

trans-Diaquabis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole]nickel(II) bis(tetrafluoridoborate)

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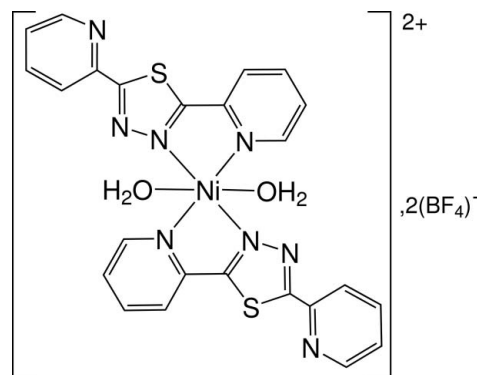
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.029; wR factor = 0.073; data-to-parameter ratio = 14.6.

The bidentate 1,3,4-thiadiazole ligand, namely, 2,5-bis(2-pyridyl)-1,3,4-thiadiazole (denoted *L*), untested as a polydentate ligand, has been found to form the monomeric title complex, $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_4\text{S})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$. The complex shows an octahedral environment of the nickel cation in which the Ni^{2+} ion is located on a center of symmetry, linked to two ligands and two water molecules. In this 1:2 complex (one metal for two organic ligands) each thiadiazole ligand uses one pyridyl and one thiadiazole N atom for chelate binding. In the second pyridyl substituent, the N atom is oriented towards the same direction as the S atom of the 1,3,4-thiadiazole ring. The mean plane of the thiadiazole and pyridyl rings linked to the nickel cation forms a dihedral angle with the other pyridine ring of $18.63(8)^\circ$. The tetrafluoridoborate ions can be regarded as free anions in the crystal lattice. Nevertheless, they are involved in an infinite two-dimensional network parallel to $(\bar{1}01)$ through $\text{O}-\text{H}\cdots\text{F}$ hydrogen bonds.

Related literature

For Ni^{II} and Cu^{II} complexes containing a five azide ring, see: Keij *et al.* (1984). For background to similar structures, see: Bentiss *et al.* (2002, 2004, 2011); Zheng *et al.* (2006). For an improved synthesis of the ligand, see: Lebrini *et al.* (2005).



Experimental

Crystal data

$[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_4\text{S})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$
 $M_r = 748.93$
 Monoclinic, $P2_1/n$
 $a = 10.8164(15)$ Å
 $b = 11.0126(13)$ Å
 $c = 13.2333(16)$ Å
 $\beta = 101.455(6)^\circ$

$V = 1544.9(3)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.85$ mm⁻¹
 $T = 100$ K
 $0.26 \times 0.21 \times 0.13$ mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\text{min}} = 0.809$, $T_{\text{max}} = 0.898$

28021 measured reflections
 3120 independent reflections
 2729 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.073$
 $S = 1.05$
 3120 reflections

214 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.60$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{O1}-\text{H1W}\cdots\text{F1}^i$ | 0.86 | 1.88 | 2.704 (2) | 160 |
| $\text{O1}-\text{H2W}\cdots\text{F4}$ | 0.86 | 1.94 | 2.7880 (19) | 171 |

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2703).

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supplementary materials

Acta Cryst. (2011). E67, m1052-m1053 [doi:10.1107/S1600536811026420]

***trans*-Diaquabis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole]nickel(II) bis(tetrafluoroborate)**

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Comment

With ligands containing a five azide ring, 3 d transition metals such as Ni^{II} and Cu^{II} have a tendency to form mono or polynuclear species (Keij *et al.*, 1984). The dinuclear species are of interest due to their potential magnetic coupling. The unpaired 3 d electrons being potentially coupled *via* the intermediary of the bridging azide ligands. The ligands related to the 1,2-diazoles with *o*-pyridine substitution at the 3 and 5 positions, such as 2,5-bis(2-pyridyl)-1,3,4 oxadiazole and thiadiazole, have been of interest for such applications. Indeed, 2,5-bis(2-pyridyl)-1,3,4-thiadiazole can be used as a molecular architect with transition metals in association with anionic Ni-ligands. In the resulting di and mononuclear complexes, a variety of coordination modes have been observed, of which the dinuclear (N'N'', N2, N'') bridging, the dinuclear (N'N'', N2, N'')₂ double bridging and the monoclear (N',N')₂ coordination mode are the most common and the most important ones (Scheme 1), the latter mode, the *trans* type is exclusively observed for featuring octahedral complexes.

The structures of monomeric complexes of the neutral 2,5-bis(2-pyridyl)-1,3,4-thiadiazole derivative with divalent Zn (tetrachloride and perchlorate), Co (nitrate, perchlorate and tetrafluoroborate), Ni (perchlorate), and Cu (nitrate, perchlorate) have been previously reported (Bentiss *et al.*, 2002; Bentiss *et al.*, 2004; Zheng *et al.* 2006; Bentiss *et al.*, 2011). We report here the synthesis and the single-crystal structure of the new monomeric complex formed by 2,5-bis(2-pyridyl)-1,3,4-thiadiazole with nickel tetrafluoroborate as counter ions.

The complex shows an almost regular octahedral environment of the nickel cation in which Ni²⁺ is located at a center of symmetry, and linked to two ligand and two water molecules as shown in Fig.1. As a matter of fact, the nickel coordination sphere is achieved by interaction with the nitrogen atom of a single pyridyl ring and with the near nitrogen of the azide group with Ni—N distances in the range of 2.052 (2)—2.132 (2) Å. Moreover, the water molecules are found in axial positions at distances and angles of Ni—O 2.120 (2) Å and all N—Ni—O angles being close to 90 °.

The dihedral angle between the thiadiazole and the pyridyl rings linked to the nickel cation is in the range of 4.16 (9)°. The mean plane of the two preceding cycles forms a dihedral angle with the (N4—C8—C9—C10—C11—C12) other pyridine ring of 18.63 (8)°. The counter ion, BF₄⁻ is involved in an infinite two-dimensional network of O—H...F hydrogen bonds parallel to the (-1 0 1) plane (Table 1, Fig.1).

Experimental

2,5-Bis(2-pyridyl)-1,3,4-thiadiazole ligand (noted *L*) was synthesized as described previously by Lebrini *et al.*, 2005. Ni(BF₄)₂·6H₂O (1.5 mmol, 0.51 g) in 8 ml of water was added to (0.42 mmol, 0.1 g) of *L* (bptd ligand) dissolved in 8 ml of ethanol. The solution was filtered and after 24 h, the colorless compound crystallized at room temperature. Crystals were washed with water and dried under vacuum. Yield: 51%. Anal. Calc. for C₂₄H₂₀B₂F₈N₈NiO₂S₂: C, 38.44; H, 2.67; N, 14.95; S, 8.56; F, 20.29%. Found: C, 38.52; H, 2.75; N, 14.90; S, 8.53; F, 20.27%.

Refinement

H atoms attached to carbon were located in a difference map but introduced in calculated position and treated as riding with C—H = 0.95 Å for the aromatic CH, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (aromatic). The O-bound H atoms were initially located in a difference map and refined with O—H distance restraints of 0.86 (1). In the last cycles of refinement, they are treated as riding on their parent O atoms with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{O})$.

Figures

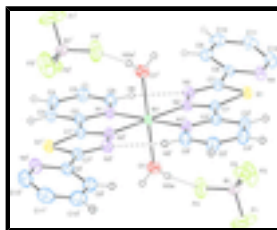


Fig. 1. Plot of the crystal structure showing the molecules linked to the nickel cation and the counter ions, BF_4^- , with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles. Hydrogen bonds are shown as dashed lines.

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$M_r = 748.93$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 10.8164$ (15) Å

$b = 11.0126$ (13) Å

$c = 13.2333$ (16) Å

$\beta = 101.455$ (6)°

$V = 1544.9$ (3) Å³

$Z = 2$

$F(000) = 756$

$D_x = 1.610$ Mg m⁻³

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

Cell parameters from 3120 reflections

$\theta = 2.7\text{--}26.3^\circ$

$\mu = 0.85$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.26 \times 0.21 \times 0.13$ mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2005)

$T_{\text{min}} = 0.809$, $T_{\text{max}} = 0.898$

28021 measured reflections

3120 independent reflections

2729 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\text{max}} = 26.3^\circ$, $\theta_{\text{min}} = 2.7^\circ$

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 13$

$l = -16 \rightarrow 16$

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.029$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.073$ | H-atom parameters constrained |
| $S = 1.05$ | $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 1.3259P]$ |
| 3120 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 214 parameters | $(\Delta/\sigma)_{\max} < 0.001$ |
| 0 restraints | $\Delta\rho_{\max} = 0.60 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$ |

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|--------------|---------------|----------------------------------|
| B1 | 0.5722 (2) | 0.6450 (2) | 0.25602 (17) | 0.0236 (4) |
| F1 | 0.67390 (15) | 0.59474 (18) | 0.32316 (11) | 0.0707 (6) |
| F2 | 0.58436 (11) | 0.62341 (12) | 0.15219 (9) | 0.0362 (3) |
| F3 | 0.46260 (14) | 0.59379 (14) | 0.27433 (14) | 0.0583 (4) |
| F4 | 0.56853 (15) | 0.77036 (12) | 0.27479 (11) | 0.0494 (4) |
| C1 | 0.40875 (16) | 0.75569 (16) | -0.02295 (14) | 0.0202 (4) |
| C2 | 0.47768 (16) | 1.25248 (17) | 0.06948 (13) | 0.0200 (4) |
| C3 | 0.43547 (18) | 1.35965 (17) | 0.10676 (14) | 0.0236 (4) |
| H3 | 0.4806 | 1.4333 | 0.1048 | 0.028* |
| C4 | 0.32542 (18) | 1.35711 (18) | 0.14729 (15) | 0.0258 (4) |
| H4 | 0.2940 | 1.4292 | 0.1726 | 0.031* |
| C5 | 0.26311 (18) | 1.24770 (18) | 0.14982 (15) | 0.0265 (4) |
| H5 | 0.1883 | 1.2433 | 0.1770 | 0.032* |
| C6 | 0.31231 (18) | 1.14360 (18) | 0.11167 (15) | 0.0248 (4) |
| H6 | 0.2696 | 1.0686 | 0.1144 | 0.030* |
| C7 | 0.22180 (17) | 0.74859 (17) | 0.04687 (14) | 0.0210 (4) |
| C8 | 0.10347 (17) | 0.71642 (18) | 0.08024 (14) | 0.0222 (4) |
| C9 | 0.01756 (18) | 0.80507 (19) | 0.09554 (16) | 0.0296 (4) |

supplementary materials

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|-----|---------------|--------------|--------------|--------------|
| H9 | 0.0335 | 0.8887 | 0.0859 | 0.036* |
| C10 | -0.09264 (19) | 0.7670 (2) | 0.12544 (17) | 0.0342 (5) |
| H10 | -0.1541 | 0.8246 | 0.1364 | 0.041* |
| C11 | -0.11154 (19) | 0.6445 (2) | 0.13902 (16) | 0.0329 (5) |
| H11 | -0.1862 | 0.6166 | 0.1591 | 0.040* |
| C12 | -0.0195 (2) | 0.5627 (2) | 0.12282 (16) | 0.0310 (5) |
| H12 | -0.0326 | 0.4787 | 0.1334 | 0.037* |
| Ni1 | 0.5000 | 1.0000 | 0.0000 | 0.01936 (10) |
| N1 | 0.41765 (14) | 1.14452 (14) | 0.07112 (12) | 0.0218 (3) |
| N2 | 0.38061 (14) | 0.85992 (14) | 0.01661 (12) | 0.0210 (3) |
| N3 | 0.27253 (14) | 0.85652 (14) | 0.05732 (12) | 0.0226 (3) |
| N4 | 0.08724 (15) | 0.59655 (15) | 0.09286 (13) | 0.0260 (4) |
| O1 | 0.61598 (13) | 0.95553 (13) | 0.14395 (11) | 0.0307 (3) |
| H1W | 0.6844 | 0.9932 | 0.1692 | 0.037* |
| H2W | 0.6090 | 0.9007 | 0.1886 | 0.037* |
| S1 | 0.30384 (4) | 0.64191 (4) | -0.01275 (4) | 0.02147 (12) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| B1 | 0.0194 (10) | 0.0233 (11) | 0.0268 (11) | 0.0023 (8) | 0.0017 (8) | 0.0008 (9) |
| F1 | 0.0620 (10) | 0.1029 (14) | 0.0388 (8) | 0.0561 (10) | -0.0106 (7) | -0.0066 (9) |
| F2 | 0.0351 (7) | 0.0440 (8) | 0.0285 (6) | -0.0059 (6) | 0.0039 (5) | -0.0035 (6) |
| F3 | 0.0514 (9) | 0.0459 (9) | 0.0907 (12) | -0.0177 (7) | 0.0457 (9) | -0.0236 (8) |
| F4 | 0.0759 (10) | 0.0240 (7) | 0.0503 (8) | -0.0093 (7) | 0.0178 (7) | -0.0030 (6) |
| C1 | 0.0189 (9) | 0.0170 (9) | 0.0231 (9) | -0.0021 (7) | 0.0004 (7) | 0.0028 (7) |
| C2 | 0.0188 (9) | 0.0196 (9) | 0.0203 (8) | -0.0010 (7) | 0.0005 (7) | 0.0021 (7) |
| C3 | 0.0248 (10) | 0.0184 (9) | 0.0270 (10) | -0.0014 (7) | 0.0034 (8) | 0.0006 (8) |
| C4 | 0.0283 (10) | 0.0214 (10) | 0.0283 (10) | 0.0025 (8) | 0.0073 (8) | -0.0018 (8) |
| C5 | 0.0248 (10) | 0.0258 (10) | 0.0302 (10) | -0.0003 (8) | 0.0090 (8) | 0.0004 (8) |
| C6 | 0.0243 (9) | 0.0213 (10) | 0.0297 (10) | -0.0038 (8) | 0.0078 (8) | 0.0001 (8) |
| C7 | 0.0197 (9) | 0.0197 (9) | 0.0226 (9) | 0.0002 (7) | 0.0015 (7) | 0.0009 (7) |
| C8 | 0.0194 (9) | 0.0246 (10) | 0.0218 (9) | -0.0032 (8) | 0.0020 (7) | -0.0011 (8) |
| C9 | 0.0247 (10) | 0.0270 (11) | 0.0362 (11) | 0.0009 (8) | 0.0040 (8) | -0.0007 (9) |
| C10 | 0.0246 (10) | 0.0425 (13) | 0.0365 (11) | 0.0058 (9) | 0.0086 (9) | -0.0034 (10) |
| C11 | 0.0244 (10) | 0.0476 (14) | 0.0295 (10) | -0.0075 (9) | 0.0116 (8) | -0.0016 (10) |
| C12 | 0.0337 (11) | 0.0290 (11) | 0.0331 (11) | -0.0092 (9) | 0.0131 (9) | 0.0009 (9) |
| Ni1 | 0.01766 (17) | 0.01400 (17) | 0.02659 (18) | -0.00261 (13) | 0.00479 (13) | -0.00057 (13) |
| N1 | 0.0205 (8) | 0.0182 (8) | 0.0264 (8) | -0.0019 (6) | 0.0039 (6) | 0.0009 (6) |
| N2 | 0.0186 (7) | 0.0179 (8) | 0.0267 (8) | -0.0013 (6) | 0.0048 (6) | 0.0000 (6) |
| N3 | 0.0193 (8) | 0.0208 (8) | 0.0282 (8) | -0.0032 (6) | 0.0056 (6) | 0.0012 (7) |
| N4 | 0.0267 (8) | 0.0233 (9) | 0.0299 (8) | -0.0047 (7) | 0.0099 (7) | -0.0014 (7) |
| O1 | 0.0270 (7) | 0.0276 (8) | 0.0337 (8) | -0.0075 (6) | -0.0030 (6) | 0.0064 (6) |
| S1 | 0.0188 (2) | 0.0158 (2) | 0.0299 (2) | -0.00252 (17) | 0.00479 (18) | 0.00033 (18) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------|-----------|-------|-------------|
| B1—F3 | 1.377 (3) | C7—S1 | 1.7517 (19) |
| B1—F1 | 1.385 (3) | C8—N4 | 1.346 (3) |

| | | | |
|------------------------|-------------|--------------------------------------|-------------|
| B1—F4 | 1.404 (3) | C8—C9 | 1.390 (3) |
| B1—F2 | 1.426 (2) | C9—C10 | 1.393 (3) |
| C1—N2 | 1.322 (2) | C9—H9 | 0.9500 |
| C1—C2 ⁱ | 1.482 (2) | C10—C11 | 1.382 (3) |
| C1—S1 | 1.7137 (18) | C10—H10 | 0.9500 |
| C2—N1 | 1.357 (2) | C11—C12 | 1.391 (3) |
| C2—C3 | 1.391 (3) | C11—H11 | 0.9500 |
| C2—C1 ⁱ | 1.482 (2) | C12—N4 | 1.345 (2) |
| C3—C4 | 1.400 (3) | C12—H12 | 0.9500 |
| C3—H3 | 0.9500 | Ni1—N2 | 2.0515 (15) |
| C4—C5 | 1.384 (3) | Ni1—N2 ⁱ | 2.0515 (15) |
| C4—H4 | 0.9500 | Ni1—O1 ⁱ | 2.1197 (14) |
| C5—C6 | 1.400 (3) | Ni1—O1 | 2.1197 (14) |
| C5—H5 | 0.9500 | Ni1—N1 ⁱ | 2.1320 (16) |
| C6—N1 | 1.352 (2) | Ni1—N1 | 2.1320 (16) |
| C6—H6 | 0.9500 | N2—N3 | 1.381 (2) |
| C7—N3 | 1.305 (2) | O1—H1W | 0.8564 |
| C7—C8 | 1.478 (2) | O1—H2W | 0.8588 |
| F3—B1—F1 | 108.98 (19) | C9—C10—H10 | 120.4 |
| F3—B1—F4 | 108.44 (17) | C10—C11—C12 | 118.91 (18) |
| F1—B1—F4 | 109.02 (18) | C10—C11—H11 | 120.5 |
| F3—B1—F2 | 110.41 (17) | C12—C11—H11 | 120.5 |
| F1—B1—F2 | 109.73 (17) | N4—C12—C11 | 123.3 (2) |
| F4—B1—F2 | 110.22 (17) | N4—C12—H12 | 118.4 |
| N2—C1—C2 ⁱ | 119.49 (16) | C11—C12—H12 | 118.4 |
| N2—C1—S1 | 113.30 (13) | N2—Ni1—N2 ⁱ | 180.00 (9) |
| C2 ⁱ —C1—S1 | 127.21 (14) | N2—Ni1—O1 ⁱ | 89.84 (6) |
| N1—C2—C3 | 123.10 (16) | N2 ⁱ —Ni1—O1 ⁱ | 90.16 (6) |
| N1—C2—C1 ⁱ | 113.09 (16) | N2—Ni1—O1 | 90.16 (6) |
| C3—C2—C1 ⁱ | 123.81 (16) | N2 ⁱ —Ni1—O1 | 89.84 (6) |
| C2—C3—C4 | 118.89 (17) | O1 ⁱ —Ni1—O1 | 180.00 (8) |
| C2—C3—H3 | 120.6 | N2—Ni1—N1 ⁱ | 79.22 (6) |
| C4—C3—H3 | 120.6 | N2 ⁱ —Ni1—N1 ⁱ | 100.78 (6) |
| C5—C4—C3 | 118.81 (18) | O1 ⁱ —Ni1—N1 ⁱ | 90.02 (6) |
| C5—C4—H4 | 120.6 | O1—Ni1—N1 ⁱ | 89.98 (6) |
| C3—C4—H4 | 120.6 | N2—Ni1—N1 | 100.78 (6) |
| C4—C5—C6 | 118.84 (17) | N2 ⁱ —Ni1—N1 | 79.22 (6) |
| C4—C5—H5 | 120.6 | O1 ⁱ —Ni1—N1 | 89.98 (6) |
| C6—C5—H5 | 120.6 | O1—Ni1—N1 | 90.02 (6) |
| N1—C6—C5 | 123.20 (17) | N1 ⁱ —Ni1—N1 | 180.0 |
| N1—C6—H6 | 118.4 | C6—N1—C2 | 117.16 (16) |
| C5—C6—H6 | 118.4 | C6—N1—Ni1 | 128.93 (13) |
| N3—C7—C8 | 123.90 (17) | C2—N1—Ni1 | 113.82 (12) |
| N3—C7—S1 | 114.75 (13) | C1—N2—N3 | 114.22 (15) |
| C8—C7—S1 | 121.34 (14) | C1—N2—Ni1 | 114.28 (12) |

supplementary materials

| | | | |
|---------------------------|--------------|----------------------------|--------------|
| N4—C8—C9 | 124.27 (17) | N3—N2—Ni1 | 131.42 (12) |
| N4—C8—C7 | 114.47 (16) | C7—N3—N2 | 110.73 (15) |
| C9—C8—C7 | 121.26 (17) | C12—N4—C8 | 116.68 (17) |
| C8—C9—C10 | 117.7 (2) | Ni1—O1—H1W | 123.4 |
| C8—C9—H9 | 121.2 | Ni1—O1—H2W | 131.6 |
| C10—C9—H9 | 121.2 | H1W—O1—H2W | 105.0 |
| C11—C10—C9 | 119.2 (2) | C1—S1—C7 | 87.00 (9) |
| C11—C10—H10 | 120.4 | | |
| N1—C2—C3—C4 | -0.5 (3) | C3—C2—N1—Ni1 | 176.49 (14) |
| C1 ⁱ —C2—C3—C4 | 178.72 (17) | C1 ⁱ —C2—N1—Ni1 | -2.83 (19) |
| C2—C3—C4—C5 | 0.7 (3) | C2 ⁱ —C1—N2—N3 | 179.76 (15) |
| C3—C4—C5—C6 | -0.1 (3) | S1—C1—N2—N3 | -0.4 (2) |
| C4—C5—C6—N1 | -0.7 (3) | C2 ⁱ —C1—N2—Ni1 | 2.7 (2) |
| N3—C7—C8—N4 | -160.31 (18) | S1—C1—N2—Ni1 | -177.46 (8) |
| S1—C7—C8—N4 | 20.7 (2) | C8—C7—N3—N2 | -178.38 (16) |
| N3—C7—C8—C9 | 20.3 (3) | S1—C7—N3—N2 | 0.6 (2) |
| S1—C7—C8—C9 | -158.62 (15) | C1—N2—N3—C7 | -0.1 (2) |
| N4—C8—C9—C10 | -0.3 (3) | Ni1—N2—N3—C7 | 176.26 (13) |
| C7—C8—C9—C10 | 179.01 (18) | C11—C12—N4—C8 | 1.1 (3) |
| C8—C9—C10—C11 | 0.3 (3) | C9—C8—N4—C12 | -0.4 (3) |
| C9—C10—C11—C12 | 0.3 (3) | C7—C8—N4—C12 | -179.74 (17) |
| C10—C11—C12—N4 | -1.0 (3) | N2—C1—S1—C7 | 0.63 (14) |
| C5—C6—N1—C2 | 0.9 (3) | C2 ⁱ —C1—S1—C7 | -179.58 (17) |
| C5—C6—N1—Ni1 | -175.27 (14) | N3—C7—S1—C1 | -0.72 (15) |
| C3—C2—N1—C6 | -0.2 (3) | C8—C7—S1—C1 | 178.31 (16) |
| C1 ⁱ —C2—N1—C6 | -179.56 (16) | | |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| O1—H1W \cdots F1 ⁱⁱ | 0.86 | 1.88 | 2.704 (2) | 160. |
| O1—H2W \cdots F4 | 0.86 | 1.94 | 2.7880 (19) | 171. |

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

Fig. 1

