

Crystal structure of bis(4-benzoylpyridine- κN)bis-(methanol- κO)bis(thiocyanato- κN)nickel(II) methanol monosolvate

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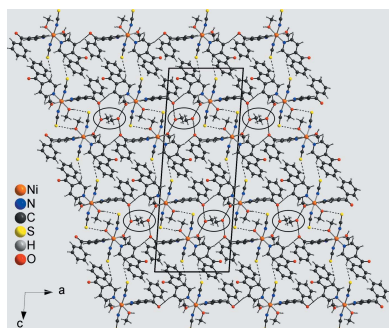
Supporting information: this article has supporting information at journals.iucr.org/e

The asymmetric unit of the title compound, $[\text{Ni}(\text{NCS})_2(\text{C}_{12}\text{H}_9\text{NO})_2(\text{CH}_3\text{OH})_2] \cdot \text{CH}_3\text{OH}$, comprises one Ni^{II} cation, two thiocyanate anions, two 4-benzoylpyridine coligands, two coordinating, as well as one non-coordinating methanol molecule. The Ni^{II} cation is coordinated by two terminally N-bonded thiocyanate anions, the N atoms of two 4-benzoylpyridine coligands and the O atoms of two methanol ligands within a slightly distorted octahedron. Individual complexes are linked by intermolecular $\text{O}-\text{H} \cdots \text{S}$ hydrogen bonding into chains parallel to $[010]$ that are further connected into layers parallel to $(10\bar{1})$ by $\text{C}-\text{H} \cdots \text{S}$ hydrogen bonds. Additional $\text{C}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions lead to the formation of a three-dimensional network that limits channels extending parallel to $[010]$ in which the non-coordinating methanol molecules are located. They are hydrogen-bonded to the coordinating methanol molecules. X-ray powder diffraction revealed that the compound could not be prepared as a pure phase.

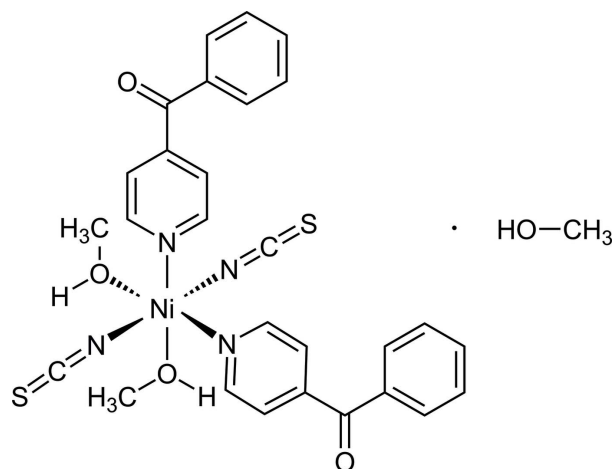
1. Chemical context

Thiocyanate anions are versatile ligands that can coordinate to metal cations in different manners, leading to a variety of structural set-ups. The most common coordination modes are the N-terminal and the μ -1,3-bridging coordination, but, as an example, there are also reports of a μ -1,1-coordination (Prananto *et al.*, 2017; Buckingham, 1994; Palion-Gazda *et al.*, 2017; Mautner *et al.*, 2016, 2017; Mahmoudi *et al.*, 2017; Hamdani *et al.*, 2018; Wöhlert *et al.*, 2014*a,b*). With respect to paramagnetic transition metal cations, the μ -1,3-bridging mode is of special importance because it can mediate the magnetic exchange (Gonzalez *et al.*, 2012; Wöhlert *et al.*, 2013*a,b*; Palion-Gazda *et al.*, 2015; Guillet *et al.*, 2016; Mekuimemba *et al.*, 2018). In this context, an increasing number of compounds with different magnetic properties are being reported (Wöhlert *et al.*, 2014*a,b*; Werner *et al.*, 2015; Suckert *et al.*, 2017*a*; Mautner *et al.*, 2018). In the majority of cases, the metal cations are linked by thiocyanate anions into chains, but there are also examples where layer formation is observed (Suckert *et al.*, 2016; Wellm *et al.*, 2018; Neumann *et al.*, 2018*a*).

Unfortunately, for most paramagnetic transition metal cations, the bridging modes are energetically less favored and thus, compounds with a terminal coordination are usually obtained. Nevertheless, we have found an alternative approach to overcome this problem by transformation of the latter compounds through thermal annealing into the desired compounds that have bridging anions. For the alternative



synthesis of such coordination polymers with bridging anionic ligands, a precursor consisting of a discrete complex can be used in which the metal cations are coordinated by two terminal N-bonded thiocyanate anions and four co-ligands that, in our cases, consist of pyridine derivatives. Upon controlled heating, two of the four co-ligands can be removed. Frequently, this treatment yields the desired compounds with bridging coordination as intermediates, which can easily be investigated by thermogravimetry. In some cases, no discrete decomposition steps are observed because all co-ligands are removed in one step. Under these circumstances, alternatives are required that are based on precursor complexes comprising only two of the pyridine derivatives as ligands and two coordinating and volatile molecules such as water or methanol. The ligand molecules are emitted in a discrete step (also observable in a thermogravimetric measurement), which directly produces the desired compounds in quantitative yield. It is also noted that this approach often leads to the formation of polymorphs or isomers that are different from the compounds obtained from solution (Werner *et al.*, 2015; Jochim *et al.*, 2018).



In this context we have reported two isotopic compounds with chain-structures that have the general composition $M(\text{NCS})_2(4\text{-benzoylpyridine})_2$ where $M = \text{Co}, \text{Ni}$ (Rams *et al.*, 2017; Jochim *et al.*, 2018). Here the metal cations are linked into linear chains with a *cis-cis-trans* coordination, in contrast to most other compounds with similar linear chains where all ligands are in *trans* positions. This is somewhat surprising because $\text{Cd}(\text{NCS})_2(4\text{-benzoylpyridine})_2$ also forms linear chains with an *all-trans* coordination of the cations (Neumann *et al.*, 2018a). Therefore, our intention was to test if a different isomer with, for example, Ni can be prepared by thermal annealing. A complex with composition $\text{Ni}(\text{NCS})_2(4\text{-benzoylpyridine})_4$ has already been reported in the literature. It decomposes in several steps, but only the intermediate after complete removal of 4-benzoylpyridine was examined (Soliman *et al.*, 2014). We have synthesized this compound again and investigated its thermal properties. The residue formed after removal of half of the 4-benzoylpyridine ligands is of poor crystallinity and does not correspond to a pure phase. Therefore, we searched for a more promising precursor;

during these investigations, crystals of the title compound were obtained and characterized by single crystal X-ray diffraction. X-ray powder diffraction revealed that the compound directly isolated from the reaction mixture is a nearly pure phase but always contaminated with a very small amount of $\text{Ni}(\text{NCS})_2(4\text{-benzoylpyridine})_4$ (see Fig. S1 in the supporting information). More importantly, if the title compound is filtered off, it decomposes very quickly into an unknown crystalline phase that does not correspond to that of $\text{Ni}(\text{NCS})_2(4\text{-benzoylpyridine})_4$ already reported in the literature. However, this sample is still contaminated with $\text{Ni}(\text{NCS})_2(4\text{-benzoylpyridine})_4$, and any attempt to completely index its powder pattern failed (Fig. S2 in the supporting information).

2. Structural commentary

The crystal structure of the title compound consists of discrete complexes in which the Ni^{II} cations are sixfold coordinated by two crystallographically independent thiocyanate anions, two methanol molecules and two 4-benzoylpyridine ligands (Fig. 1). The Ni–N bond lengths to the anionic ligands of 2.009 (3) and 2.034 (3) Å are shorter than those to the 4-benzoylpyridine ligands [2.092 (2) and 2.104 (2) Å; the Ni–O distances to the methanol ligands are longer again at 2.108 (2) and 2.154 (2) Å. The coordination sphere around Ni^{II} can be described as a slightly distorted octahedron. This is also obvious from the angle variance and the quadratic elon-

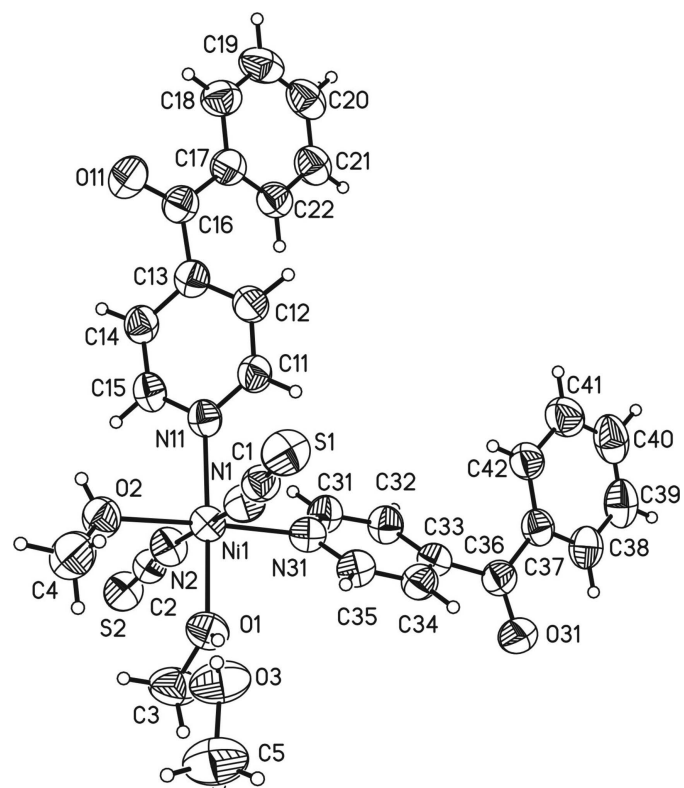


Figure 1
The asymmetric unit of the solvated title complex with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C32–H32 \cdots S2 ⁱ	0.95	3.01	3.865 (3)	151
C34–H34 \cdots O11 ⁱⁱ	0.95	2.50	3.406 (4)	160
C35–H35 \cdots N1	0.95	2.65	3.113 (4)	111
O1–H1 \cdots O3	0.84	1.83	2.643 (3)	163
O2–H2 \cdots S1 ⁱⁱⁱ	0.84	2.44	3.246 (2)	160
O3–H3 \cdots O11 ⁱⁱⁱ	0.84	1.98	2.808 (3)	166

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

gation, which were calculated to be 4.7 and 1.022 (Robinson *et al.*, 1971). The 4-benzoylpyridine ligand is not planar. The dihedral angle between the pyridine ring (N11, C11–C15) and the carbonyl plane (C13, C16, C17, O11) amounts to 56.86 (16)° and that between the phenyl ring (C17–C22) and the carbonyl group (C13, C16, C17, O11) to 12.49 (17)°. The second ligand has corresponding values of 48.61 (17)° between the pyridine ring (N31, C31–C35) and the carbonyl group (C33, C36, C37, O31) and 16.69 (18)° between the phenyl ring (C37–C42) and the carbonyl group (C33, C36, C37, O31). There is a short intramolecular contact between one of the aromatic hydrogen atoms (H35) and one of the thiocyanate N

atoms (N1); however, the corresponding C–H \cdots N angle deviates strongly from linearity, indicating only a weak interaction (Table 1).

3. Supramolecular features

The crystal structure of the title compound is dominated by extensive intermolecular classical and non-classical hydrogen-bonding interactions of medium-to-weak strengths (Table 1). Discrete complexes are linked by intermolecular O–H \cdots S hydrogen bonds into chains extending parallel to [010] (Fig. 2, top). Within such a chain, the complexes are related by the 2₁-screw axis, resulting in a helical arrangement (Fig. 2, bottom). These chains are further linked by pairs of centrosymmetric C–H \cdots S hydrogen bonds into layers extending parallel to (10 $\bar{1}$) (Fig. 3). Adjacent layers are linked into a three-dimensional network by C–H \cdots O hydrogen bonding between a hydrogen atom (H34) of one of the phenyl rings and the carbonyl O atom (O11) of a neighboring 4-benzoylpyridine ligand (Fig. 4). Within this network channels are formed in which the non-coordinating methanol molecules are embedded (Fig. 4). The solvent molecules are linked by O–H \cdots O hydrogen bonding and act both as a donor (O3) to a neighbouring carbonyl O atom (O11) and as an acceptor for a hydroxyl group (O1) of a methanol ligand (Fig. 4).

4. Database survey

In the Cambridge Structure Database (Version 5.39, last update Aug 2018; Groom *et al.*, 2016) several structures of

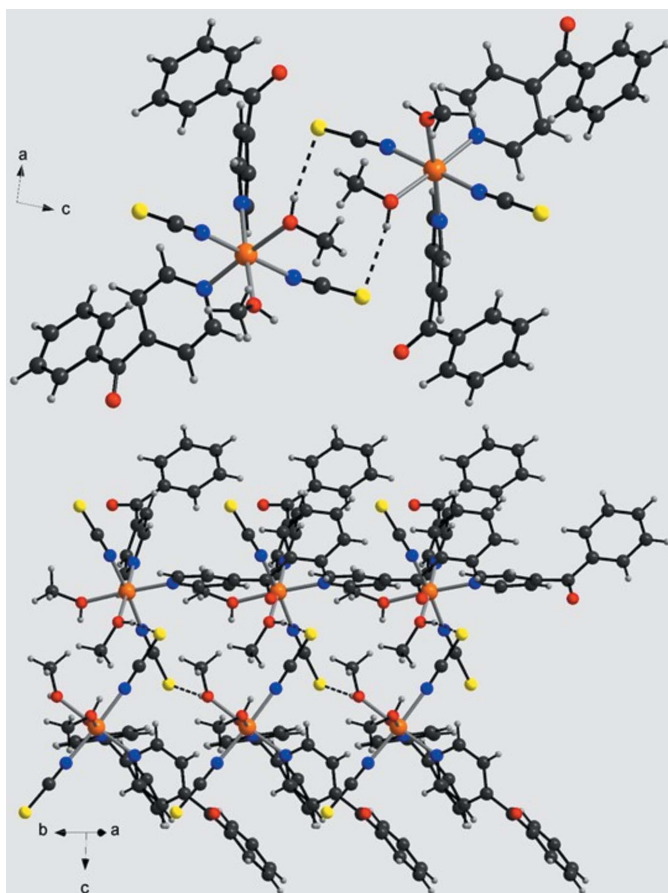


Figure 2
Crystal structure of the title compound in a view along (top) and perpendicular (bottom) to the hydrogen-bonded chains. Intermolecular O–H \cdots S hydrogen bonding is shown as dashed lines.

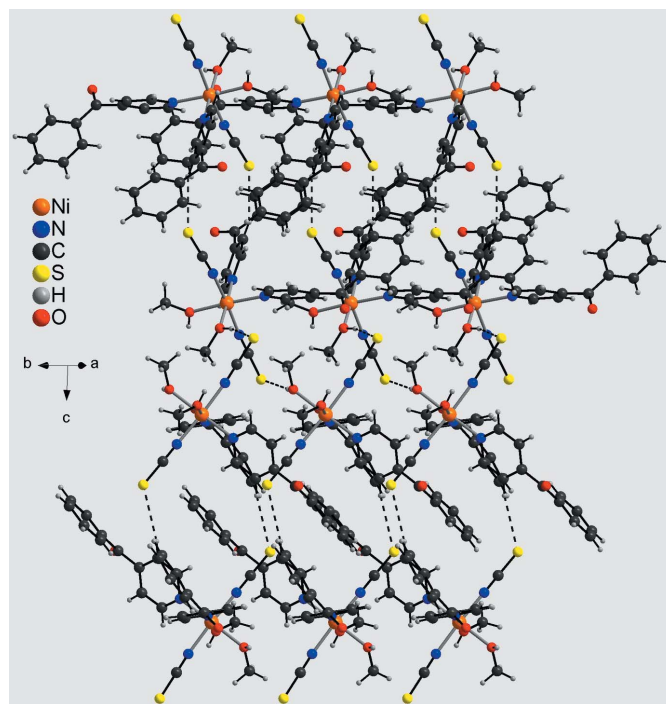
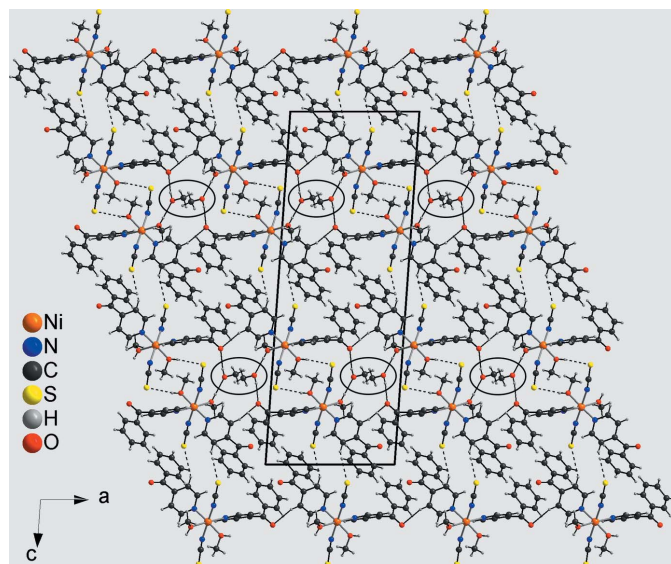


Figure 3
Crystal structure of the title compound in a view approximately [110] showing the layers formed by intermolecular O–H \cdots S and C–H \cdots S hydrogen bonding (shown as dashed lines).


Figure 4

Crystal structure of the title compound in a view along [010] showing the channels that are filled with the non-coordinating methanol molecules. Intermolecular O—H...S, C—H...S, C—H...O and O—H...O hydrogen bonding is shown as dashed lines; the oval channels are marked with thick lines.

transition-metal thiocyanate coordination compounds with 4-benzoylpyridine as ligand have been deposited. They include three compounds with the composition $[M(\text{NCS})_2(4\text{-benzoylpyridine})_2]_n$ ($M = \text{Cd}, \text{Co}, \text{Ni}$), in which the metal cations are octahedrally coordinated and linked into chains by pairs of μ -1,3 bridging thiocyanate anions (Neumann *et al.*, 2018a; Rams *et al.*, 2017; Jochim *et al.*, 2018). Discrete complexes with general composition $M(\text{NCS})_2(4\text{-benzoylpyridine})_4$ ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{Cd}$ and Zn) are also reported in which the metal cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and four 4-benzoylpyridine co-ligands (Drew *et al.*, 1985; Soliman *et al.*, 2014; Wellm & Näther, 2018; Neumann *et al.*, 2018b). There are also compounds where the metal cations are fourfold coordinated by the two N-bonded terminal thiocyanate anions and two 4-benzoylpyridine co-ligands, forming either a tetrahedral (Zn^{II} complex) or a square-planar (Cu^{II} complex) coordination sphere (Neumann *et al.*, 2018a; Bai *et al.*, 2011). The last group consists of octahedrally coordinated Co^{II} cations that either contain two acetonitrile (Suckert *et al.*, 2017b) or two methanol molecules (Suckert *et al.*, 2017c) as coordinating solvent molecules.

5. Synthesis and crystallization

$\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ and 4-benzoylpyridine were purchased from Alfa Aesar. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was purchased from Merck. All solvents and reactants were used without further purification. $\text{Ni}(\text{NCS})_2$ was prepared by the reaction of equimolar amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Ba}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ in water. The resulting white precipitate of BaSO_4 was filtered off, and the solvent was evaporated from the filtrate. The product was dried at

Table 2

Experimental details.

Crystal data	
Chemical formula	$[\text{Ni}(\text{NCS})_2(\text{C}_{12}\text{H}_9\text{NO})_2(\text{CH}_4\text{O})_2] \cdot \text{CH}_4\text{O}$
M_r	637.40
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	12.0588 (6), 7.5515 (3), 33.0408 (16)
β (°)	94.021 (4)
V (Å ³)	3001.4 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.83
Crystal size (mm)	0.25 × 0.15 × 0.08
Data collection	
Diffractometer	Stoe <i>IPDS2</i>
Absorption correction	Numerical (<i>X-SHAPE</i> and <i>X-RED32</i> ; Stoe, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.638, 0.875
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17675, 4726, 4004
R_{int}	0.036
θ_{max} (°)	24.1
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.574
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.105, 1.10
No. of reflections	4726
No. of parameters	371
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.46, -0.26

Computer programs: *X-AREA* (Stoe, 2008), *XP* in *SHELXTL* and *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

room temperature. Crystals of the title compound suitable for single-crystal X-ray diffraction were obtained within a few days by the reaction of 52.5 mg $\text{Ni}(\text{NCS})_2$ (0.30 mmol) with 27.5 mg 4-benzoylpyridine (0.15 mmol) in methanol (1.5 ml) at 354 K using culture tubes.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms were positioned with idealized geometry (C—H = 0.95–0.98 Å; methyl H atoms in part were allowed to rotate but not to tip) and were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (1.5 for methyl H atoms) using a riding model. The OH hydrogen atoms were located in a difference-Fourier map; their bond lengths were set to ideal values and finally they were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ using a riding model.

Acknowledgements

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supporting information

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Crystal structure of bis(4-benzoylpyridine- κ N)bis(methanol- κ O)bis(thiocyanato- κ N)nickel(II) methanol monosolvate

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Computing details

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-AREA* (Stoe, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(4-benzoylpyridine- κ N)bis(methanol- κ O)bis(thiocyanato- κ N)nickel(II) methanol monosolvate

Crystal data

$[\text{Ni}(\text{NCS})_2(\text{C}_{12}\text{H}_9\text{NO})_2(\text{CH}_4\text{O})_2] \cdot \text{CH}_4\text{O}$

$M_r = 637.40$

Monoclinic, $P2_1/n$

$a = 12.0588$ (6) Å

$b = 7.5515$ (3) Å

$c = 33.0408$ (16) Å

$\beta = 94.021$ (4)°

$V = 3001.4$ (2) Å³

$Z = 4$

$F(000) = 1328$

$D_x = 1.411$ Mg m⁻³

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

Cell parameters from 17675 reflections

$\theta = 1.2$ – 24.1 °

$\mu = 0.83$ mm⁻¹

$T = 200$ K

Block, green

$0.25 \times 0.15 \times 0.08$ mm

Data collection

Stoe IPDS-2
diffractometer

ω scans

Absorption correction: numerical
(*X-SHAPE* and *X-RED32*; Stoe, 2008)

$T_{\min} = 0.638$, $T_{\max} = 0.875$

17675 measured reflections

4726 independent reflections

4004 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 24.1$ °, $\theta_{\min} = 1.2$ °

$h = -13$ → 13

$k = -8$ → 8

$l = -37$ → 37

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.105$

$S = 1.10$

4726 reflections

371 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.7722P]$

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

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

$\Delta\rho_{\max} = 0.46$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.58556 (3)	0.48583 (5)	0.16271 (2)	0.04735 (13)
N1	0.5502 (2)	0.3421 (3)	0.21226 (7)	0.0550 (6)
C1	0.5445 (2)	0.2585 (4)	0.24141 (9)	0.0488 (7)
S1	0.53684 (8)	0.13868 (12)	0.28229 (2)	0.0659 (2)
N2	0.6201 (2)	0.6432 (3)	0.11620 (8)	0.0584 (6)
C2	0.6290 (2)	0.7419 (4)	0.08932 (8)	0.0488 (6)
S2	0.64295 (7)	0.87918 (12)	0.05253 (2)	0.0638 (2)
N11	0.7197 (2)	0.3188 (3)	0.15150 (7)	0.0487 (5)
C11	0.7138 (3)	0.1421 (4)	0.15605 (9)	0.0528 (7)
H11	0.6443	0.0913	0.1614	0.063*
C12	0.8037 (3)	0.0310 (4)	0.15339 (9)	0.0545 (7)
H12	0.7950	-0.0936	0.1556	0.065*
C13	0.9062 (2)	0.1032 (4)	0.14754 (8)	0.0516 (7)
C14	0.9127 (3)	0.2864 (4)	0.14232 (9)	0.0534 (7)
H14	0.9819	0.3406	0.1378	0.064*
C15	0.8191 (3)	0.3869 (4)	0.14378 (8)	0.0524 (7)
H15	0.8244	0.5107	0.1391	0.063*
C16	1.0109 (3)	-0.0051 (4)	0.14785 (9)	0.0543 (7)
C17	1.0192 (3)	-0.1532 (4)	0.11893 (9)	0.0538 (7)
C18	1.1107 (3)	-0.2650 (5)	0.12354 (11)	0.0645 (8)
H18	1.1639	-0.2506	0.1459	0.077*
C19	1.1240 (3)	-0.3976 (5)	0.09531 (12)	0.0723 (10)
H19	1.1861	-0.4751	0.0985	0.087*
C20	1.0476 (3)	-0.4176 (4)	0.06269 (11)	0.0689 (9)
H20	1.0577	-0.5080	0.0433	0.083*
C21	0.9566 (3)	-0.3071 (4)	0.05800 (10)	0.0638 (8)
H21	0.9038	-0.3216	0.0355	0.077*
C22	0.9424 (3)	-0.1748 (4)	0.08619 (9)	0.0555 (7)
H22	0.8797	-0.0986	0.0830	0.067*
O11	1.08903 (18)	0.0371 (3)	0.17175 (7)	0.0681 (6)
N31	0.4723 (2)	0.3367 (3)	0.12595 (7)	0.0496 (6)
C31	0.4886 (3)	0.2922 (4)	0.08771 (9)	0.0536 (7)
H31	0.5575	0.3230	0.0773	0.064*
C32	0.4118 (3)	0.2047 (4)	0.06254 (9)	0.0553 (7)
H32	0.4283	0.1743	0.0357	0.066*
C33	0.3094 (2)	0.1610 (4)	0.07678 (9)	0.0510 (7)
C34	0.2925 (3)	0.2062 (4)	0.11660 (9)	0.0541 (7)
H34	0.2241	0.1780	0.1277	0.065*
C35	0.3740 (3)	0.2911 (4)	0.13971 (9)	0.0534 (7)

H35	0.3608	0.3194	0.1670	0.064*
C36	0.2167 (3)	0.0776 (4)	0.05069 (9)	0.0556 (7)
C37	0.2378 (3)	-0.0814 (4)	0.02630 (9)	0.0529 (7)
C38	0.1594 (3)	-0.1303 (5)	-0.00466 (9)	0.0626 (8)
H38	0.0944	-0.0608	-0.0100	0.075*
C39	0.1759 (4)	-0.2788 (5)	-0.02748 (11)	0.0747 (10)
H39	0.1228	-0.3105	-0.0488	0.090*
C40	0.2696 (4)	-0.3824 (5)	-0.01951 (12)	0.0828 (12)
H40	0.2800	-0.4858	-0.0352	0.099*
C41	0.3480 (3)	-0.3361 (5)	0.01117 (12)	0.0758 (10)
H41	0.4120	-0.4077	0.0167	0.091*
C42	0.3325 (3)	-0.1839 (4)	0.03387 (10)	0.0596 (8)
H42	0.3869	-0.1501	0.0546	0.071*
O31	0.1247 (2)	0.1446 (3)	0.05102 (8)	0.0762 (7)
O1	0.45471 (18)	0.6547 (3)	0.17699 (6)	0.0590 (5)
H1	0.4265	0.6291	0.1988	0.089*
C3	0.4305 (3)	0.8282 (5)	0.16255 (13)	0.0801 (11)
H3A	0.3642	0.8727	0.1747	0.120*
H3B	0.4937	0.9062	0.1700	0.120*
H3C	0.4171	0.8256	0.1330	0.120*
O2	0.69448 (18)	0.6461 (3)	0.20203 (6)	0.0604 (5)
H2	0.7622	0.6195	0.2026	0.091*
C4	0.6653 (3)	0.7267 (6)	0.23878 (12)	0.0854 (12)
H4A	0.7293	0.7924	0.2510	0.128*
H4B	0.6030	0.8082	0.2330	0.128*
H4C	0.6437	0.6349	0.2577	0.128*
O3	0.3644 (2)	0.6458 (4)	0.24757 (8)	0.0844 (8)
H3	0.3838	0.5988	0.2700	0.127*
C5	0.2807 (4)	0.7704 (7)	0.25548 (14)	0.1051 (15)
H5A	0.2179	0.7090	0.2666	0.158*
H5B	0.2553	0.8303	0.2302	0.158*
H5C	0.3109	0.8580	0.2752	0.158*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0524 (2)	0.0467 (2)	0.0431 (2)	-0.00002 (16)	0.00477 (15)	0.00073 (15)
N1	0.0544 (15)	0.0607 (15)	0.0499 (13)	0.0041 (12)	0.0036 (11)	0.0030 (12)
C1	0.0465 (16)	0.0523 (16)	0.0477 (15)	0.0025 (13)	0.0045 (12)	-0.0028 (13)
S1	0.0660 (5)	0.0740 (5)	0.0582 (4)	0.0013 (4)	0.0086 (4)	0.0192 (4)
N2	0.0653 (17)	0.0552 (15)	0.0551 (14)	-0.0033 (12)	0.0074 (12)	-0.0009 (12)
C2	0.0482 (16)	0.0511 (16)	0.0471 (15)	-0.0007 (13)	0.0036 (13)	-0.0006 (13)
S2	0.0660 (5)	0.0682 (5)	0.0574 (4)	-0.0027 (4)	0.0056 (4)	0.0168 (4)
N11	0.0527 (14)	0.0484 (13)	0.0454 (12)	-0.0049 (11)	0.0066 (11)	-0.0028 (10)
C11	0.0473 (16)	0.0508 (17)	0.0609 (17)	-0.0061 (13)	0.0089 (14)	-0.0011 (13)
C12	0.0552 (18)	0.0482 (16)	0.0607 (17)	-0.0008 (14)	0.0076 (14)	-0.0016 (13)
C13	0.0521 (17)	0.0562 (17)	0.0468 (14)	-0.0021 (14)	0.0064 (13)	-0.0059 (13)
C14	0.0509 (17)	0.0540 (17)	0.0566 (16)	-0.0069 (14)	0.0129 (14)	-0.0041 (13)

C15	0.0595 (18)	0.0475 (15)	0.0508 (15)	-0.0096 (14)	0.0091 (14)	-0.0030 (12)
C16	0.0503 (17)	0.0591 (18)	0.0542 (16)	-0.0020 (14)	0.0084 (14)	0.0003 (14)
C17	0.0517 (17)	0.0541 (17)	0.0568 (17)	-0.0014 (14)	0.0114 (14)	0.0025 (13)
C18	0.0559 (19)	0.065 (2)	0.074 (2)	0.0064 (16)	0.0109 (16)	0.0085 (16)
C19	0.074 (2)	0.0584 (19)	0.087 (2)	0.0152 (17)	0.029 (2)	0.0090 (18)
C20	0.082 (2)	0.0527 (18)	0.075 (2)	0.0000 (17)	0.028 (2)	-0.0030 (16)
C21	0.072 (2)	0.0563 (18)	0.0642 (19)	-0.0028 (17)	0.0143 (16)	-0.0047 (15)
C22	0.0573 (18)	0.0527 (17)	0.0571 (16)	0.0004 (14)	0.0092 (14)	-0.0001 (13)
O11	0.0538 (13)	0.0825 (16)	0.0674 (13)	-0.0034 (11)	0.0007 (12)	-0.0082 (12)
N31	0.0513 (14)	0.0516 (13)	0.0464 (12)	0.0024 (11)	0.0056 (11)	0.0013 (10)
C31	0.0535 (17)	0.0590 (17)	0.0492 (15)	-0.0048 (14)	0.0096 (13)	-0.0017 (13)
C32	0.0594 (19)	0.0586 (17)	0.0481 (15)	-0.0037 (15)	0.0053 (14)	-0.0052 (13)
C33	0.0511 (17)	0.0450 (15)	0.0566 (16)	0.0026 (13)	0.0021 (14)	0.0010 (13)
C34	0.0506 (17)	0.0531 (17)	0.0591 (17)	0.0005 (14)	0.0084 (14)	0.0016 (14)
C35	0.0545 (18)	0.0576 (17)	0.0486 (15)	0.0014 (14)	0.0070 (14)	0.0013 (13)
C36	0.0528 (19)	0.0538 (17)	0.0594 (17)	-0.0007 (14)	-0.0019 (14)	0.0020 (14)
C37	0.0575 (18)	0.0497 (16)	0.0520 (16)	-0.0070 (14)	0.0083 (14)	0.0016 (13)
C38	0.067 (2)	0.068 (2)	0.0534 (17)	-0.0148 (17)	0.0042 (15)	0.0026 (15)
C39	0.085 (3)	0.080 (2)	0.0602 (19)	-0.029 (2)	0.0132 (18)	-0.0120 (18)
C40	0.096 (3)	0.073 (2)	0.084 (3)	-0.027 (2)	0.037 (2)	-0.025 (2)
C41	0.076 (2)	0.062 (2)	0.092 (3)	-0.0005 (18)	0.025 (2)	-0.0069 (19)
C42	0.0594 (19)	0.0527 (17)	0.0674 (19)	-0.0043 (15)	0.0101 (15)	-0.0008 (15)
O31	0.0551 (14)	0.0694 (15)	0.1020 (18)	0.0078 (12)	-0.0103 (13)	-0.0142 (13)
O1	0.0676 (14)	0.0550 (12)	0.0551 (11)	0.0074 (10)	0.0087 (10)	0.0036 (9)
C3	0.080 (3)	0.063 (2)	0.099 (3)	0.0178 (19)	0.021 (2)	0.023 (2)
O2	0.0602 (13)	0.0646 (13)	0.0567 (11)	-0.0027 (10)	0.0057 (10)	-0.0121 (10)
C4	0.069 (2)	0.111 (3)	0.076 (2)	0.004 (2)	0.0030 (19)	-0.042 (2)
O3	0.0767 (17)	0.108 (2)	0.0711 (15)	0.0280 (15)	0.0213 (13)	0.0161 (14)
C5	0.095 (3)	0.129 (4)	0.092 (3)	0.033 (3)	0.018 (3)	-0.002 (3)

Geometric parameters (Å, °)

Ni1—N2	2.009 (3)	C31—H31	0.9500
Ni1—N1	2.034 (3)	C32—C33	1.392 (4)
Ni1—N31	2.092 (2)	C32—H32	0.9500
Ni1—N11	2.104 (2)	C33—C34	1.388 (4)
Ni1—O1	2.108 (2)	C33—C36	1.501 (4)
Ni1—O2	2.154 (2)	C34—C35	1.362 (4)
N1—C1	1.158 (4)	C34—H34	0.9500
C1—S1	1.634 (3)	C35—H35	0.9500
N2—C2	1.170 (4)	C36—O31	1.220 (4)
C2—S2	1.615 (3)	C36—C37	1.478 (4)
N11—C11	1.345 (4)	C37—C42	1.387 (5)
N11—C15	1.345 (4)	C37—C38	1.394 (4)
C11—C12	1.378 (4)	C38—C39	1.373 (5)
C11—H11	0.9500	C38—H38	0.9500
C12—C13	1.378 (4)	C39—C40	1.384 (6)
C12—H12	0.9500	C39—H39	0.9500

C13—C14	1.397 (4)	C40—C41	1.382 (6)
C13—C16	1.503 (4)	C40—H40	0.9500
C14—C15	1.364 (4)	C41—C42	1.393 (5)
C14—H14	0.9500	C41—H41	0.9500
C15—H15	0.9500	C42—H42	0.9500
C16—O11	1.228 (4)	O1—C3	1.417 (4)
C16—C17	1.479 (4)	O1—H1	0.8401
C17—C22	1.383 (4)	C3—H3A	0.9800
C17—C18	1.389 (5)	C3—H3B	0.9800
C18—C19	1.386 (5)	C3—H3C	0.9800
C18—H18	0.9500	O2—C4	1.424 (4)
C19—C20	1.376 (5)	O2—H2	0.8400
C19—H19	0.9500	C4—H4A	0.9800
C20—C21	1.380 (5)	C4—H4B	0.9800
C20—H20	0.9500	C4—H4C	0.9800
C21—C22	1.384 (4)	O3—C5	1.418 (5)
C21—H21	0.9500	O3—H3	0.8402
C22—H22	0.9500	C5—H5A	0.9800
N31—C31	1.335 (4)	C5—H5B	0.9800
N31—C35	1.343 (4)	C5—H5C	0.9800
C31—C32	1.369 (4)		
N2—Ni1—N1	175.96 (10)	N31—C31—C32	123.9 (3)
N2—Ni1—N31	92.09 (10)	N31—C31—H31	118.0
N1—Ni1—N31	90.85 (10)	C32—C31—H31	118.0
N2—Ni1—N11	90.95 (10)	C31—C32—C33	119.1 (3)
N1—Ni1—N11	91.66 (9)	C31—C32—H32	120.4
N31—Ni1—N11	93.10 (9)	C33—C32—H32	120.4
N2—Ni1—O1	90.70 (10)	C34—C33—C32	117.1 (3)
N1—Ni1—O1	86.56 (9)	C34—C33—C36	119.6 (3)
N31—Ni1—O1	89.25 (9)	C32—C33—C36	123.2 (3)
N11—Ni1—O1	177.08 (8)	C35—C34—C33	119.9 (3)
N2—Ni1—O2	88.77 (10)	C35—C34—H34	120.0
N1—Ni1—O2	88.15 (9)	C33—C34—H34	120.0
N31—Ni1—O2	176.81 (9)	N31—C35—C34	123.4 (3)
N11—Ni1—O2	89.96 (9)	N31—C35—H35	118.3
O1—Ni1—O2	87.67 (8)	C34—C35—H35	118.3
C1—N1—Ni1	171.3 (2)	O31—C36—C37	122.2 (3)
N1—C1—S1	179.4 (3)	O31—C36—C33	117.5 (3)
C2—N2—Ni1	172.8 (3)	C37—C36—C33	120.2 (3)
N2—C2—S2	179.2 (3)	C42—C37—C38	119.5 (3)
C11—N11—C15	117.0 (3)	C42—C37—C36	121.7 (3)
C11—N11—Ni1	121.87 (19)	C38—C37—C36	118.8 (3)
C15—N11—Ni1	120.7 (2)	C39—C38—C37	120.2 (4)
N11—C11—C12	123.3 (3)	C39—C38—H38	119.9
N11—C11—H11	118.3	C37—C38—H38	119.9
C12—C11—H11	118.3	C38—C39—C40	120.3 (4)
C13—C12—C11	119.1 (3)	C38—C39—H39	119.8

C13—C12—H12	120.5	C40—C39—H39	119.8
C11—C12—H12	120.5	C41—C40—C39	120.3 (4)
C12—C13—C14	117.9 (3)	C41—C40—H40	119.9
C12—C13—C16	123.0 (3)	C39—C40—H40	119.9
C14—C13—C16	119.0 (3)	C40—C41—C42	119.5 (4)
C15—C14—C13	119.5 (3)	C40—C41—H41	120.2
C15—C14—H14	120.2	C42—C41—H41	120.2
C13—C14—H14	120.2	C37—C42—C41	120.2 (3)
N11—C15—C14	123.0 (3)	C37—C42—H42	119.9
N11—C15—H15	118.5	C41—C42—H42	119.9
C14—C15—H15	118.5	C3—O1—Ni1	128.6 (2)
O11—C16—C17	121.9 (3)	C3—O1—H1	114.5
O11—C16—C13	118.0 (3)	Ni1—O1—H1	114.0
C17—C16—C13	120.1 (3)	O1—C3—H3A	109.5
C22—C17—C18	119.8 (3)	O1—C3—H3B	109.5
C22—C17—C16	121.5 (3)	H3A—C3—H3B	109.5
C18—C17—C16	118.6 (3)	O1—C3—H3C	109.5
C19—C18—C17	119.6 (3)	H3A—C3—H3C	109.5
C19—C18—H18	120.2	H3B—C3—H3C	109.5
C17—C18—H18	120.2	C4—O2—Ni1	125.3 (2)
C20—C19—C18	120.3 (3)	C4—O2—H2	112.4
C20—C19—H19	119.9	Ni1—O2—H2	115.5
C18—C19—H19	119.9	O2—C4—H4A	109.5
C19—C20—C21	120.3 (3)	O2—C4—H4B	109.5
C19—C20—H20	119.8	H4A—C4—H4B	109.5
C21—C20—H20	119.8	O2—C4—H4C	109.5
C20—C21—C22	119.7 (3)	H4A—C4—H4C	109.5
C20—C21—H21	120.1	H4B—C4—H4C	109.5
C22—C21—H21	120.1	C5—O3—H3	106.0
C17—C22—C21	120.2 (3)	O3—C5—H5A	109.5
C17—C22—H22	119.9	O3—C5—H5B	109.5
C21—C22—H22	119.9	H5A—C5—H5B	109.5
C31—N31—C35	116.6 (3)	O3—C5—H5C	109.5
C31—N31—Ni1	123.5 (2)	H5A—C5—H5C	109.5
C35—N31—Ni1	119.82 (19)	H5B—C5—H5C	109.5

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C32—H32 \cdots S2 ⁱ	0.95	3.01	3.865 (3)	151
C34—H34 \cdots O11 ⁱⁱ	0.95	2.50	3.406 (4)	160
C35—H35 \cdots N1	0.95	2.65	3.113 (4)	111
O1—H1 \cdots O3	0.84	1.83	2.643 (3)	163
O2—H2 \cdots S1 ⁱⁱⁱ	0.84	2.44	3.246 (2)	160
O3—H3 \cdots O11 ⁱⁱⁱ	0.84	1.98	2.808 (3)	166

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