O5A hydrogen bonds to form a three-dimensional network. The hydrogen-bond lengths and angles are summarized in Table 1.

In summary, a separation of dissimilar interactions can be observed between the non-covalent lipophilic  $\pi$ - $\pi$  stacking and C—H $\cdots$  $\pi$  interactions in the interior of the double-chains and the polar hydrogen bonds in the exterior of the double-chains, further stabilizing the crystal structure.

#### 4. Synthesis and crystallization

Anhydrous NiCO<sub>3</sub> (0.67 mmol, 79.15 mg), 2,6-pyridine dicarboxylic acid (0.67 mmol, 111.41 mg), and pyrazine (1.00 mmol, 80.09 mg) were dissolved in 10 ml dimethyl sulfoxide. The resulting mixture was transferred into a stainless steel autoclave which was heated at 373 K for 24 h and cooled to room temperature at a cooling rate of 0.1 K per minute.

Green needle-like crystals of the title compound were collected by filtration. Selected IR bands (KBr,  $\text{cm}^{-1}$ ): 1640.6 (C=O), 1367.9 (C–O), 950.9 (S=O), 480.6 (bridging pyrazine).

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically (C–H = 0.93/1.00 Å) and allowed to ride with  $U_{\text{iso}}(\text{H}) = 1.2/1.5U_{\text{eq}}(\text{C})$ . Methyl H atoms were allowed to rotate around the corresponding C–C bond. There are two disordered parts, both of which are in molecule *A*. The carboxylate atom O2*A* sits just outside of the mirror plane (occupancy 0.5) and one of the DMSO methyl groups is disordered over two positions in a ratio of 0.54 (2):0.46 (2). The C atom of this group was refined with isotropic displacement parameters.

## Acknowledgements

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## supporting information

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## Crystal structure of *catena*-poly[[*(dimethyl sulfoxide-κO)*(pyridine-2,6-dicarboxylato- $\kappa^3O,N,O'$ )nickel(II)]- $\mu$ -pyrazine- $\kappa^2N:N'$ ]

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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* (Bruker, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### *catena*-Poly[[*(dimethyl sulfoxide-κO)*(pyridine-2,6-dicarboxylato- $\kappa^3O,N,O'$ )nickel(II)]- $\mu$ -pyrazine- $\kappa^2N:N'$ ]

#### Crystal data

[Ni(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)(C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>6</sub>OS)]

$M_r = 382.03$

Monoclinic,  $P2_1/m$

$a = 10.5631$  (7) Å

$b = 7.0296$  (4) Å

$c = 20.3710$  (13) Å

$\beta = 90.6447$  (11)°

$V = 1512.54$  (16) Å<sup>3</sup>

$Z = 4$

$F(000) = 784$

$D_x = 1.678$  Mg m<sup>-3</sup>

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

Cell parameters from 9922 reflections

$\theta = 2.0$ – $28.0$ °

$\mu = 1.45$  mm<sup>-1</sup>

$T = 100$  K

Needle, green

$0.37 \times 0.15 \times 0.05$  mm

#### Data collection

Bruker APEXII DUO CCD

diffractometer

Radiation source: fine-focus sealed tube

$\phi$  and  $\omega$  scans

Absorption correction: analytical

based on measured indexed crystal faces;

*XPREP* (Bruker, 2014)

$T_{\min} = 0.730$ ,  $T_{\max} = 0.965$

56634 measured reflections

3756 independent reflections

3549 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 1.0$ °

$h = -13 \rightarrow 13$

$k = -9 \rightarrow 9$

$l = -26 \rightarrow 26$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.055$

$S = 1.07$

3756 reflections

256 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

$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 1.0377P]$

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

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

$\Delta\rho_{\max} = 0.43$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.31$  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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1A	0.19703 (2)	0.7500	0.11633 (2)	0.00831 (6)	
Ni1B	0.27491 (2)	0.2500	0.36354 (2)	0.00767 (6)	
S1B	0.54518 (4)	0.2500	0.28209 (2)	0.01208 (9)	
S1A	-0.08847 (4)	0.7500	0.16036 (2)	0.01425 (10)	
O1B	0.10195 (12)	0.2500	0.30920 (6)	0.0113 (2)	
O1A	0.11570 (12)	0.7500	0.02161 (6)	0.0132 (3)	
O2B	-0.10902 (13)	0.2500	0.32425 (7)	0.0233 (3)	
O2A	0.17059 (18)	0.7205 (10)	-0.08458 (9)	0.0253 (15)	0.5
O3B	0.39180 (12)	0.2500	0.44805 (6)	0.0111 (2)	
O3A	0.34526 (12)	0.7500	0.18730 (6)	0.0120 (3)	
O4A	0.55732 (14)	0.7500	0.19630 (8)	0.0263 (4)	
O4B	0.38006 (13)	0.2500	0.55830 (7)	0.0182 (3)	
O5B	0.40109 (12)	0.2500	0.28824 (6)	0.0121 (3)	
O5A	0.05126 (12)	0.7500	0.18052 (6)	0.0133 (3)	
N1B	0.14803 (14)	0.2500	0.43438 (7)	0.0096 (3)	
N1A	0.34951 (14)	0.7500	0.06078 (8)	0.0115 (3)	
N2B	0.27691 (9)	0.55104 (16)	0.36044 (5)	0.0099 (2)	
N2A	0.18744 (9)	0.44903 (16)	0.11862 (5)	0.0106 (2)	
C1A	0.19489 (19)	0.7500	-0.02550 (10)	0.0191 (4)	
C1B	0.33304 (17)	0.2500	0.50290 (9)	0.0116 (3)	
C2B	0.18885 (17)	0.2500	0.49647 (9)	0.0114 (3)	
C2A	0.33379 (18)	0.7500	-0.00413 (9)	0.0145 (4)	
C3B	0.10332 (18)	0.2500	0.54760 (9)	0.0156 (4)	
H3BA	0.1317	0.2500	0.5920	0.019*	
C3A	0.4378 (2)	0.7500	-0.04533 (10)	0.0186 (4)	
H3AA	0.4274	0.7500	-0.0917	0.022*	
C4B	-0.02551 (19)	0.2500	0.53191 (10)	0.0178 (4)	
H4BA	-0.0861	0.2500	0.5660	0.021*	
C4A	0.55810 (19)	0.7500	-0.01630 (11)	0.0206 (4)	
H4AA	0.6310	0.7500	-0.0432	0.025*	
C5B	-0.06604 (18)	0.2500	0.46662 (10)	0.0157 (4)	
H5BA	-0.1537	0.2500	0.4556	0.019*	
C5A	0.57227 (18)	0.7500	0.05169 (11)	0.0183 (4)	
H5AA	0.6540	0.7500	0.0717	0.022*	
C6B	0.02532 (17)	0.2500	0.41808 (9)	0.0114 (3)	
C6A	0.46371 (17)	0.7500	0.08948 (9)	0.0135 (4)	
C7B	0.00208 (17)	0.2500	0.34383 (9)	0.0127 (3)	
C7A	0.45721 (17)	0.7500	0.16448 (9)	0.0141 (4)	
C11B	0.21031 (11)	0.65089 (18)	0.31586 (6)	0.0107 (2)	

H11B	0.1620	0.5849	0.2835	0.013*	
C11A	0.25161 (12)	0.34864 (19)	0.16410 (6)	0.0129 (2)	
H11A	0.2982	0.4144	0.1972	0.015*	
C12B	0.34543 (11)	0.65142 (18)	0.40430 (6)	0.0115 (2)	
H12B	0.3951	0.5856	0.4361	0.014*	
C12A	0.11868 (12)	0.34903 (19)	0.07512 (7)	0.0157 (3)	
H12A	0.0686	0.4149	0.0435	0.019*	
C21B	0.60288 (13)	0.4416 (2)	0.33098 (7)	0.0209 (3)	
H21A	0.6954	0.4467	0.3284	0.031*	
H21B	0.5669	0.5614	0.3148	0.031*	
H21C	0.5781	0.4221	0.3767	0.031*	
C21A	-0.1608 (4)	0.5556 (5)	0.1942 (4)	0.0179 (12)*	0.46 (2)
H21D	-0.2505	0.5546	0.1814	0.027*	0.46 (2)
H21E	-0.1201	0.4393	0.1783	0.027*	0.46 (2)
H21F	-0.1530	0.5616	0.2421	0.027*	0.46 (2)
C22A	-0.1502 (4)	0.5609 (5)	0.2133 (4)	0.0196 (10)*	0.54 (2)
H22A	-0.2413	0.5458	0.2051	0.029*	0.54 (2)
H22B	-0.1068	0.4412	0.2036	0.029*	0.54 (2)
H22C	-0.1356	0.5949	0.2594	0.029*	0.54 (2)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1A	0.00710 (11)	0.00803 (11)	0.00981 (11)	0.000	-0.00020 (8)	0.000
Ni1B	0.00712 (11)	0.00684 (11)	0.00903 (11)	0.000	-0.00055 (8)	0.000
S1B	0.0106 (2)	0.0141 (2)	0.0116 (2)	0.000	0.00228 (15)	0.000
S1A	0.0095 (2)	0.0211 (2)	0.0121 (2)	0.000	0.00003 (15)	0.000
O1B	0.0099 (6)	0.0118 (6)	0.0122 (6)	0.000	-0.0019 (5)	0.000
O1A	0.0128 (6)	0.0142 (6)	0.0125 (6)	0.000	-0.0013 (5)	0.000
O2B	0.0098 (6)	0.0403 (9)	0.0198 (7)	0.000	-0.0042 (5)	0.000
O2A	0.0269 (9)	0.038 (5)	0.0115 (7)	-0.0012 (11)	-0.0023 (6)	-0.0008 (10)
O3B	0.0108 (6)	0.0104 (6)	0.0120 (6)	0.000	-0.0013 (5)	0.000
O3A	0.0105 (6)	0.0127 (6)	0.0129 (6)	0.000	-0.0007 (5)	0.000
O4A	0.0115 (7)	0.0433 (10)	0.0239 (8)	0.000	-0.0050 (6)	0.000
O4B	0.0181 (7)	0.0235 (7)	0.0129 (6)	0.000	-0.0057 (5)	0.000
O5B	0.0101 (6)	0.0158 (6)	0.0104 (6)	0.000	-0.0005 (5)	0.000
O5A	0.0079 (6)	0.0187 (7)	0.0133 (6)	0.000	0.0002 (5)	0.000
N1B	0.0100 (7)	0.0073 (7)	0.0116 (7)	0.000	-0.0001 (5)	0.000
N1A	0.0115 (7)	0.0093 (7)	0.0135 (7)	0.000	0.0014 (6)	0.000
N2B	0.0089 (5)	0.0089 (5)	0.0118 (5)	0.0000 (4)	0.0020 (4)	-0.0003 (4)
N2A	0.0091 (5)	0.0101 (5)	0.0128 (5)	0.0004 (4)	0.0015 (4)	-0.0001 (4)
C1A	0.0179 (9)	0.0238 (10)	0.0156 (9)	0.000	-0.0018 (7)	0.000
C1B	0.0131 (8)	0.0067 (8)	0.0151 (9)	0.000	-0.0019 (7)	0.000
C2B	0.0137 (8)	0.0083 (8)	0.0120 (8)	0.000	-0.0008 (7)	0.000
C2A	0.0166 (9)	0.0123 (8)	0.0145 (9)	0.000	0.0023 (7)	0.000
C3B	0.0195 (9)	0.0161 (9)	0.0113 (8)	0.000	0.0016 (7)	0.000
C3A	0.0233 (10)	0.0171 (9)	0.0155 (9)	0.000	0.0057 (8)	0.000
C4B	0.0169 (9)	0.0194 (10)	0.0172 (9)	0.000	0.0080 (7)	0.000

C4A	0.0169 (9)	0.0183 (10)	0.0268 (11)	0.000	0.0123 (8)	0.000
C5B	0.0116 (8)	0.0160 (9)	0.0196 (9)	0.000	0.0018 (7)	0.000
C5A	0.0113 (9)	0.0159 (9)	0.0278 (11)	0.000	0.0037 (8)	0.000
C6B	0.0102 (8)	0.0096 (8)	0.0144 (8)	0.000	-0.0002 (7)	0.000
C6A	0.0118 (8)	0.0098 (8)	0.0190 (9)	0.000	0.0010 (7)	0.000
C7B	0.0119 (8)	0.0114 (8)	0.0149 (9)	0.000	-0.0015 (7)	0.000
C7A	0.0111 (8)	0.0123 (9)	0.0188 (9)	0.000	-0.0011 (7)	0.000
C11B	0.0119 (5)	0.0108 (6)	0.0094 (5)	-0.0005 (5)	0.0014 (4)	-0.0009 (5)
C11A	0.0169 (6)	0.0122 (6)	0.0095 (5)	-0.0007 (5)	0.0000 (4)	-0.0009 (5)
C12B	0.0095 (5)	0.0106 (6)	0.0144 (6)	0.0004 (5)	-0.0009 (4)	0.0007 (5)
C12A	0.0121 (6)	0.0122 (7)	0.0226 (7)	0.0006 (5)	-0.0067 (5)	0.0009 (5)
C21B	0.0136 (6)	0.0194 (7)	0.0295 (7)	-0.0040 (5)	0.0011 (5)	-0.0080 (6)

*Geometric parameters (Å, °)*

Ni1A—N1A	1.9788 (15)	C1A—O2A <sup>i</sup>	1.245 (3)
Ni1A—O5A	2.0313 (13)	C1A—C2A	1.526 (3)
Ni1A—O1A	2.1032 (13)	C1B—C2B	1.527 (2)
Ni1A—N2A <sup>i</sup>	2.1186 (11)	C2B—C3B	1.386 (3)
Ni1A—N2A	2.1186 (11)	C2A—C3A	1.390 (3)
Ni1A—O3A	2.1191 (13)	C3B—C4B	1.394 (3)
Ni1B—N1B	1.9804 (15)	C3B—H3BA	0.9500
Ni1B—O5B	2.0434 (13)	C3A—C4A	1.395 (3)
Ni1B—O3B	2.1073 (13)	C3A—H3AA	0.9500
Ni1B—N2B	2.1172 (11)	C4B—C5B	1.393 (3)
Ni1B—N2B <sup>ii</sup>	2.1173 (11)	C4B—H4BA	0.9500
Ni1B—O1B	2.1255 (12)	C4A—C5A	1.391 (3)
S1B—O5B	1.5286 (13)	C4A—H4AA	0.9500
S1B—C21B <sup>ii</sup>	1.7786 (14)	C5B—C6B	1.389 (3)
S1B—C21B	1.7786 (14)	C5B—H5BA	0.9500
S1A—O5A	1.5276 (13)	C5A—C6A	1.388 (3)
S1A—C21A	1.713 (4)	C5A—H5AA	0.9500
S1A—C21A <sup>i</sup>	1.713 (4)	C6B—C7B	1.530 (3)
S1A—C22A	1.836 (4)	C6A—C7A	1.530 (3)
S1A—C22A <sup>i</sup>	1.836 (4)	C11B—C11B <sup>i</sup>	1.393 (3)
O1B—C7B	1.276 (2)	C11B—H11B	0.9500
O1A—C1A	1.280 (2)	C11A—C11A <sup>ii</sup>	1.387 (3)
O2B—C7B	1.235 (2)	C11A—H11A	0.9500
O2A—O2A <sup>i</sup>	0.414 (15)	C12B—C12B <sup>i</sup>	1.386 (3)
O2A—C1A	1.245 (3)	C12B—H12B	0.9500
O3B—C1B	1.284 (2)	C12A—C12A <sup>ii</sup>	1.392 (3)
O3A—C7A	1.276 (2)	C12A—H12A	0.9500
O4A—C7A	1.234 (2)	C21B—H21A	0.9800
O4B—C1B	1.228 (2)	C21B—H21B	0.9800
N1B—C2B	1.332 (2)	C21B—H21C	0.9800
N1B—C6B	1.334 (2)	C21A—H21D	0.9800
N1A—C2A	1.331 (2)	C21A—H21E	0.9800
N1A—C6A	1.335 (2)	C21A—H21F	0.9800



N2B—C11B	1.3408 (16)	C22A—H22A	0.9800
N2B—C12B	1.3438 (16)	C22A—H22B	0.9800
N2A—C12A	1.3388 (17)	C22A—H22C	0.9800
N2A—C11A	1.3423 (16)		
N1A—Ni1A—O5A	174.81 (6)	N1B—C2B—C3B	120.45 (17)
N1A—Ni1A—O1A	78.58 (6)	N1B—C2B—C1B	113.16 (15)
O5A—Ni1A—O1A	106.61 (5)	C3B—C2B—C1B	126.39 (17)
N1A—Ni1A—N2A <sup>i</sup>	92.98 (3)	N1A—C2A—C3A	120.61 (18)
O5A—Ni1A—N2A <sup>i</sup>	87.08 (3)	N1A—C2A—C1A	113.10 (16)
O1A—Ni1A—N2A <sup>i</sup>	90.06 (3)	C3A—C2A—C1A	126.30 (18)
N1A—Ni1A—N2A	92.98 (3)	C2B—C3B—C4B	118.06 (17)
O5A—Ni1A—N2A	87.08 (3)	C2B—C3B—H3BA	121.0
O1A—Ni1A—N2A	90.06 (3)	C4B—C3B—H3BA	121.0
N2A <sup>i</sup> —Ni1A—N2A	173.95 (6)	C2A—C3A—C4A	117.80 (18)
N1A—Ni1A—O3A	77.89 (6)	C2A—C3A—H3AA	121.1
O5A—Ni1A—O3A	96.92 (5)	C4A—C3A—H3AA	121.1
O1A—Ni1A—O3A	156.48 (5)	C5B—C4B—C3B	120.50 (17)
N2A <sup>i</sup> —Ni1A—O3A	91.15 (3)	C5B—C4B—H4BA	119.8
N2A—Ni1A—O3A	91.15 (3)	C3B—C4B—H4BA	119.8
N1B—Ni1B—O5B	178.13 (6)	C5A—C4A—C3A	120.61 (18)
N1B—Ni1B—O3B	78.45 (6)	C5A—C4A—H4AA	119.7
O5B—Ni1B—O3B	103.42 (5)	C3A—C4A—H4AA	119.7
N1B—Ni1B—N2B	91.65 (3)	C6B—C5B—C4B	118.12 (17)
O5B—Ni1B—N2B	88.32 (3)	C6B—C5B—H5BA	120.9
O3B—Ni1B—N2B	91.06 (3)	C4B—C5B—H5BA	120.9
N1B—Ni1B—N2B <sup>ii</sup>	91.65 (3)	C6A—C5A—C4A	118.14 (18)
O5B—Ni1B—N2B <sup>ii</sup>	88.32 (3)	C6A—C5A—H5AA	120.9
O3B—Ni1B—N2B <sup>ii</sup>	91.06 (3)	C4A—C5A—H5AA	120.9
N2B—Ni1B—N2B <sup>ii</sup>	176.38 (6)	N1B—C6B—C5B	120.23 (17)
N1B—Ni1B—O1B	78.15 (6)	N1B—C6B—C7B	112.99 (15)
O5B—Ni1B—O1B	99.97 (5)	C5B—C6B—C7B	126.78 (16)
O3B—Ni1B—O1B	156.61 (5)	N1A—C6A—C5A	120.34 (18)
N2B—Ni1B—O1B	89.61 (3)	N1A—C6A—C7A	112.76 (16)
N2B <sup>ii</sup> —Ni1B—O1B	89.61 (3)	C5A—C6A—C7A	126.89 (17)
O5B—S1B—C21B <sup>ii</sup>	106.82 (6)	O2B—C7B—O1B	127.59 (18)
O5B—S1B—C21B	106.82 (6)	O2B—C7B—C6B	117.43 (16)
C21B <sup>ii</sup> —S1B—C21B	98.42 (11)	O1B—C7B—C6B	114.98 (15)
O5A—S1A—C21A	109.0 (2)	O4A—C7A—O3A	126.94 (18)
O5A—S1A—C21A <sup>i</sup>	109.0 (2)	O4A—C7A—C6A	118.47 (17)
C21A—S1A—C21A <sup>i</sup>	105.8 (3)	O3A—C7A—C6A	114.59 (16)
O5A—S1A—C22A	101.00 (18)	N2B—C11B—C11B <sup>i</sup>	121.57 (7)
O5A—S1A—C22A <sup>i</sup>	101.00 (18)	N2B—C11B—H11B	119.2
C22A—S1A—C22A <sup>i</sup>	92.8 (3)	C11B <sup>i</sup> —C11B—H11B	119.2
C7B—O1B—Ni1B	115.04 (11)	N2A—C11A—C11A <sup>ii</sup>	121.72 (7)
C1A—O1A—Ni1A	115.10 (12)	N2A—C11A—H11A	119.1
O2A <sup>i</sup> —O2A—C1A	80.4 (3)	C11A <sup>ii</sup> —C11A—H11A	119.1
C1B—O3B—Ni1B	115.23 (11)	N2B—C12B—C12B <sup>i</sup>	121.67 (7)

C7A—O3A—Ni1A	115.61 (12)	N2B—C12B—H12B	119.2
S1B—O5B—Ni1B	136.06 (8)	C12B <sup>i</sup> —C12B—H12B	119.2
S1A—O5A—Ni1A	124.34 (8)	N2A—C12A—C12A <sup>ii</sup>	121.68 (7)
C2B—N1B—C6B	122.64 (16)	N2A—C12A—H12A	119.2
C2B—N1B—Ni1B	118.53 (12)	C12A <sup>ii</sup> —C12A—H12A	119.2
C6B—N1B—Ni1B	118.83 (12)	S1B—C21B—H21A	109.5
C2A—N1A—C6A	122.50 (16)	S1B—C21B—H21B	109.5
C2A—N1A—Ni1A	118.36 (13)	H21A—C21B—H21B	109.5
C6A—N1A—Ni1A	119.14 (13)	S1B—C21B—H21C	109.5
C11B—N2B—C12B	116.75 (11)	H21A—C21B—H21C	109.5
C11B—N2B—Ni1B	122.56 (8)	H21B—C21B—H21C	109.5
C12B—N2B—Ni1B	120.69 (8)	S1A—C21A—H21D	109.5
C12A—N2A—C11A	116.53 (12)	S1A—C21A—H21E	109.5
C12A—N2A—Ni1A	122.38 (9)	H21D—C21A—H21E	109.5
C11A—N2A—Ni1A	121.09 (9)	S1A—C21A—H21F	109.5
O2A—C1A—O2A <sup>i</sup>	19.2 (7)	H21D—C21A—H21F	109.5
O2A—C1A—O1A	126.5 (2)	H21E—C21A—H21F	109.5
O2A <sup>i</sup> —C1A—O1A	126.5 (2)	S1A—C22A—H22A	109.5
O2A—C1A—C2A	117.57 (19)	S1A—C22A—H22B	109.5
O2A <sup>i</sup> —C1A—C2A	117.57 (19)	H22A—C22A—H22B	109.5
O1A—C1A—C2A	114.86 (17)	S1A—C22A—H22C	109.5
O4B—C1B—O3B	127.24 (17)	H22A—C22A—H22C	109.5
O4B—C1B—C2B	118.13 (16)	H22B—C22A—H22C	109.5
O3B—C1B—C2B	114.63 (15)		

Symmetry codes: (i)  $x, -y+3/2, z$ ; (ii)  $x, -y+1/2, z$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11B—H11B $\cdots$ O1B	0.95	2.50	3.0442 (13)	117
C11B—H11B $\cdots$ O5A	0.95	2.66	3.2871 (18)	124
C11A—H11A $\cdots$ O3A	0.95	2.42	3.0252 (14)	121
C11A—H11A $\cdots$ O5B	0.95	2.43	3.0462 (17)	122
C12B—H12B $\cdots$ O3B	0.95	2.37	2.9978 (13)	123
C12A—H12A $\cdots$ O1A	0.95	2.45	3.0221 (14)	119
C12A—H12A $\cdots$ O1A <sup>iii</sup>	0.95	2.61	3.2230 (18)	122
C21B—H21A $\cdots$ O2B <sup>iv</sup>	0.98	2.49	3.3321 (19)	144
C21A—H21D $\cdots$ O4A <sup>v</sup>	0.98	2.47	3.277 (4)	139
C21A—H21E $\cdots$ O2A <sup>iii</sup>	0.98	2.27	2.959 (9)	126
C21A—H21E $\cdots$ O2A <sup>vi</sup>	0.98	2.50	3.246 (9)	132
C22A—H22A $\cdots$ O4A <sup>v</sup>	0.98	2.57	3.377 (4)	140

Symmetry codes: (iii)  $-x, -y+1, -z$ ; (iv)  $x+1, -y+1/2, z$ ; (v)  $x-1, -y+3/2, z$ ; (vi)  $-x, y-1/2, -z$ .