Syntheses and crystal structures of the ethanol, acetonitrile and diethyl ether Werner clathrates bis(isothiocyanato-κN)tetrakis(3-methylpyridine-κN)nickel(II)

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The reaction of nickel(II)thiocyanate with 3-methylpyridine (3-picoline; C₆H₇N) in different solvents leads to the formation of crystals of bis(isothiocyanato-κN)tetrakis(3-methylpyridine-κN)nickel(II) as the ethanol disolvate, [Ni(NCS)₂(C₆H₇N)₄]·2C₂H₅OH (1), the acetonitrile disolvate, [Ni(NCS)₂(C₆H₇N)₄]·2CH₃CN (2), and the diethyl ether monosolvate, [Ni(NCS)₂(C₆H₇N)₄]·C₄H₁₀O (3). The crystal structures of these compounds consist of NiN₆ octahedra with the thiocyanate groups in a trans orientation. In compounds 1 and 2 these complexes are located on centers of inversion, whereas in compound 3, they occupy general positions. In the crystal structures, the complexes are packed in such a way that cavities are formed in which the solvent molecules are located. Compounds 1 and 2 are isotypic, which is not the case for compound 3. In compounds 1 and 2 the solvate molecules are disordered, whereas they are fully ordered in compound 3. Disorder is also observed for one of the 3-methylpyridine ligands in compound 2. Powder X-ray diffraction and IR measurements show that at room temperature all compounds decompose almost immediately into the same phase, as a result of the loss of the solvent molecules.

1. Chemical context

The synthesis and structural characterization of new compounds is still an important topic in coordination chemistry, because some of them might have the potential for future applications such as magnetic behavior. In this context, coordination compounds in which the cations are linked by small-sized anionic ligands into networks of different dimensionality are of special interest. Therefore, many compounds based on, for example, cyanide or azide ligands have been reported in the literature. Magnetic exchange can also be mediated by thiocyanate anions and this is one reason why we and others have been interested in this class of compounds for many years (Mautner et al., 2018, Rams et al., 2020, Böhme et al., 2020). Regarding this, compounds are of interest in which the paramagnetic metal cations are linked by thiocyanate anions into chains or layers (Werner et al., 2014, 2015a,b; Suckert et al., 2016). In contrast to azides or cyanides, the synthesis of thiocyanates with bridging coordination is more difficult to achieve, because metal cations such as Mn²⁺, Fe²⁺, Co²⁺ and Ni²⁺ are less chalcophilic and therefore prefer a terminal N coordination. Nevertheless, a large number of compounds with μ-1,3-bridging thiocyanate anions have been...
reported in recent years (Mautner et al., 2018 and Werner et al., 2015a,b).

In our own investigations, we are particularly interested in the influence of the neutral co-ligand on the chemical reactivity, the crystal structure and the magnetic properties of thiocyanate coordination polymers of 3d metal cations. In most cases, we used pyridine derivatives that are substituted in the 4-position as co-ligands, but recently we also became interested in such ligands where the substituent is located in the 3-position, including 3-methylpyridine (also called 3-picoline), C₆H₇N. With Co(NCS)₂, two discrete complexes with the composition Co(NCS)₂(C₆H₇N)₄ (refcodes EYAROM and EYAROM01; Boeckmann et al., 2011 and Malecki et al., 2012) and Co(NCS)₂(C₆H₇N)₂(H₂O)₂ (EYAREC; Boeckmann et al., 2011) are deposited in the Cambridge Structural Database, in which the cobalt cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and two 3-methylpyridine in the former compound and two 3-methylpyridine and two water ligands in the latter. Upon heating, these complexes lose half of their co-ligands and transform into Co(NCS)₂(C₆H₇N)₂ (EYARIG; Boeckmann et al., 2011) before a decomposition into Co(NCS)₂ is observed. Surprisingly, in contrast to most other compounds with pyridine derivatives substituted in the 4-position where chains or layers are formed, in this compound the CoII cations are tetrahedrally coordinated by two terminal N-bonded thiocyanate anions and two 3-methylpyridine co-ligands, forming discrete complexes.

Most compounds with 3-methylpyridine as co-ligand are reported with Ni(NCS)₂, but surprisingly in none of them are the NiII cations linked by the thiocyanate anions. This includes, for example, Ni(NCS)₂(C₆H₇N)₂(H₂O)₂ (MEGCEH; Tan et al., 2006), which is isotypic to its cobalt analog. Moreover, a number of compounds consist of discrete complexes with the general composition Ni(NCS)₂(C₆H₇N)₄ in which the NiII cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions as well as by four 3-methylpyridine co-ligands. In all of these compounds, the discrete complexes are packed in such a way that cavities are formed, in which additional solvate molecules are embedded. Altogether, three different structure types are observed. The mono-dichloromethane (Laylus, Pang et al., 1992), mono-trichloromethane (CIVJEW and CIFJEW01; Nassimbeni et al., 1984, 1986), mono-tetrachloromethane, mono-dibromo-dichloromethane and mono-2,2-dichloropropane clathrates (JICMIR, LAYLAY and LAYLEC; Pang et al., 1990, 1992) crystallize in the orthorhombic space group P2₁2₁2₁. If two molecules of trichloromethane are incorporated, the clathrate crystallizes with triclinic symmetry in space group P₁ (LAYLIG; Pang et al., 1992). It is noted that the two latter unit cells are crystallographically unrelated. The formation of these clathrates for such simple nickel complexes is surprising because this is not observed in practically all other complexes with Ni(NCS)₂ and pyridine derivatives as co-ligands. However, it might be traced back to the fact that all of these solvents are non-polar and cannot coordinate to NiII cations to form, for example, solvato octahedral complexes with the composition Ni(NCS)₂(L)₂ (L = co-ligand).

Based on these assumptions, we tried to prepare additional compounds based on Ni(NCS)₂ and 3-methylpyridine as co-ligand, for which we used diethyl ether, ethanol and acetonitrile as solvents. All of them can coordinate to NiII cations, which might lead to solvato complexes that afterwards might be transformed into the desired compounds with a bridging coordination by thermal decomposition. On the other hand, they are not very strong donor ligands, which means that compounds with a bridging coordination of the anionic ligands might form directly. With all three solvents, suitable crystals were obtained, which were characterized by single-crystal X-ray diffraction. Structure analysis reveals that even in this case, clathrates with the composition Ni(NCS)₂(C₆H₇N)₂ · 2 ethanol (1), Ni(NCS)₂(C₆H₇N)₂ · 2 acetonitrile (2) and Ni(NCS)₂(C₆H₇N)₂ · diethyl ether (3) have formed, which crystallize in two different structure types, with compounds 1 and 2 isotypic to the bis(dichloromethane) clathrate reported by Pang et al. (1992). Unfortunately, all of these compounds lose their solvents almost immediately at room temperature and X-ray powder diffraction shows that the same crystalline phase is obtained (Fig. S1 in the supporting information). In their IR spectra, the CN stretching vibration is observed at 2074 cm⁻¹, indicating that the anionic ligands are still terminally N-bonded (Fig. S2). Therefore, one can assume that a solvent-free compound with the composition Ni(NCS)₂(C₆H₇N)₄ has formed, that still consists of discrete complexes and for which the crystal structure is unknown.

2. Structural commentary
The asymmetric units of Ni(NCS)₂(C₆H₇N)₄ · 2 ethanol (1) and Ni(NCS)₂(C₆H₇N)₂ · 2 acetonitrile (2) consist of half of an NiII cation that is located on a center of inversion, one thiocyanate anion and two 3-methylpyridine ligands as well as one ethanol (1) and one acetonitrile (2) solvate molecules in general positions (Figs. 1 and 2). The asymmetric unit in
Ni(NCS)₂(C₆H₇N)₄·diethyl ether (3) consists of one Ni II cation, two thiocyanate anions, four 3-methylpyridine ligands and one diethyl ether solvate molecule that occupy general positions (Fig. 3). In compounds 1 and 2, the solvate molecules are disordered and were refined using a split model (see Refinement), whereas in compound 3 they are fully ordered. The ethanol and acetonitrile solvates 1 and 2 crystallize in the monoclinic C-centered space group C2/c and are isotypic to the bis(dichloromethane) clathrate reported by Pang et al. (1992). Compound 3 crystallizes in space group P2₁/n and its structure type is different from that of the solvates of Ni(NCS)₂(C₆H₇N)₄ already reported in the literature (see Chemical Context).

In all three compounds the nickel(II) cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and four 3-methylpyridine co-ligands, forming discrete complexes. In compound 1 and 2 the discrete complexes are located on centers of inversion, whereas in compound 3 the complexes are located in general positions. The Ni—N bond lengths are comparable in all three compounds (Tables 1–3) and from the bonding angles, it is obvious that all octahedra are slightly distorted (see supporting information). This is reflected in the octahedral angle variance and the mean octahedral quadratic elongation calculated by the method of Robinson et al. (1971), which amount to 0.0857/2 and 1.0004, respectively, for compound 1, 0.3299/2 and 1.0006 for compound 2 and 1.0694/2 and 1.0010 for compound 3.

| Table 1 | Selected bond lengths (Å) for 1. |
|---------|---------------------------------|
| Ni1—N1 | 2.0597 (13) Ni1—N21 2.1200 (11) |
| Ni1—N11| 2.1196 (12) |

| Table 2 | Selected bond lengths (Å) for 2. |
|---------|---------------------------------|
| Ni1—N1 | 2.0528 (16) Ni1—N21 2.1224 (13) |
| Ni1—N11| 2.1235 (14) |

| Table 3 | Selected bond lengths (Å) for 3. |
|---------|---------------------------------|
| Ni1—N1 | 2.0517 (11) Ni1—N21 2.1266 (10) |
| Ni1—N2 | 2.0552 (11) Ni1—N31 2.1523 (11) |
| Ni1—N11| 2.1358 (10) Ni1—N41 2.1291 (11) |

![Figure 1](image1.png) The molecular structure of compound 1 with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: (A) −x + 1, y, −z + 3/2.

![Figure 2](image2.png) The molecular structure of compound 2 with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: (A) −x + 1, y, −z + 3/2.

![Figure 3](image3.png) The molecular structure of compound 3 with labeling and displacement ellipsoids drawn at the 50% probability level.

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3. Supramolecular features

In the crystal structures, the Ni(NCS)₂(C₆H₇N)₄ complexes are packed in such a way that cavities are formed, in which the solvate molecules are embedded (Figs. 4 and 5). In compound 1, both ethanol molecules are linked to the complex by O—H···S hydrogen bonding between the hydroxyl hydrogen atom of the ethanol molecule and the thiocyanate S atom (Fig. 4). The H···S distance amounts to 2.464 (4) Å and the O—H···S angle to 172 (2)°, which indicates that this is a strong interaction (Table 4). There is one additional intermolecular contact between a pyridine H atom and the ethanol O atom, but the distance and geometry of this contact shows that this should be only a very weak interaction (Table 4). In the isotypic compound 2, no pronounced intermolecular interactions are observed and the packing seems to be dominated by van der Waals interactions. This is similar in the diethyl ether solvate 3, where the complexes are arranged in stacks along the c-axis direction (Fig. 5). For all compounds, the void spaces occupied by the solvate molecules were calculated, leading to values of 221 Å³ (6.5%) for 1, 162 Å³ (4.8%) for 2 and 165 Å³ (5.1%) for 3. The higher value for compound 1 might be traced back to the intermolecular hydrogen bonding.

4. Database survey

Several thiocyanate compounds with transition metal cations and 3-methylpyridine as co-ligand are reported in the Cambridge Structure Database CSD (version 5.43, last update November 2021; Groom et al., 2016), including the Co and Ni compounds mentioned above.

With Cd(NCS)₂, one compound with the composition Cd(NCS)₂(C₆H₇N)₂ (FIYGUP; Taniguchi et al., 1987) is reported, in which the Cd II cations are octahedrally coordinated and linked by pairs of thiocyanate anions into chains. With copper, discrete complexes with the composition Cu(NCS)₂(C₆H₇N)₂ (ABOTET; Handy et al., 2017) and Cu(NCS)₂(C₆H₇N)₃ (VEPBAT; Kabešová & Kožíšková, 1989) are reported. There is also one chain compound with the composition Cu(NCS)₂(C₆H₇N)₂ (CUHBEM; Healy et al., 1984), in which the copper cations are tetrahedrally coordinated. With Zn(NCS)₂, the discrete complex Zn(NCS)₂(C₆H₇N)₂ with a tetrahedral structure is found (ETUSAO; Boeckmann & Näther, 2011), which is isotypic to Co(NCS)₂(C₆H₇N)₂. With Mn II and Fe II, two discrete complexes with the composition M(NCS)₂(C₆H₇N)₄ (M = Mn, Fe) are reported (Ceglarska et al., 2022). Additionally there is also a mixed-metal compound with manganese and mercury with the composition catena-[tetrakis(thiocyanato)bis[3-methylpyridine]manganese-mercury] (NAQYOW; Malecki, 2017).

5. Synthesis and crystallization

Synthesis

3-Methylpyridine was purchased from Alfa Aesar. Ni(NCS)₂ was purchased from Santa Cruz Biotechnology.
Acetonitrile was dried over CaH$_2$ and ethanol over sodium before use.

$\text{Ni}$(NCS)$_2$(C$_6$H$_7$N)$_4$: 2 ethanol (1): 0.25 mmol $\text{Ni}$(NCS)$_2$ (43.7 mg) and 2.5 mmol 3-methylpyridine (243 µl) were added to 1.5 ml of ethanol and stored under hydrothermal conditions at 403 K to form light-purple single crystals.

$\text{Ni}$(NCS)$_2$(C$_6$H$_7$N)$_4$: 2 acetonitrile (2): To synthesize single crystals suitable for single-crystal X-ray analysis, 0.25 mmol of $\text{Ni}$(NCS)$_2$ (43.7 mg) and 2.5 mmol of 3-methylpyrididine (243 µl) were combined in a snap-cap vial and 1.5 ml of acetonitrile were added. After two days at room temperature, light-purple blocks were obtained.

$\text{Ni}$(NCS)$_2$(C$_6$H$_7$N)$_4$: diethyl ether (3): In a mixture of diethyl ether and H$_2$O, 0.25 mmol of $\text{Ni}$(NCS)$_2$ (43.7 mg) and 2.5 mmol of 3-methylpyrididine (243 µl) were added. Single crystals in the form of light-purple blocks were obtained after heating the reaction mixture to 353 K and storing it at this temperature for two days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. 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 $U_{	ext{iso}}$(H) = 1.2 $U_{	ext{eq}}$(C) (1.5 for methyl H atoms) using a riding model.

Funding information

Financial support by the State of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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Syntheses and crystal structures of the ethanol, acetonitrile and diethyl ether Werner clathrates bis(isothiocyanato-κN)tetrakis(3-methylpyridine-κN)nickel(II)

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Computing details
For all structures, 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).

Bis(isothiocyanato-κN)tetrakis(3-methylpyridine-κN)nickel(II) ethanol disolvate (1)

Crystal data
[Ni(NCS)2(C6H7N)4]·2C2H6O
Mr = 639.51
Monoclinic, C2/c
a = 18.5763 (1) Å
b = 11.6179 (1) Å
c = 15.8998 (1) Å
β = 97.448 (1)°
V = 3402.51 (4) Å³
Z = 4

F(000) = 1352
Dc = 1.248 Mg m⁻³
Cu Kα radiation, λ = 1.54184 Å
Cell parameters from 28027 reflections
θ = 4.5–79.4°
µ = 2.24 mm⁻¹
T = 100 K
Block, light purple
0.2 × 0.1 × 0.05 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: 10.0000 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2021)
Tmin = 0.857, Tmax = 1.000
36997 measured reflections
3672 independent reflections
3589 reflections with I > 2σ(I)
Rint = 0.018
θmax = 79.7°, θmin = 4.5°
h = −23→21
k = −14→14
l = −19→20

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.036
wR(F²) = 0.098
S = 1.09
3672 reflections
213 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(Fo²) + (0.0454P)² + 3.9194P]
where P = (Fo² + 2Fe²)/3
(Δ/σ)max = 0.001
Δρmax = 0.44 e Å⁻³
Δρmin = −0.38 e Å⁻³
Extinction correction: SHELXL-2016/6
(Sheldrick 2015b),
\[
F_{c}^* = k F_{c} [1 + 0.001 x F_{c}^{2} / \lambda^{2} / \sin(2 \theta)]^{1/4}
\]
Extinction coefficient: 0.00015 (4)

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* | Ueq | Occ. (<1) |
|------|------|------|------|-------|-----|-----------|
| Ni1  | 0.500000 | 0.25420 (2) | 0.750000 | 0.01790 (12) |
| N1   | 0.42011 (7) | 0.25422 (10) | 0.82854 (8) | 0.0245 (3) |
| C1   | 0.36585 (8) | 0.25217 (11) | 0.85683 (9) | 0.0221 (3) |
| S1   | 0.28878 (2) | 0.24794 (3) | 0.89699 (2) | 0.03098 (12) |
| N11  | 0.55731 (6) | 0.33824 (10) | 0.82555 (7) | 0.0245 (2) |
| C11  | 0.52238 (9) | 0.47165 (12) | 0.85584 (9) | 0.0288 (3) |
| H11  | 0.470896 | 0.473317 | 0.844620 | 0.035* |
| C12  | 0.55721 (10) | 0.56143 (14) | 0.90293 (11) | 0.0398 (4) |
| C13  | 0.63193 (12) | 0.5568 (2) | 0.91929 (16) | 0.0632 (7) |
| H13  | 0.657909 | 0.615808 | 0.951651 | 0.076* |
| C14  | 0.66863 (11) | 0.4666 (2) | 0.88857 (16) | 0.0678 (7) |
| H14  | 0.720101 | 0.462974 | 0.899044 | 0.081* |
| C15  | 0.62980 (9) | 0.38109 (16) | 0.84226 (11) | 0.0393 (4) |
| H15  | 0.655461 | 0.318635 | 0.821579 | 0.047* |
| C16  | 0.51427 (13) | 0.65865 (17) | 0.93377 (14) | 0.0536 (5) |
| H16A | 0.506739 | 0.718348 | 0.889971 | 0.080* |
| H16B | 0.540910 | 0.691251 | 0.985543 | 0.080* |
| H16C | 0.467130 | 0.629800 | 0.945930 | 0.080* |
| N21  | 0.44290 (6) | 0.12465 (10) | 0.67471 (7) | 0.0212 (2) |
| C21  | 0.43798 (7) | 0.12692 (12) | 0.58975 (8) | 0.0220 (3) |
| H21  | 0.406160 | 0.189164 | 0.564102 | 0.026* |
| C22  | 0.40237 (7) | 0.04368 (12) | 0.53708 (8) | 0.0248 (3) |
| C23  | 0.37036 (9) | −0.04668 (14) | 0.57566 (10) | 0.0329 (3) |
| H23  | 0.345507 | −0.105716 | 0.542233 | 0.039* |
| C24  | 0.37492 (10) | −0.05012 (15) | 0.66333 (10) | 0.0381 (4) |
| H24  | 0.353266 | −0.111351 | 0.690695 | 0.046* |
| C25  | 0.41140 (8) | 0.03678 (13) | 0.71022 (9) | 0.0294 (3) |
| H25  | 0.414269 | 0.034090 | 0.770276 | 0.035* |
| C26  | 0.39962 (9) | 0.05215 (14) | 0.44214 (9) | 0.0323 (3) |
| H26A | 0.361753 | 0.106922 | 0.419902 | 0.048* |
| H26B | 0.388635 | −0.023684 | 0.416676 | 0.048* |
| H26C | 0.446699 | 0.078720 | 0.428104 | 0.048* |
| O31  | 0.21100 (8) | 0.26594 (14) | 0.69605 (11) | 0.0553 (4) |
| H31  | 0.2297 (17) | 0.253 (2) | 0.749 (2) | 0.081 (10)* |
| C31  | 0.2139 (2) | 0.1760 (4) | 0.6416 (3) | 0.0422 (8) | 0.5 |
Atomic displacement parameters (Å²)

|       | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|-------|-----|-----|-----|-----|-----|-----|
| Ni1   | 0.01946 (19) | 0.01906 (18) | 0.01550 (18) | 0.0000 | 0.00346 (12) | 0.0000 |
| N1    | 0.0232 (6) | 0.0273 (6) | 0.0235 (6) | 0.0014 (4) | 0.0054 (5) | 0.0020 (4) |
| C1    | 0.0271 (7) | 0.0214 (6) | 0.0178 (6) | 0.0030 (5) | 0.0024 (5) | 0.0015 (4) |
| S1    | 0.0215 (2) | 0.0433 (2) | 0.0295 (2) | 0.00391 (13) | 0.00857 (15) | 0.00623 (14) |
| N11   | 0.0283 (6) | 0.0239 (6) | 0.0218 (5) | -0.0037 (5) | 0.0046 (4) | -0.0031 (4) |
| C11   | 0.0368 (8) | 0.0249 (7) | 0.0257 (7) | -0.0014 (6) | 0.0079 (6) | -0.0026 (5) |
| C12   | 0.0528 (10) | 0.0317 (8) | 0.0383 (8) | -0.0107 (7) | 0.0190 (7) | -0.0116 (7) |
| C13   | 0.0501 (11) | 0.0683 (14) | 0.0754 (15) | -0.0315 (10) | 0.0244 (10) | -0.0458 (12) |
| C14   | 0.0319 (9) | 0.0880 (17) | 0.0852 (16) | -0.0214 (10) | 0.0138 (10) | -0.0533 (14) |
| C15   | 0.0272 (7) | 0.0477 (10) | 0.0435 (9) | -0.0073 (7) | 0.0067 (7) | -0.0188 (8) |
| C16   | 0.0740 (14) | 0.0356 (9) | 0.0547 (11) | -0.0057 (9) | 0.0221 (10) | -0.0198 (8) |
| N21   | 0.0231 (5) | 0.0233 (5) | 0.0172 (5) | -0.0032 (4) | 0.0031 (4) | -0.0004 (4) |
| C21   | 0.0230 (6) | 0.0247 (6) | 0.0184 (6) | -0.0016 (5) | 0.0034 (5) | 0.0015 (5) |
| C22   | 0.0242 (6) | 0.0297 (7) | 0.0202 (6) | -0.0010 (5) | 0.0019 (5) | -0.0022 (5) |
| C23   | 0.0371 (8) | 0.0324 (8) | 0.0290 (7) | -0.0132 (6) | 0.0034 (6) | -0.0058 (6) |
| C24   | 0.0504 (10) | 0.0354 (8) | 0.0295 (8) | -0.0206 (7) | 0.0091 (7) | 0.0001 (6) |
| C25   | 0.0379 (8) | 0.0315 (7) | 0.0195 (6) | -0.0102 (6) | 0.0057 (6) | 0.0019 (5) |
| C26   | 0.0393 (8) | 0.0371 (8) | 0.0197 (7) | -0.0045 (6) | 0.0014 (6) | -0.0043 (6) |
| O31   | 0.0430 (8) | 0.0768 (11) | 0.0444 (8) | 0.0050 (7) | -0.0006 (6) | -0.0149 (7) |
| C31   | 0.0380 (19) | 0.048 (2) | 0.041 (2) | -0.0017 (16) | 0.0067 (16) | -0.0083 (19) |
| C32   | 0.052 (3) | 0.041 (2) | 0.089 (4) | -0.016 (2) | 0.018 (2) | -0.013 (3) |
| C31'  | 0.075 (4) | 0.068 (4) | 0.050 (3) | -0.007 (3) | -0.006 (3) | 0.001 (3) |
| C32'  | 0.093 (4) | 0.077 (3) | 0.058 (3) | 0.021 (3) | -0.010 (3) | -0.020 (3) |

Geometric parameters (Å, °)

|       | Ni1—Ni1 | C22—C23 | C22—C26 |
|-------|---------|---------|---------|
| Ni1   | 2.0596 (13) | 1.388 (2) | 1.5070 (19) |
| N1    | 2.0597 (13) | 2.1195 (12) | 1.386 (2) |
| N11   | 2.1195 (12) | 0.9500 | 0.9500 |
| N21   | 2.1200 (11) | 0.9500 | 0.9500 |

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| Bond Pair     | Distance (Å) | Bond Angle (°) |Torsion Angle (°) |
|--------------|--------------|----------------|------------------|
| Ni1—N21i     | 2.1200 (11)  |                |                  |
| N1—C1        | 1.156 (2)    |                |                  |
| C1—S1        | 1.6423 (15)  |                |                  |
| N11—C11      | 1.3375 (19)  |                |                  |
| N11—C15      | 1.339 (2)    |                |                  |
| C11—H11      | 0.9500       |                |                  |
| C11—C12      | 1.393 (2)    |                |                  |
| C12—C13      | 1.380 (3)    |                |                  |
| C12—C16      | 1.501 (2)    |                |                  |
| C13—H13      | 0.9500       |                |                  |
| C13—C14      | 1.375 (3)    |                |                  |
| C14—H14      | 0.9500       |                |                  |
| C14—C15      | 1.382 (2)    |                |                  |
| C15—H15      | 0.9500       |                |                  |
| C16—H16A     | 0.9800       |                |                  |
| C16—H16B     | 0.9800       |                |                  |
| C16—H16C     | 0.9800       |                |                  |
| N21—C21      | 1.3423 (16)  |                |                  |
| N21—C25      | 1.3376 (17)  |                |                  |
| C21—H21      | 0.9500       |                |                  |
| C21—C22      | 1.3894 (19)  |                |                  |
| N1—Ni1—N1    | 179.98 (6)   | C22—C21—H21   | 118.0            |
| N1—Ni1—N11   | 90.27 (5)    | C21—C22—C26   | 120.66 (13)      |
| N1—Ni1—N11i  | 89.72 (5)    | C23—C22—C21   | 117.25 (12)      |
| N1—Ni1—N1i   | 90.27 (5)    | C23—C22—C26   | 122.09 (13)      |
| N1—Ni1—N21   | 90.27 (4)    | C22—C23—H23   | 120.2            |
| N1—Ni1—N21i  | 89.74 (5)    | C24—C23—C22   | 119.50 (14)      |
| N1—Ni1—N21i  | 90.27 (4)    | C24—C23—H23   | 120.2            |
| N1—Ni1—N21   | 89.74 (5)    | C23—C24—C22   | 120.5            |
| N11i—Ni1—N11 | 89.96 (7)    | C25—C24—C23   | 118.95 (14)      |
| N11i—Ni1—N21 | 90.25 (5)    | C25—C24—H24   | 120.5            |
| N11i—Ni1—N21i| 89.53 (6)    | C22—C26—H26A  | 109.5            |
| N11—Ni1—N21i | 90.25 (5)    | C22—C26—H26B  | 109.5            |
| C1—N1—Ni1    | 165.69 (12)  | C22—C26—H26C  | 109.5            |
| N1—C1—S1     | 179.47 (12)  | H26A—C26—H26B | 109.5            |
| C11—N11—Ni1  | 121.04 (10)  | H26A—C26—H26C | 109.5            |
| C11—N11—C15  | 117.74 (13)  | H26B—C26—H26C | 109.5            |
| C15—N11—Ni1  | 121.18 (10)  | C31—O31—H31   | 116.0 (18)       |
| N11—C11—H11  | 118.1        | C31′—O31—H31  | 90.7 (18)        |
| N11—C11—C12  | 123.72 (15)  | O31—C31—H31A  | 110.3            |
| C12—C11—H11  | 118.1        | O31—C31—H31B  | 110.3            |
| C11—C12—C16  | 120.62 (17)  | O31—C31—C32   | 107.2 (4)        |
| C13—C12—C11  | 117.27 (16)  | H31A—C31—H31B | 108.5            |
| C13—C12—C16  | 122.11 (17)  | C32—C31—H31A  | 110.3            |
C12—C13—H13  120.1  C32—C31—H31B  110.3
C14—C13—C12  119.71 (17)  C31—C32—H32A  109.5
C14—C13—H13  120.1  C31—C32—H32B  109.5
C13—C14—H14  120.4  C31—C32—H32C  109.5
C13—C14—C15  119.27 (18)  H32A—C32—H32B  109.5
C15—C14—H14  120.4  H32A—C32—H32C  109.5
N11—C15—C14  118.9  O31—C31′—H31C  111.0
N11—C15—H15  118.9  O31—C31′—H31D  111.0
C14—C15—H15  118.9  H32A—C32—H32B  109.5
C12—C16—H16A  109.5  C32′—C31′—O31  103.9 (5)
C12—C16—H16B  109.5  C32′—C31′—H31C  111.0
C12—C16—H16C  109.5  C32′—C31′—H31D  111.0
H16A—C16—H16B  109.5  C32′—C31′—H31D  111.0
H16A—C16—H16C  109.5  C31′—C32′—H32D  109.5
H16B—C16—H16C  109.5  C31′—C32′—H32D  109.5
C21—N21—Ni1  121.21 (9)  C31′—C32′—H32F  109.5
C25—N21—Ni1  121.18 (9)  C31′—C32′—H32F  109.5
C25—N21—C21  117.61 (12)  H32D—C32′—H32E  109.5
N21—C21—H21  118.0  H32D—C32′—H32E  109.5
N21—C21—C22  123.90 (12)  H32D—C32′—H32F  109.5

Symmetry code: (i) −x,y,−z+3/2.

Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H | H···A | D···A     | D—H···A |
|---------------|-----|-------|-----------|---------|
| C15—H15···O31′i | 0.95 | 2.61  | 3.373 (2) | 138     |
| O31···S1       | 0.88 (4) | 2.46 (4) | 3.3379 (17) | 172 (2) |

Symmetry code: (i) −x+1, y, −z+3/2.

Bis(isothiocyanato-κN)tetrakis(3-methylpyridine-κN) nickel(II) acetonitrile disolvate (2)

Crystal data

[Ni(NCS)2(C6H7N)4]·2C2H3N

F(000) = 1320
M_r = 629.48
Monoclinic, C2/c
a = 18.7990 (1) Å
b = 11.3033 (1) Å
R = 15.8639 (1) Å
β = 96.825 (1)°
V = 3347.04 (4) Å³
Z = 4

Cell parameters from 26840 reflections
θ = 4.5–79.2°
µ = 2.25 mm⁻¹
T = 100 K
Block, light purple
0.25 × 0.15 × 0.05 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2021)
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm⁻¹
ω scans

35196 measured reflections
3605 independent reflections
3462 reflections with I > 2σ(I)
R_max = 0.746, T_max = 1.000

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sup-5
θ_{max} = 79.7°, θ_{min} = 4.6°

Refinement

Refinement on F^2

Least-squares matrix: full

\( R(F^2 > 2\sigma(F^2)) = 0.046 \)

\( wR(F^2) = 0.153 \)

S = 1.07

3605 reflections

264 parameters

82 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\( \frac{\Delta}{\sigma}_{\text{max}} = 0.001 \)

\( \Delta \rho_{\text{max}} = 0.80 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.46 \text{ e Å}^{-3} \)

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 (Å^2)

| Atom | x     | y     | z     | U_{iso}/U_{eq} | Occ. (<1) |
|------|-------|-------|-------|----------------|-----------|
| Ni1  | 0.50000 | 0.24890 (3) | 0.750000 | 0.02595 (17) |
| N1   | 0.42021 (9) | 0.24892 (10) | 0.82781 (11) | 0.0345 (4)  |
| C1   | 0.36511 (10) | 0.24794 (11) | 0.85346 (11) | 0.0284 (4)  |
| S1   | 0.28727 (2) | 0.24611 (4) | 0.88985 (3) | 0.04010 (18) |
| N11  | 0.55665 (7) | 0.38053 (12) | 0.82637 (9) | 0.0330 (3)  |
| C11  | 0.52259 (10) | 0.47154 (15) | 0.85750 (11) | 0.0386 (4)  |
| H11  | 0.472097 | 0.476613 | 0.843833 | 0.046* |
| C12  | 0.55697 (12) | 0.55942 (17) | 0.90889 (13) | 0.0503 (5)  |
| C13  | 0.63026 (13) | 0.5497 (2) | 0.92937 (16) | 0.0608 (6)  |
| H13  | 0.655637 | 0.607165 | 0.964830 | 0.073* |
| C14  | 0.66640 (11) | 0.4564 (2) | 0.89825 (16) | 0.0612 (6)  |
| H14  | 0.716769 | 0.448707 | 0.911946 | 0.073* |
| C15  | 0.62794 (9) | 0.37415 (17) | 0.84660 (12) | 0.0449 (4)  |
| H15  | 0.653079 | 0.310505 | 0.824553 | 0.054* |
| C16  | 0.51514 (16) | 0.6613 (2) | 0.93882 (19) | 0.0760 (8)  |
| H16A | 0.509929 | 0.722969 | 0.895090 | 0.114* |
| H16B | 0.540591 | 0.693673 | 0.991274 | 0.114* |
| H16C | 0.467636 | 0.633742 | 0.949620 | 0.114* |
| N21  | 0.44432 (7) | 0.11538 (12) | 0.67464 (8) | 0.0310 (3)  |
| C21  | 0.43764 (9) | 0.12022 (14) | 0.58979 (10) | 0.0337 (3)  |
| H21  | 0.460555 | 0.183760 | 0.564569 | 0.040* |
| H21A | 0.452665 | 0.188327 | 0.561597 | 0.040* |
| C22  | 0.4005 (3) | 0.0410 (5) | 0.5368 (4) | 0.0347 (12) |
| C23  | 0.3683 (3) | -0.0535 (4) | 0.5741 (3) | 0.0400 (9) |
| H23  | 0.343460 | -0.112681 | 0.539724 | 0.048* |
| C24  | 0.3730 (2) | -0.0603 (3) | 0.6615 (2) | 0.0453 (8) |
| H24  | 0.350897 | -0.123617 | 0.687939 | 0.054* |
| Atomic displacement parameters (Å²) | U₁₁ | U₁₂ | U₁₃ | U₂₂ | U₂₃ | U₃₃ |
|-----------------------------------|-----|-----|-----|-----|-----|-----|
| Ni1                              | 0.0266 (3) | 0.0241 (3) | 0.0272 (3) | 0.000 | 0.00339 (17) | 0.000 |
| N1                               | 0.0328 (8) | 0.0347 (8) | 0.0367 (8) | -0.0004 (4) | 0.0076 (6) | 0.0012 (5) |
| C1                               | 0.0336 (8) | 0.0257 (8) | 0.0254 (8) | 0.0016 (5) | 0.0009 (6) | 0.0006 (4) |
| S1                               | 0.0297 (3) | 0.0488 (3) | 0.0431 (3) | 0.00236 (14) | 0.0093 (2) | 0.00200 (15) |
| N11                              | 0.0360 (7) | 0.0286 (6) | 0.0346 (7) | -0.0035 (5) | 0.0044 (5) | -0.0037 (5) |
| C11                              | 0.0452 (9) | 0.0324 (8) | 0.0395 (8) | -0.0026 (7) | 0.0099 (7) | -0.0057 (6) |
| C12                              | 0.0649 (12) | 0.0391 (9) | 0.0491 (10) | -0.0099 (8) | 0.0166 (9) | -0.0137 (8) |
| C13                              | 0.0609 (13) | 0.0601 (13) | 0.0611 (13) | -0.0223 (11) | 0.0067 (10) | -0.0259 (11) |
| C14                              | 0.0425 (10) | 0.0660 (14) | 0.0729 (14) | -0.0132 (9) | -0.0023 (9) | -0.0211 (11) |
| C15                              | 0.0364 (8) | 0.0431 (9) | 0.0538 (10) | -0.0042 (7) | 0.0001 (7) | -0.0112 (8) |
| C16                              | 0.0889 (19) | 0.0580 (14) | 0.0850 (18) | -0.0064 (12) | 0.0269 (15) | -0.0332 (13) |
| N21                              | 0.0352 (7) | 0.0295 (6) | 0.0276 (6) | -0.0048 (5) | 0.0008 (5) | 0.0009 (5) |
| C21                              | 0.0393 (8) | 0.0330 (8) | 0.0288 (7) | -0.0021 (6) | 0.0038 (6) | 0.0018 (6) |
| C22                              | 0.0409 (18) | 0.031 (2) | 0.0324 (18) | -0.0011 (17) | 0.0058 (14) | 0.0012 (12) |
| C23                              | 0.046 (2) | 0.037 (2) | 0.0369 (16) | -0.0138 (16) | 0.0011 (16) | -0.0052 (13) |
supporting information

| Atom  | U1   | U2   | U3   | U12  | U13  | U23  |
|-------|------|------|------|------|------|------|
| C24   | 0.054 (2) | 0.0409 (17) | 0.0411 (14) | −0.0197 (15) | 0.0044 (15) | 0.0019 (12) |
| C25   | 0.041 (3) | 0.0412 (18) | 0.0315 (15) | −0.014 (2) | 0.001 (2) | 0.0053 (12) |
| C26   | 0.0616 (15) | 0.0482 (14) | 0.0294 (11) | −0.0122 (11) | 0.0032 (10) | −0.0058 (9) |
| C22'  | 0.064 (8) | 0.037 (7) | 0.019 (4) | 0.014 (5) | −0.020 (4) | −0.012 (4) |
| C23'  | 0.053 (8) | 0.042 (6) | 0.045 (4) | 0.000 (5) | −0.012 (5) | −0.009 (4) |
| C24'  | 0.034 (5) | 0.036 (4) | 0.038 (3) | −0.004 (3) | −0.004 (3) | −0.004 (3) |
| C25'  | 0.021 (6) | 0.030 (4) | 0.029 (4) | −0.006 (4) | −0.008 (4) | −0.002 (3) |
| C26'  | 0.063 (5) | 0.045 (4) | 0.050 (4) | −0.025 (4) | −0.010 (4) | 0.001 (3) |
| N31   | 0.188 (4) | 0.153 (7) | 0.146 (7) | 0.007 (4) | 0.003 (4) | 0.067 (6) |
| C31   | 0.178 (4) | 0.098 (5) | 0.096 (5) | 0.025 (3) | −0.002 (4) | 0.040 (4) |
| C32   | 0.172 (5) | 0.099 (9) | 0.202 (14) | 0.038 (4) | 0.000 (5) | 0.092 (9) |
| N31'  | 0.128 (7) | 0.131 (5) | 0.221 (5) | 0.049 (5) | −0.016 (4) | 0.031 (4) |
| C31'  | 0.051 (3) | 0.087 (4) | 0.197 (5) | 0.011 (3) | −0.001 (4) | 0.062 (3) |
| C32'  | 0.100 (5) | 0.077 (4) | 0.184 (5) | 0.025 (4) | 0.000 (4) | 0.076 (3) |

Geometric parameters (Å, º)

| Bond         | Distance    | Bond         | Distance    |
|--------------|-------------|--------------|-------------|
| Ni1—N1i      | 2.0528 (16) | C22—C26      | 1.506 (6)   |
| Ni1—N1       | 2.0528 (16) | C23—H23      | 0.9500      |
| Ni1—N11      | 2.1235 (14) | C23—C24      | 1.381 (5)   |
| Ni1—N11i     | 2.1235 (13) | C24—H24      | 0.9500      |
| Ni1—N21      | 2.1224 (13) | C24—C25      | 1.370 (7)   |
| Ni1—N21i     | 2.1224 (13) | C25—H25      | 0.9500      |
| N1—C1        | 1.157 (3)   | C26—H26A     | 0.9800      |
| C1—S1        | 1.6358 (19) | C26—H26B     | 0.9800      |
| N11—C11      | 1.337 (2)   | C26—H26C     | 0.9800      |
| N11—C15      | 1.342 (2)   | C22'—H22'    | 0.9500      |
| C11—H11      | 0.9500      | C22'—C23'    | 1.34 (2)    |
| C11—C12      | 1.394 (2)   | C23'—H23'    | 0.9500      |
| C12—C13      | 1.382 (3)   | C23'—C24'    | 1.363 (19)  |
| C12—C16      | 1.503 (3)   | C24'—C25'    | 1.423 (19)  |
| C13—H13      | 0.9500      | C24'—C26'    | 1.516 (13)  |
| C13—C14      | 1.377 (3)   | C25'—H25'    | 0.9500      |
| C14—H14      | 0.9500      | C26'—H26D    | 0.9800      |
| C14—C15      | 1.385 (3)   | C26'—H26E    | 0.9800      |
| C15—H15      | 0.9500      | C26'—H26F    | 0.9800      |
| C16—H16A     | 0.9800      | N31—C31      | 1.121 (11)  |
| C16—H16B     | 0.9800      | C31—C32      | 1.449 (14)  |
| C16—H16C     | 0.9800      | C32—H32A     | 0.9800      |
| N21—C21      | 1.3381 (19) | C32—H32B     | 0.9800      |
| N21—C25      | 1.537 (6)   | C32—H32C     | 0.9800      |
| N21—C25'     | 1.312 (19)  | N31'—C31'    | 1.151 (12)  |
| C21—H21      | 0.9500      | C31'—C32'    | 1.381 (15)  |
| C21—H21A     | 0.9500      | C32'—H32D    | 0.9800      |
| C21—C22      | 1.363 (6)   | C32'—H32E    | 0.9800      |
| C21—C22'     | 1.490 (19)  | C32'—H32F    | 0.9800      |
| C22—C23      | 1.394 (6)   |               |             |
N1i—Ni1—N1 179.99 (7)  C22′—C21—H21A  120.6
N1i—Ni1—N11i 90.55 (6)  C21—C22—C23  117.3 (4)
N1—Ni1—N11i 89.44 (6)  C21—C22—C26  120.5 (3)
N1—Ni1—N11 90.55 (6)  C23—C22—C26  122.1 (5)
N1i—Ni1—N21i 90.46 (6)  C24—C23—H23  119.3 (4)
N1—Ni1—N21 90.46 (6)  C24—C23—H23  120.3
N1i—Ni1—N21 89.46 (6)  C23—C24—H24  120.4
N1i—Ni1—N21i 89.44 (6)  C25—C24—C23  119.1 (4)
N11—Ni1—N11i 91.03 (8)  C25—C24—H24  120.4
N21i—Ni1—N11 89.80 (6)  N21—C25—C24  122.5 (5)
N21i—Ni1—N11 89.80 (6)  N21—C25—H25  118.7
N21—Ni1—N11i 91.03 (8)  N21—C25—C24  118.7
N21—Ni1—N11 91.03 (8)  C22—C26—H26A  109.5
N21—Ni1—N21i 90.36 (7)  C22—C26—H26B  109.5
C1—Ni1—Ni1 163.77 (15)  C22—C26—H26C  109.5
C1—Ni1—Ni1 163.77 (15)  H26A—C26—H26B  109.5
C1—C1—S1 179.81 (16)  H26A—C26—H26C  109.5
C11—Ni1—N11i 121.35 (11)  C21—C22′—H22′  120.2
C11—Ni1—N11 121.35 (11)  C23′—C22′—C21  119.6 (14)
C11—Ni1—N11 121.35 (11)  C23′—C22′—H22′  120.2
C11—Ni1—N11i 121.35 (11)  C22′—C23′—H23′  120.0
N11—C1—C11 120.1  C22′—C23′—H23′  120.0
N11—C11—H11 118.1  C23′—C24′—C25′  117.9 (13)
N11—C11—C12 123.73 (17)  C23′—C24′—C26′  123.3 (10)
C12—C11—H11 118.1  C25′—C24′—C26′  118.7 (11)
C12—C11—C12 120.5 (2)  C21—C25′—C24′  124.1 (15)
C12—C11—H11 118.1  C24′—C25′—C24′  118.0
C11—C12—C16 122.1 (2)  C24′—C25′—H25′  118.0
C11—C12—C16 122.1 (2)  C24′—C26′—H26D  109.5
N11—C15—C14 122.78 (18)  C24′—C26′—H26E  109.5
N11—C15—H15 118.6  C24′—C26′—H26F  109.5
C14—C15—H15 118.6  H26D—C26′—H26E  109.5
C12—C16—H16A 109.5  H26D—C26′—H26F  109.5
C12—C16—H16B 109.5  N31—C31—C32  173.6 (12)
C12—C16—H16C 109.5  C31—C32—H32A  109.5
C16A—C16—H16B 109.5  C31—C32—H32B  109.5
C16A—C16—H16C 109.5  C31—C32—H32C  109.5
C21—N21—Ni1 121.24 (10)  H32A—C32—H32B  109.5
C21—N21—C25 118.6  C31′—C32′—H32D  109.5
C25—N21—Ni1 117.8 (8)  N31′—C31′—C32′  178.5 (12)
C25′—N21—Ni1 117.8 (8)  C31′—C32′—H32E  109.5
N21—C21—H21 117.5  C31′—C32′—H32F  109.5
N21—C21—H21A 117.5  C31′—C32′—H32F  109.5

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N21—C21—C22 125.0 (2) H32D—C32′—H32E 109.5
N21—C21—C22′ 118.8 (8) H32D—C32′—H32F 109.5
C22—C21—H21 117.5 H32E—C32′—H32F 109.5

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

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|------|-------|-------|---------|
| C25′—H25′···N21i | 0.95 | 2.48  | 2.991 (15) | 114 |
| C32—H32···S1ii  | 0.98 | 2.93  | 3.791 (17) | 147 |
| C32′—H32···S1   | 0.98 | 2.89  | 3.779 (10) | 152 |

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

Bis(isothiocyanato-κN)tetrakis(3-methylpyridine-κN)\ nickel(II) diethyl ether monosolvate (3)

Crystal data

[Ni(NCS)2(C6H7N)4]·C4H10O

Mr = 621.49

Monoclinic, $P2_1/n$

$a = 10.2275$ (10) Å

$b = 25.0468$ (1) Å

$c = 12.7180$ (1) Å

$\beta = 94.600$ (1)°

$V = 3247.4$ (3) Å³

$Z = 4$

$F(000) = 1312$

$D_x = 1.271$ Mg m⁻³

Cu Kα radiation, $\lambda = 1.54184$ Å

Cell parameters from 43692 reflections

$\theta = 3.5–79.0$°

$\mu = 2.31$ mm⁻¹

$T = 100$ K

Block, light purple

$0.2 \times 0.2 \times 0.15$ 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: 10.0000 pixels mm⁻¹

$\omega$ scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.076$

$S = 1.03$

6974 reflections

368 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 1.9652P]$

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

$(\Delta\sigma)_{max} = 0.002$

$\Delta \rho_{max} = 0.54$ e Å⁻³

$\Delta \rho_{min} = -0.32$ e Å⁻³

Extinction correction: SHELXL-2016/6 (Sheldrick 2015b),

Fc = kFc[1+0.001xFc²/sin(2θ)]^1/4

Extinction coefficient: 0.00020 (4)
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/Unq |
|------|------|------|------|----------|
| Ni1  | 0.24076 (2) | 0.61197 (2) | 0.27926 (2) | 0.01630 (7) |
| N1   | 0.24400 (11) | 0.60562 (4) | 0.44028 (9)  | 0.0217 (2)  |
| C1   | 0.24082 (12) | 0.62304 (5) | 0.52491 (10) | 0.0188 (2)  |
| S1   | 0.23850 (4)  | 0.64887 (2) | 0.64199 (3)  | 0.0324 (4)  |
| N2   | 0.23270 (11) | 0.61727 (4) | 0.11760 (9)  | 0.0209 (2)  |
| C2   | 0.26680 (12) | 0.62259 (5) | 0.03386 (10) | 0.0195 (2)  |
| S2   | 0.31719 (4)  | 0.63063 (2) | −0.08404 (3) | 0.0280 (5)  |
| N11  | 0.11637 (10) | 0.54346 (4) | 0.26359 (8)  | 0.0182 (2)  |
| C11  | 0.12071 (12) | 0.51046 (5) | 0.18089 (10) | 0.0195 (2)  |
| H11  | 0.180894    | 0.518406   | 0.129934     | 0.023*      |
| C12  | 0.04240 (12) | 0.46529 (5) | 0.16522 (10) | 0.0212 (2)  |
| C13  | −0.04471 (13)| 0.45407 (5) | 0.24070 (11) | 0.0252 (3)  |
| H13  | −0.100594   | 0.423786   | 0.233060     | 0.030*      |
| C14  | −0.04931 (13)| 0.48748 (6)| 0.32726 (11) | 0.0259 (3)  |
| H14  | −0.107695   | 0.480129   | 0.379882     | 0.031*      |
| C15  | 0.03222 (12) | 0.53170 (5) | 0.33612 (10) | 0.0218 (2)  |
| H15  | 0.028503    | 0.554484   | 0.395516     | 0.026*      |
| C16  | 0.05390 (14) | 0.42992 (6)| 0.07075 (11) | 0.0286 (3)  |
| H16A | 0.090667    | 0.450425   | 0.014493     | 0.043*      |
| H16B | −0.033150   | 0.416564   | 0.045699     | 0.043*      |
| H16C | 0.111655    | 0.399722   | 0.090543     | 0.043*      |
| N21  | 0.40489 (10) | 0.55986 (4)| 0.27878 (8)  | 0.0181 (2)  |
| C21  | 0.48770 (12) | 0.56126 (5)| 0.20234 (10) | 0.0209 (2)  |
| H21  | 0.479956    | 0.589974   | 0.153433     | 0.025*      |
| C22  | 0.58430 (13) | 0.52316 (5)| 0.19038 (11) | 0.0249 (3)  |
| C23  | 0.59499 (13) | 0.48144 (5)| 0.26294 (11) | 0.0251 (3)  |
| H23  | 0.658347    | 0.454105   | 0.256871     | 0.030*      |
| C24  | 0.51244 (13) | 0.48016 (5)| 0.34399 (11) | 0.0240 (3)  |
| H24  | 0.519758    | 0.452469   | 0.395165     | 0.029*      |
| C25  | 0.41891 (12) | 0.51993 (5)| 0.34931 (10) | 0.0208 (2)  |
| H25  | 0.362470    | 0.518900   | 0.405078     | 0.025*      |
| C26  | 0.67263 (16) | 0.52747 (7)| 0.10169 (14) | 0.0393 (4)  |
| H26A | 0.632509    | 0.551229   | 0.046997     | 0.059*      |
| H26B | 0.685163    | 0.492004   | 0.071558     | 0.059*      |
| H26C | 0.757741    | 0.541995   | 0.128735     | 0.059*      |
| N31  | 0.36520 (10) | 0.68134 (4)| 0.29236 (8)  | 0.0190 (2)  |
| C31  | 0.44241 (12) | 0.69197 (5)| 0.38051 (10) | 0.0206 (2)  |
| H31  | 0.445853    | 0.666502   | 0.436028     | 0.025*      |
| C32  | 0.51760 (12) | 0.73812 (5)| 0.39515 (10) | 0.0220 (3)  |
Atomic displacement parameters (Å²)

|     | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U²³  |
|-----|------|------|------|------|------|------|
| Ni1 | 0.01686 (11) | 0.01632 (11) | 0.01561 (11) | 0.00084 (7) | 0.00063 (8) | −0.00079 (7) |
| N1  | 0.0249 (5)  | 0.0217 (5)  | 0.0185 (5)  | 0.0001 (4)  | 0.0018 (4)  | −0.0013 (4)  |
| C1  | 0.0193 (6)  | 0.0166 (5)  | 0.0206 (6)  | −0.0011 (4) | 0.0021 (4)  | 0.0029 (4)   |
| S1  | 0.0513 (2)  | 0.02888 (18) | 0.01775 (16) | 0.00010 (15) | 0.00635 (14) | −0.00430 (12) |
| N2  | 0.0198 (5)  | 0.0204 (5)  | 0.0223 (6)  | 0.0006 (4)  | 0.0008 (4)  | 0.0006 (4)   |

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### Geometric parameters (Å, °)

|     | Ni1—N1   | Ni1—N2   | Ni1—N11  | Ni1—N21  | Ni1—N31  | Ni1—N41  | C1—S1   | C2—S1   | C3—S1   | C4—S1   | C5—S1   | C6—S1   | C7—S1   | C8—S1   | C9—S1   | C10—S1  | C11—S1  | C12—S1  | C13—S1  | C14—S1  | C15—S1  | C16—S1  | C17—S1  | C18—S1  | C19—S1  | C20—S1  | C21—S1  | C22—S1  | C23—S1  | C24—S1  | C25—S1  | C26—S1  | C27—S1  |
|-----|----------|----------|----------|----------|----------|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| C2  | 0.0214 (6) | 0.0145 (5) | 0.0216 (6) | 0.0021 (4) | −0.0046 (5) | −0.0029 (4) | 2.0517 (11) | 2.0552 (11) | 2.1358 (10) | 2.1026 (11) | 2.1523 (11) | 2.1291 (11) | 1.6254 (13) | 1.1546 (18) | 1.6366 (13) | 0.9500 | 1.3926 (18) | 1.3928 (19) | 1.5047 (18) | 0.9500 | 1.382 (2) | 0.9500 | 1.3858 (19) | 0.9500 | 0.9800 | 0.9800 |
N11—C11   1.3413 (16)
N11—C15   1.3437 (16)
C11—H11   0.9500
C11—C12   1.3912 (17)
C12—C13   1.3898 (19)
C12—C16   1.5050 (18)
C13—H13   0.9500
C13—C14   1.387 (2)
C14—H14   0.9500
C14—C15   1.3855 (18)
C15—H15   0.9500
C16—H16A  0.9800
C16—H16B  0.9800
C16—H16C  0.9800
N21—C21   1.3400 (16)
N21—C25   1.3436 (16)
C21—H21   0.9500
C21—C22   1.3907 (18)
C22—C23   1.3927 (19)
C22—C26   1.5045 (19)
C23—H23   0.9500
C23—C24   1.3841 (19)
C24—H24   0.9500
C24—C25   1.3864 (18)
C25—H25   0.9500
C26—H26A  0.9800
C26—H26B  0.9800
C26—H26C  0.9800
N31—C31   1.3452 (16)
N31—C35   1.3437 (17)
N1—Ni1—N2  178.45 (4)
N1—Ni1—N11 89.58 (4)
N1—Ni1—N21 90.33 (4)
N1—Ni1—N31 91.33 (4)
N1—Ni1—N41 89.18 (4)
N2—Ni1—N11 90.29 (4)
N2—Ni1—N21 90.07 (4)
N2—Ni1—N31 90.18 (4)
N11—Ni1—N31 179.05 (4)
N21—Ni1—N11 88.35 (4)
N21—Ni1—N21 90.72 (4)
N21—Ni1—N31 91.93 (4)
N41—Ni1—N31 89.02 (4)
C1—Ni1—Ni1 153.43 (4)
S1—C1—Ni1 178.36 (12)
C36—H36B 0.9800
C36—H36C 0.9800
N41—C41 1.3409 (17)
C41—H41 0.9500
N41—C45 1.3423 (17)
C42—C43 1.391 (2)
C42—C46 1.508 (2)
C43—H43 0.9500
C44—C45 1.3872 (19)
C45—H45 0.9500
C46—H46A 0.9800
C46—H46B 0.9800
O1—C52 1.4195 (19)
C51—H51A 0.9800
C51—H51B 0.9800
C51—H51C 0.9800
C52—C53 1.503 (2)
C52—H52A 0.9900
C52—H52B 0.9900
C52—H52C 0.9900
C53—C54 1.503 (2)
C54—H54A 0.9800
C54—H54B 0.9800
C54—H54C 0.9800
N31—C31 1.3452 (16)
N31—C35 1.3437 (17)
N31—C31—H31 118.1
N31—C31—C32 123.82 (12)
C32—C31—H31 118.1
C32—C31—C32 117.51 (12)
C33—C32—C36 120.55 (12)
C33—C32—C32 121.94 (12)
C34—C33—C32 120.3
C34—C33—C33 119.32 (12)
C34—C33—C33 120.3
C33—C34—C34 120.4
C33—C34—C35 119.14 (13)
C35—C34—H34 120.4
C35—C34—C35 122.78 (12)
N31—C35—H35 118.6
N31—C35—H35 118.6
C32—C36—H36A 109.5
C32—C36—H36B 109.5
C2—N2—Ni1 159.93 (10) C32—C36—H36C 109.5
N2—C2—S2 179.10 (13) H36A—C36—H36B 109.5
C11—N11—Ni1 120.75 (8) H36A—C36—H36C 109.5
C11—N11—C15 117.80 (11) H36B—C36—H36C 109.5
C15—N11—Ni1 121.44 (8) C41—N41—Ni1 121.14 (9)
N11—C11—H11 118.0 C41—N41—C45 117.88 (11)
N11—C11—C12 123.96 (12) C45—N41—Ni1 120.95 (9)
C12—C11—H11 118.0 N41—C41—H41 118.1
C11—C12—C16 120.81 (12) N41—C41—C42 123.82 (13)
C13—C12—C11 117.33 (12) C42—C41—H41 118.1
C13—C12—C16 121.86 (12) C41—C42—C43 117.17 (13)
C12—C13—H13 120.3 C41—C42—C46 121.06 (14)
C14—C13—C12 119.39 (12) C43—C42—C46 121.76 (13)
C14—C13—H13 120.3 C42—C43—H43 120.1
C13—C14—C13 119.24 (12) C44—C43—C42 119.85 (13)
C15—C14—H14 120.4 C44—C43—H44 120.1
C11—C15—C14 122.27 (12) C43—C44—C45 118.89 (13)
C11—C15—H15 118.9 C45—C44—C42 118.6
C14—C15—H15 118.9 N41—C45—C44 122.38 (13)
C12—C16—H16A 109.5 N41—C45—H45 118.8
C12—C16—H16B 109.5 C52—O1—C53 113.17 (12)
C12—C16—H16C 109.5 C51—C52—H52A 110.0
H16A—C16—H16B 109.5 C51—C52—H52B 110.0
H16A—C16—H16C 109.5 C52—C53—H53A 110.0
H16B—C16—H16C 109.5 C52—C53—H53B 110.0
N21—C21—Ni1 122.07 (8) C52—O1—C53 113.17 (12)
C21—N21—Ni1 117.64 (11) C51—C52—H52A 110.0
C25—N21—Ni1 119.80 (8) C51—C52—H52B 110.0
N21—C21—H21 118.1 C52—O1—C53 113.17 (12)
N21—C21—C22 123.87 (12) C51—C52—H52A 110.0
C22—C21—H21 118.1 C51—C52—H52B 110.0
C21—C22—C23 117.46 (12) C51—C52—H52B 110.0
C21—C22—C26 120.49 (13) C51—C52—H52B 110.0
C23—C22—C26 122.06 (12) C51—C52—H52B 110.0
C22—C23—H23 120.3 O1—C52—C51 108.25 (12)
C24—C23—C22 119.38 (12) O1—C52—H52A 110.0
C24—C23—H23 120.3 O1—C52—H52B 110.0
C23—C24—H24 120.5 C51—C52—H52A 110.0
C23—C24—C25 118.96 (12) C51—C52—H52B 110.0
C25—C24—H24 120.5 H52A—C52—H52B 108.4
N21—C25—C24 122.64 (12) O1—C53—H53A 110.0
N21—C25—H25 118.7 O1—C53—H53B 110.0
C24—C25—H25 118.7 O1—C53—C54 108.46 (13)
C22—C26—H26A 109.5 H53A—C53—H53B 108.4
C22—C26—H26B 109.5 C54—C53—H53A 110.0
C22—C26—H26C 109.5 C54—C53—H53B 110.0
H26A—C26—H26B 109.5 C53—C54—H54A 109.5
| Bond Type          | Angle (°) | Bond Type          | Angle (°) |
|--------------------|-----------|--------------------|-----------|
| H26A—C26—H26C     | 109.5     | C53—C54—H54B      | 109.5     |
| H26B—C26—H26C     | 109.5     | C53—C54—H54C      | 109.5     |
| C31—N31—Ni1       | 121.89 (8)| H54A—C54—H54B     | 109.5     |
| C35—N31—Ni1       | 120.64 (9)| H54A—C54—H54C     | 109.5     |
| C35—N31—C31       | 117.39 (11)| H54B—C54—H54C    | 109.5     |
| Ni1—N11—C11—C12   | −179.71 (9)| C23—C24—C25—N21  | 0.0 (2)   |
| Ni1—N11—C15—C14   | 179.93 (10)| C25—N21—C21—C22  | 1.80 (19) |
| Ni1—N21—C21—C22   | −170.21 (10)| C26—C22—C23—C24  | 178.84 (14)|
| Ni1—N21—C25—C24   | 170.56 (10)| N31—C31—C32—C33  | −1.89 (19)|
| Ni1—N31—C31—C32   | −175.46 (9)| N31—C31—C32—C36  | 178.29 (12)|
| Ni1—N31—C35—C34   | 177.39 (10)| C31—N31—C35—C34  | 0.66 (19)|
| Ni1—N41—C41—C42   | −177.75 (10)| C31—C32—C33—C34  | 0.66 (19)|
| Ni1—N41—C45—C44   | 177.81 (10)| C32—C33—C34—C35  | 1.1 (2)   |
| N11—C11—C12—C13   | −0.29 (19)| C33—C34—C35—N31  | −1.8 (2)   |
| N11—C11—C12—C16   | −179.46 (12)| C35—N31—C31—C32  | 1.23 (19)|
| C11—N11—C15—C14   | −0.57 (18)| C36—C32—C33—C34  | −179.52 (13)|
| C11—C12—C13—C14   | −0.44 (19)| N41—C41—C42—C43  | −0.1 (2)   |
| C12—C13—C14—C15   | 0.6 (2)  | N41—C41—C42—C46  | 179.09 (14)|
| C13—C14—C15—N11   | −0.1 (2) | C41—N41—C45—C44  | −0.3 (2)   |
| C15—N11—C11—C12   | 0.79 (18)| C41—C42—C43—C44  | −0.2 (2)   |
| C16—C12—C13—C14   | 178.71 (13)| C42—C43—C44—C45  | 0.2 (2)   |
| N21—C21—C22—C23   | −0.3 (2) | C43—C44—C45—N41  | 0.0 (2)   |
| N21—C21—C22—C26   | 179.49 (14)| C45—N41—C41—C42  | 0.4 (2)   |
| C21—N21—C25—C24   | −1.63 (18)| C46—C42—C43—C44  | −179.38 (15)|
| C21—C22—C23—C24   | −1.4 (2) | C52—O1—C53—C54  | 174.86 (13)|
| C22—C23—C24—C25   | 1.5 (2)  | C53—O1—C52—C51  | 176.55 (12)|