Synthesis, crystal structure and properties of catena-poly[[[bis(3-methylpyridine-κN)n]ickel(II)]-di-μ-1,3-thiocyanato] acetonitrile monosolvate]

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In the crystal structure of the title compound, [[Ni(NCS)₂(C₆H₇N)₂]·CH₃CN]ₙ, the Ni²⁺ cation is octahedrally coordinated by two N-bonding and two S-bonding thiocyanate anions, as well as two 3-methylpyridine coligands, with the thiocyanate S atoms and the 3-methylpyridine N atoms in cis-positions. The metal cations are linked by pairs of thiocyanate anions into chains that, because of the cis–cis–trans coordination, are corrugated. These chains are arranged in such a way that channels are formed in which disordered acetonitrile solvate molecules are located. This overall structural motif is very similar to that observed in Ni(NCS)₂[4-(boc-amino)pyridine]₂·CH₃CN reported in the literature. At room temperature, the title compound loses its solvent molecules within a few hours, leading to a crystalline phase that is structurally related to that of the pristine material. If the ansovlate is stored in an acetonitrile atmosphere, the solvate is formed again. Single-crystal X-ray analysis at room-temperature proves that the crystals decompose immediately, presumably because of the loss of solvent molecules, and from the reciprocal space plots it is obvious that this reaction, in contrast to that in Ni(NCS)₂[4-(boc-amino)pyridine]₂·CH₃CN, does not proceed via a topotactic reaction.

1. Chemical context

Over the past several years, we and others have been interested in the synthesis and crystal structures of coordination polymers based on transition-metal cations and thiocyanate anions. For this anionic ligand, two major coordination modes are known, which include terminal coordination and the μ-1,3-bridging mode. The latter mode is of special interest if magnetic coordination polymers are to be prepared, because thiocyanate anions can mediate reasonable magnetic exchange (Palion-Gazda et al., 2015; Mekuimemba et al., 2018; Böhme & Plass, 2019; Rams et al., 2020). In the majority of such compounds, the metal cations are octahedrally coordinated by each of two trans thiocyanate S and N atoms as well as two N atoms of neutral coligands that mostly consist of pyridine derivatives. The metal cations are linked by pairs of anionic ligands into chains that, because of the all-trans coordination, are linear (Shurdha et al., 2013; Prananto et al., 2017; Mautner, Traber et al., 2018; Jochim et al., 2020a,b).

For octahedrally coordinated metal cations, however, five different isomers exist, which include the all-trans, all-cis and three cis–cis–trans coordinations. For compounds based on thiocyanate anions, the all-trans coordination is the most common, the all-cis coordination is unknown and the cis–cis–trans-coordination is very rare. It is noted that the latter coordination leads to the formation of linear chains if the...
coligands are in the trans-position (Werner et al., 2014, 2015a,b), whereas corrugated chains are observed if they are in the cis-position (Böhme et al., 2020; Suckert et al., 2017). In this context, we have reported on a compound with the composition \( \text{Ni(NCS)}_2[4-(\text{boc-aminoo})\text{pyridine}]_2\cdot \text{CH}_3\text{CN} \) in which the \( \text{Ni}^{II} \) cations are octahedrally coordinated by four \( \mu-1,3 \)-bridging thiocyanate anions as well as two \( 4-(\text{boc-aminoo})\text{pyridine} \) ligands (Suckert et al., 2017). The coligands and the S-bonding thiocyanate anions are in cis-positions, whereas the two N-bonding anionic ligands are trans, leading to the formation of corrugated chains (Fig. 1: top). These chains are interconnected by strong N–H⋯O hydrogen bonding into layers that are packed in such a way that channels are formed in which disordered acetonitrile solvate molecules are located (Fig. 1: bottom). The acetonitrile molecules can be removed under vacuum and reincorporated via the gas phase without any loss in crystallinity. More importantly, single-crystal structure analysis of one crystal showed that the solvent removal is accompanied by a change in symmetry from primitive to \( C \)-centered. If this crystal is stored in an acetonitrile atmosphere, the solvent is reincorporated and the reflections violating the \( C \)-centering are observed again. Images of reciprocal space at different acetonitrile contents look like that of a single crystal, but the mosaic spread increases during formation of the anisolute and reformation of the solvate, which proves that these reactions proceed via a topotactic reaction (Suckert et al., 2017).

In the course of our systematic work we became interested in \( \text{Ni(NCS)}_2 \) compounds based on 3-methylpyridine (3-picoline) as coligand. Many compounds have been reported with this ligand, but with nickel only discrete complexes with a terminal coordination are known and most of these compounds consist of solvates (see Database survey). An \( \text{Ni(NCS)}_2 \) compound with 3-methylpyridine that shows a bridging coordination of the anionic ligands does not exist. However, in the course of our systematic investigations we accidentally obtained crystals of a further crystalline phase with the composition \( \text{Ni(NCS)}_2(3\text{-methylpyridine})_2\cdot \text{acetonitrile} \). Single-crystal structure analysis shows that a network has formed, which is very similar to that observed in \( \text{Ni(NCS)}_2[4-(\text{boc-aminoo})\text{pyridine}]_2\cdot \text{acetonitrile} \) mentioned above. That both compounds are structurally related is already obvious from their similar unit-cell parameters, but also from the crystal symmetry (see Structural commentary). X-ray powder diffraction proves the formation of a pure crystalline phase (Fig. S1 in the supporting information). In the IR spectrum, the CN-stretching vibration of the thiocyanate anion is observed at 2109 cm\(^{-1}\), in agreement with the presence of \( \mu-1,3 \)-bridging thiocyanate anions and that of the acetonitrile solvate molecules at 2164 cm\(^{-1}\), proving the presence of acetonitrile (Fig. S2). In view of these results, we investigated whether the acetonitrile solvate molecules can be removed from the title compound and if this proceeds via a topotactic reaction as observed in \( \text{Ni(NCS)}_2[4-(\text{boc-aminoo})\text{pyridine}]_2\cdot \text{CH}_3\text{CN} \) mentioned above (Suckert et al., 2017).

Figure 1
Crystal structure of dithiocyanatobis[4-(boc-aminoo)pyridine]nickel(II) acetonitrile solvate retrieved from the literature showing a view of the chains with intermolecular N–H⋯O hydrogen bonding indicated by dashed lines (top) and with a view along the crystallographic \( c \)-axis (bottom).
Experiments using X-ray powder diffraction show that the crystals have already decomposed at room temperature because of the loss of the solvate molecules, leading to the formation of a crystalline phase. The IR spectrum is very similar to that of the pristine phase but the CN-stretching vibration of the acetonitrile ligands have disappeared, proving that the ansolvate has formed (Fig. S3). The X-ray powder pattern of the ansolvate obtained by storing the title compound for 24 h at room temperature is very similar to that of the pristine material, which indicates that both structures must be strongly related (Fig. S4). In particular, the first three intense reflections are shifted to higher Bragg angles, which is in agreement with a decrease of the unit-cell volume. If the ansolvate is stored for 3 d in a desiccator in an acetonitrile atmosphere, the powder pattern is identical to that calculated for the title compound, which proves that this process is reversible. We also tried to determine the crystal structure of the title compound at room temperature, but during the measurement the crystal started to decompose and no reasonable data were obtained. However, the lattice parameters were determined from indexing the reflections and used for the calculation of the powder patterns. Moreover, from the reciprocal space plots of this data set, it is obvious that the mosaic spread strongly increases, which would be in agreement with a topotactic reaction, but the diffraction pattern does not look like that of a single crystal, as was the case for Ni(NCS)$_2$(4-(boc-amino)pyridine)$_2$/C$_3$H$_7$N mentioned above (Suckert et al., 2017).

2. Structural commentary

The asymmetric unit of the title compound consists of one Ni$^{II}$ cation, two thiocyanate anions, two 3-methylpyridine ligands and one acetonitrile molecule, all of them located in general positions (Fig. 2). The Ni cations are octahedrally coordinated by two 3-methylpyridine coligands and two N- as well two S-bonding thiocyanate anions in a $cis$–$cis$–$trans$ coordination with the thiocyanate S atoms and the 3-methylpyridine N atoms in $cis$-positions. The Ni–N and Ni–S bond lengths correspond to those in similar compounds (Table 1). From the bonding angles, it is obvious that the octahedra are slightly distorted (Table 1). This is also obvious from the values of the octahedral angle variance and the mean octahedral quadratic elongation calculated by the method of Robinson et al. (1971), which amount to 12.7996 and 1.0190.

3. Supramolecular features

In the crystal structure of the title compound, the chains proceed in the direction of the crystallographic c-axis and are arranged in such a way that cavities are formed, in which disordered acetonitrile molecules are embedded (Figs. 4 and 5). This arrangement is very similar to that observed in Ni(NCS)$_2$(4-(boc-amino)pyridine)$_2$/C$_3$H$_7$N already reported in the literature (please compare Fig. 1 with Figs. 4 and 5, Suckert et al., 2017). That this structure is structurally related to that of the title compound is also indicated by comparing their unit-cell parameters and their space groups. Ni(NCS)$_2$(4-(boc-amino)pyridine)$_2$/C$_3$H$_7$N crystallizes in space group

| Table 1 | Selected geometric parameters ($\text{Å}$, $\text{°}$). |
|-----------------|-----------------|-----------------|
| Ni1–N1          | 2.0285 (11)     | Ni1–Si$^1$      | 2.5508 (4)     |
| Ni1–N1$^1$      | 2.0286 (11)     | Ni1–N11         | 2.0836 (11)    |
| Ni1–N11         | 175.54 (6)      | Si$^1$–Ni1–Si$^1$ | 87.022 (18)   |
| Ni1–N11–Si$^1$  | 83.43 (3)       | N1–N11–Si$^1$   | 173.74 (3)     |
| Ni1–N11–Si$^1$  | 93.32 (3)       | N1–N11–Si$^1$   | 89.87 (3)      |
| Ni1–N11–N11     | 91.71 (4)       | N1–N11–N11$^1$  | 93.73 (6)      |
| Ni1–N11–N11$^1$ | 91.34 (4)       |                 |                |

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

Figure 2
Crystal structure of the title compound with labeling and displacement parameters drawn at the 50% probability level. Symmetry codes: (A) $-x+1, y, -z+\frac{1}{2}$; (B) $-x+1, -y, -z$; (C) $x, -y, z+\frac{1}{2}$.

Figure 3
Crystal structure of the title compound with view of part of a chain showing the Ni coordination along the crystallographic a-axis.
Finally, it is noted that there are no pronounced intermolecular hydrogen bonds in the title compound, except for one C—H⋯N contact that is much too long for any significant interaction [C22—H22A⋯N21(1 — x, y, 1/2 — z), H⋯N = 1.61 Å, C⋯N = 2.57 (2) Å, C—H⋯N = 162°]. This is in contrast to Ni(NCS)₂{4-(boc-amino)pyridine}_₂CH₃CN where the chains are linked by strong N—H⋯O hydrogen bonding, which might be the reason why this compound is much more stable than the title compound.

4. Database survey

A search in the Cambridge Structure Database (CSD, version 5.43, last update November 2021; Groom et al., 2016) for transition-metal thiocyanate compounds with 3-methylpyridine as coligand leads to several hits. There are a couple of known compounds containing nickel, all of which are discrete complexes of the composition Ni(NCS)₂(3-methylpyridine)₄ that contain additional solvate molecules such as one molecule per complex of a mixture of dibromo and dichloromethane, of 2,2-dichloropropane and of dichloromethane, as well as two molecules of dichloromethane and trichloromethane (LAYLAY, LAYLEC, LAYLUS, LAYLIG and LAYLOM; Pang et al., 1992). Moreover, crystal structures of the monochloromethane (CIVJEW and CIFJEW01; Nassimbeni et al., 1984, 1986) and monotetrachloromethane solvate (JICMIR; Pang et al., 1990) have also been reported. In Ni(NCS)₂(3-methylpyridine)₂(H₂O)₂, two of the coligands are substituted by aqua ligands and no solvate molecules are present (MEGCEH; Tan et al., 2006).

In the discrete copper complex Cu(NCS)₂(3-methylpyridine)₂ (ABOTET; Handy et al., 2017) the metal center is fourfold and in Cu(NCS)₂(3-methylpyridine), (VEPBAT; Kabešová & Kožíšková, 1989) fivefold coordinated. Also one more copper compound with the composition Cu(NCS)(3-methylpyridine)₂ (CUHBEM; Healy et al., 1984) has been reported in which the cations are tetrahedrally coordinated by two coligands and also two thiocyanate anions, linking them into chains. Some compounds with Co(NCS)₂ and 3-methylpyridine can also be found in the CSD. All are discrete complexes, but Co(NCS)₂(3-methylpyridine)_₂ (EYARIG; Boeckmann et al., 2011) has a tetrahedral coordination around the metal center compared to the octahedral complexes Co(NCS)₂(3-methylpyridine)₄ (EYAROM and EYAROM01; Boeckmann et al., 2011 and Malecki et al., 2012) and Co(NCS)₂(3-methylpyridine)₂(H₂O)₂ (EYAREC; Boeckmann et al., 2011).

With zinc and cadmium, just one compound could be found each, viz. the discrete tetrahedral complex Zn(NCS)₂(3-methylpyridine)₂ (ETUSAO; Boeckmann & Näther, 2011) and Cd(NCS)₂(3-methylpyridine)₂ (FIYGUP; Taniguchi et al., 1987) with octahedrally coordinated cations that are linked into chains by the thiocyanate anions. Although not yet included in this CSD version, an octahedral iron complex is known, with the cations coordinated by two thiocyanate anions and four 3-methylpyridine ligands (Ceglarska et al., 2022), which was reported analogously also as an isotypic
complex with manganese in the same publication. Otherwise, only one more manganese compound is reported, which however contains 3-methylpyridine-N-oxide ligands and consists of a chain structure (KESSAF; Mautner, Berger et al., 2018). There are also two compounds with a mixed-metal composition, on the one hand with catena-[tetakis(thiocyanato)bis(3-methylpyridine)manganese] (NAQYOW; Malecki, 2017a) and on the other hand with catena-[tetakis-(μ-thiocyanato)bis(3-methylpyridine)mercury] (OAMS-IJ; Malecki, 2017b).

5. Synthesis and crystallization

Synthesis

Ni(NCS)2 was purchased from Santa Cruz Biotechnology and 3-methylpyridine was purchased from Alfa Aesar. Acetonitrile, which was used as the solvent, was dried over CaH2 before use.

Ni(NCS)2(3-methylpyridine)2-acetonitrile: The reaction mixture containing 0.25 mmol of Ni(NCS)2 (43.7 mg) and 0.25 mmol of 3-methylpyridine (24.3 mg) in 1.5 mL of acetonitrile was stirred for 2 days at room temperature, resulting in light-green crystals suitable for single-crystal X-ray diffraction measurements.

Experimental details

The data collection for single-crystal structure analysis was performed using an XtaLAB Synergy, Dualflex, HyPix diffractometer from Rigaku with Cu Ka radiation. The PXRD measurements were performed with a Stoe Transmission Powder Diffraction System (STADI P) that is equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator using Cu Ka radiation (λ = 1.540598 Å). The IR spectra were measured using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Matson. The instruments were calibrated using standard reference materials.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. The C-bound H atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with Uiso(H) = 1.2Ueq(C) (1.5 for methyl H atoms) using a riding model. The acetonitrile solvate molecules are disordered within the channels around a center of inversion, which is located in the middle of two acetonitrile N atoms that show an N–N distance of 1.151 Å. Therefore, they were refined with an sof of 0.5, leading to reasonable anisotropic displacement parameters. The situation is similar to that in Ni(NCS)2[4-(bocamino)pyridine]2-acetonitrile mentioned above.

It is noted that some additional reflections are observed, leading to a doubling of the unit cell and change from C-centered to primitive. The relation between the sub-cell and the super cell is obvious if the super cell [a = 16.3542 (5) Å, b = 23.4916 (8) Å, c = 9.7358 (3) Å and β = 94.977 (3)°, space group P21/c] is compared with the sub-cell in space group P21/a instead of C2/c [a = 9.3838 (1) Å, b = 11.7493 (1) Å, c = 16.3513 (1) Å and β = 94.927 (1)°]. However, only very few reflections were observed and their intensity is close to zero (Fig. S5). Nevertheless, the structure can easily be refined in space group P21/c, leading to two crystallographically independent NiII cations and two unique acetonitrile ligands, but a closer look reveals that even in the super cell the solvate molecules are disordered. Therefore, the very few and weak additional reflections were neglected.

Acknowledgements

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Synthesis, crystal structure and properties of catena-poly[[bis(3-methylpyridine-κN)nickel(II)]-di-μ-1,3-thiocyanato] acetonitrile monosolvate

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Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2016/6 (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg & Putz, 1999); software used to prepare material for publication: publCIF (Westrip, 2010).

catena-Poly[[bis(3-methylpyridine-κN)nickel(II)]-di-μ-1,3-thiocyanato] acetonitrile monosolvate

Crystal data
[Ni(NCS)₂(C₆H₇N)₂]·C₂H₃N
Mr = 402.17
Monoclinic, C2/c
a = 18.2934 (9) Å
b = 11.7472 (4) Å
c = 9.7341 (5) Å
β = 117.043 (6)°
V = 1863.11 (17) Å³
Z = 4

F(000) = 832
Dx = 1.434 Mg m⁻³
Cu Kα radiation, λ = 1.54178 Å
Cell parameters from 9752 reflections
θ = 4.6–77.2°
µ = 3.65 mm⁻¹
T = 100 K
Plate, light green
0.15 × 0.15 × 0.03 mm

Data collection
XtaLAB Synergy, Dualflex, HyPix
diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.000 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2021)

Tmin = 0.705, Tmax = 1.000
11840 measured reflections
1966 independent reflections
1955 reflections with I > 2σ(I)
Rint = 0.015
θmax = 77.7°, θmin = 4.6°
h = −23→21
k = −13→14
l = −10→12

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.024
wR(F²) = 0.066
S = 1.07
1966 reflections
125 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
w = 1/[σ²(Fo²) + (0.0356P)² + 1.9913P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max = 0.001
Δρmax = 0.27 e Å⁻³
Δρmin = −0.37 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 (Å²)**

| Atom  | x      | y      | z      | Uiso  | Occ. (<1) |
|-------|--------|--------|--------|-------|-----------|
| Ni1   | 0.500000 | 0.11950 (2) | 0.250000 | 0.01509 (10) |           |
| N1    | 0.54965 (7) | 0.11278 (9) | 0.10148 (12) | 0.0185 (2) |           |
| C1    | 0.57231 (7) | 0.08251 (10) | 0.01406 (14) | 0.0165 (2) |           |
| S1    | 0.60344 (2) | 0.03798 (3) | −0.11091 (4) | 0.01977 (10) |           |
| N11   | 0.58540 (6) | 0.24076 (9) | 0.38595 (12) | 0.0181 (2) |           |
| C11   | 0.62454 (8) | 0.22828 (11) | 0.53994 (15) | 0.0204 (3) |           |
| H11   | 0.607248 | 0.168907 | 0.584775 | 0.025* |           |
| C12   | 0.68901 (8) | 0.29758 (12) | 0.63729 (16) | 0.0244 (3) |           |
| C13   | 0.71270 (9) | 0.38429 (13) | 0.56974 (18) | 0.0297 (3) |           |
| H13   | 0.756660 | 0.433386 | 0.631780 | 0.036* |           |
| C14   | 0.67207 (10) | 0.39913 (13) | 0.41148 (19) | 0.0309 (3) |           |
| H14   | 0.683754 | 0.458893 | 0.363972 | 0.037* |           |
| C15   | 0.60876 (9) | 0.32557 (12) | 0.32326 (16) | 0.0240 (3) |           |
| H15   | 0.581066 | 0.335802 | 0.214608 | 0.029* |           |
| C16   | 0.73170 (9) | 0.27472 (15) | 0.80794 (17) | 0.0336 (3) |           |
| H16A  | 0.696992 | 0.226009 | 0.835783 | 0.050* |           |
| H16B  | 0.741856 | 0.346916 | 0.864123 | 0.050* |           |
| H16C  | 0.784063 | 0.236346 | 0.835127 | 0.050* |           |
| N21   | 0.4958 (3) | 0.5343 (3) | 0.0380 (4) | 0.0525 (8) | 0.5       |
| C21   | 0.4990 (2) | 0.5882 (3) | 0.1369 (4) | 0.0366 (7) | 0.5       |
| C22   | 0.4981 (19) | 0.6557 (4) | 0.238 (3) | 0.059 (3) | 0.5       |
| H22A  | 0.511446 | 0.613590 | 0.333381 | 0.089* | 0.5       |
| H22B  | 0.443345 | 0.689575 | 0.200183 | 0.089* | 0.5       |
| H22C  | 0.538683 | 0.716083 | 0.258413 | 0.089* | 0.5       |

**Atomic displacement parameters (Å²)**

|   | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|---|------|------|------|------|------|------|
| Ni1 | 0.01446 (16) | 0.01706 (17) | 0.01370 (16) | 0.000 | 0.00635 (12) | 0.000 |
| N1  | 0.0076 (5) | 0.0192 (5) | 0.0184 (5) | −0.0016 (4) | 0.00080 (4) | −0.0005 (4) |
| C1  | 0.0134 (5) | 0.0164 (6) | 0.0163 (6) | −0.0017 (4) | 0.0039 (4) | 0.0010 (4) |
| S1  | 0.0090 (5) | 0.0184 (5) | 0.0196 (5) | −0.0010 (4) | 0.0018 (4) | −0.0021 (4) |
| C11 | 0.00190 (6) | 0.00237 (6) | 0.0189 (6) | −0.0030 (5) | 0.0087 (5) | −0.0027 (5) |
| C12 | 0.0096 (6) | 0.00288 (7) | 0.0245 (6) | −0.0049 (5) | 0.0101 (5) | −0.0068 (5) |
| C13 | 0.0025 (7) | 0.00305 (8) | 0.0057 (8) | −0.0012 (4) | 0.0148 (6) | −0.0105 (6) |
| C14 | 0.0035 (8) | 0.00266 (7) | 0.0054 (8) | −0.0010 (4) | 0.0203 (7) | −0.0018 (6) |
| C15 | 0.0027 (6) | 0.00223 (6) | 0.0045 (6) | −0.0022 (5) | 0.0135 (5) | −0.0006 (5) |
| C16 | 0.0028 (7) | 0.00454 (9) | 0.0219 (7) | −0.0141 (7) | 0.0070 (6) | −0.0098 (6) |
Geometric parameters (Å, °)

| Bond/Angle | Value (Å/°) |
|------------|-------------|
| Ni1—N1     | 2.0285 (11) |
| Ni1—N1i    | 2.0286 (11) |
| Ni1—S1î    | 2.5508 (4)  |
| Ni1—S1îi   | 2.5508 (4)  |
| Ni1—N1îi   | 2.0836 (11) |
| Ni1—N1i    | 2.0836 (11) |
| Ni1—C1     | 1.1590 (17) |
| C1—S1      | 1.6456 (13) |
| N11—C11    | 1.3435 (16) |
| N11—C15    | 1.3360 (17) |
| C11—C15    | 0.9500      |
| C11—C12    | 1.3912 (18) |
| C12—C13    | 1.384 (2)   |
| C12—C16    | 1.504 (2)   |
| N1—Ni1—N1i | 175.54 (6)  |
| N1—Ni1—S1îi| 83.43 (3)   |
| N1—Ni1—S1î | 93.32 (3)   |
| N1—Ni1—N1îi| 93.32 (3)   |
| N1—Ni1—N1i | 83.43 (3)   |
| N1—Ni1—N11 | 91.71 (4)   |
| N1—Ni1—N1îi| 91.71 (4)   |
| S1î—Ni1—S1îii| 87.022 (18) |
| N1îi—Ni1—S1îii| 173.74 (3) |
| N1îi—Ni1—S1î| 173.74 (3) |
| N1îi—Ni1—S1îi | 89.87 (3)  |
| N1îi—Ni1—S1î | 89.87 (3)  |
| N1îi—Ni1—N1îi| 93.73 (6)  |
| C1—N1—Ni1  | 163.89 (10) |
| N1—C1—S1   | 179.13 (12) |
| C1—C1—N1   | 101.56 (4)  |
| C1—N1—N1i  | 119.96 (9)  |
| C1—C1—N1i  | 121.53 (9)  |
| C1—C1—N1îi | 118.17 (11) |
| C1—C1—H1i  | 118.2       |
| C1—C1—H1i  | 123.56 (12) |
| C1—C1—H1i  | 118.2       |
| C1—C1—C16  | 120.10 (13) |
| N1—N1i—C11—C12| 172.20 (10) |

**Supporting Information**

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Ni1—N11—C15—C14  -172.51 (11)  C12—C13—C14—C15  -0.8 (2)
N11—C11—C12—C13  0.6 (2)  C13—C14—C15—N11  0.2 (2)
N11—C11—C12—C16  -177.52 (13)  C15—N11—C11—C12  -1.20 (19)
C11—N11—C15—C14  0.8 (2)  C16—C12—C13—C14  178.47 (15)

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