The reaction of Mn(NCS)₂ or Fe(NCS)₂ with 3-methylpyridine (C₆H₇N) leads to the formation of two isostructural compounds with compositions [Mn(NCS)₂(C₆H₇N)₄] (1) and [Fe(NCS)₂(C₆H₇N)₄] (2). IR spectroscopic investigations indicate that only terminally coordinated thiocyanate anions are present. This is confirmed by single-crystal structure analysis, which shows that their crystal structures consist of discrete centrosymmetric complexes, in which the metal cations are octahedrally coordinated by two N-bonded thiocyanate anions and four 3-methylpyridine ligands. X-ray powder diffraction (XRPD) proves that pure samples have been obtained. Thermogravimetric measurements show that decomposition starts at about 90°C and that the two coligands are removed in one step for 1 whereas for 2 no clearly resolved steps are visible. XRPD measurements of the residue obtained after the first mass loss of 1 show that a new and unknown crystalline compound has been formed.

1. Chemical context

For many years we and others have been interested in the synthesis of coordination compounds based on thio cyanate anions. In this context, we are especially interested in compounds where paramagnetic metal cations are linked by the anionic ligands into networks, because they can show interesting magnetic properties (Mautner et al., 2018; Rams et al., 2020; Böhme et al., 2020). Unfortunately, the synthesis of such compounds is sometimes difficult to achieve, because metal cations such as, for example Mn¹¹, Fe¹¹, Co¹¹ or Ni¹¹ are not very chalcophilic and prefer to coordinate only to the terminal thiocyanate N atom. With mono-coordinating ligands this leads to the formation of discrete complexes instead of the desired networks. In several cases, this problem can be solved by using discrete complexes as precursors that on heating lose their coligands stepwise, which can lead to the desired compounds with bridging coordination (Werner et al., 2015a; Suckert et al., 2016).
In the past, many such compounds were prepared following this route, using predominantly pyridine-based ligands that are substituted at the 4-position. In the course of our systematic work, we became interested in 3-methylpyridine (3-picoline; C₆H₇N) as a ligand. Some compounds have already been reported with this ligand, but bridging coordination of the anionic ligands is observed in only a very few of them (see Database survey). This includes compounds with chalcophilic metal cations like Cu²⁺, Hg²⁺ or Cd²⁺ (see Database survey).

Some time ago we tried to prepare compounds based on cobalt and 3-methylpyridine as a coligand, but only octahedral discrete complexes were observed (Boeckmann et al., 2011a).

When the compound Co(NCS)₂(3-methylpyridine)₄ is investigated by thermogravimetry, the removal of two 3-methylpyridine molecules can be detected but, instead of the desired compounds with bridging thiocyanate anions, only a mononuclear tetrahedral complex is obtained in which the Co²⁺ cations are coordinated by two terminal N-bonded thiocyanate anions and two 3-methylpyridine coligands. With Ni(NCS)₂, many compounds are known, but all of them consist of discrete complexes with the composition Ni(NCS)₂(3-methylpyridine)₄ that form channels in which additional solvate molecules are embedded. Two compounds are reported in the Cambridge Structural Database with Mn(NCS)₂ and Fe(NCS)₂ and 3-methylpyridine as ligand, except for one mixed-metal compound based on manganese and mercury (Małecki, 2017a) and therefore, we tried to prepare compounds based on these metal cations. From the reaction of Mn(NCS)₂ and Fe(NCS)₂ with 3-methylpyridine, two compounds with the composition Mn(NCS)₂(3-methylpyridine)₄ (1) and Fe(NCS)₂(3-methylpyridine)₄ (2) where obtained. IR spectroscopic investigations reveal that the CN stretching vibration of the anionic ligands is observed at 2048 cm⁻¹ for 1 and 2046 cm⁻¹ for 2, indicating that only terminal N-bonded thiocyanate anions are present (Figures S1 and S2 in the supporting information), which was confirmed by structural analysis. Comparison of the experimental X-ray powder diffraction pattern with that calculated from the structure analysis using lattice parameters obtained by measurements performed at room-temperature proves that pure samples have been obtained (Figs. 1 and 2). Measurements simultaneously using thermogravimetry and differential thermoanalysis (TG–DTA) reveal that decomposition already starts at about 90 °C for both compounds (Figures S3 and S4).

2. Structural commentary

Mn(NCS)₂(3-methylpyridine)₄ (1) and Fe(NCS)₂(3-methylpyridine)₄ (2) are isotypic to Co(NCS)₂(3-methylpyridine)₄ reported in the literature (Boeckmann et al., 2011a) and form discrete complexes, in which the metal cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and two 3-methylpyridine coligands (Figs. 3 and 4). The asymmetric unit consists of one metal cation that is located on a crystallographic center of inversion as well as one thiocyanate anion and two 3-methylpyridine ligands in general positions. As expected, the M—N bond lengths to the negatively charged thiocyanate anions are shorter than those to the 3-methylpyridine coligands and all M—N bond lengths are shorter for the Fe compound 2 than for the Mn compound 1 (Tables 1 and 2). From the N—M—N bonding angles, it is obvious that both octahedra are slightly distorted, which can also be seen from the mean octahedral quadratic elongation...
(1.0018 for 1 and 1.0023 for 2) and the octahedral angle variance (1.259° for 1 and 1.096° for 2) calculated by the method of Robinson et al. (1971).

3. Supramolecular features
In the extended structures of both compounds, the discrete complexes are arranged into columns that propagate along the crystallographic b-axis direction (Fig. 5). Between these columns, neighboring 3-methylpyridine ligands overlap but their ring planes are not parallel, which would be indicative of π–π stacking interactions (Fig. 5). There are some contacts between the C—H hydrogen atoms and the thiocyanate N and S atoms, but at distances and angles far from those expected for hydrogen bonding (Tables 3 and 4).

Table 1
Selected geometric parameters (Å, °) for 1.

| Bond/Angle | Value (Å/°) |
|------------|------------|
| Mn1—N1     | 2.1880 (11) |
| Mn1—N11    | 2.3306 (11) |
| N1—Mn1—N11 | 91.56 (4)  |
| N1—Mn1—N11 | 89.63 (4)  |
| N1—Mn1—N21 | 90.37 (4)  |
| N1—Mn1—N21 | 89.63 (4)  |

Symmetry code: (i) x+1, y+1, z+1.

Table 2
Selected geometric parameters (Å, °) for 2.

| Bond/Angle | Value (Å/°) |
|------------|------------|
| Fe1—N1     | 2.1103 (10) |
| Fe1—N11    | 2.2779 (10) |
| N1—Fe1—N11 | 91.23 (4)  |
| N1—Fe1—N11 | 89.75 (4)  |
| N1—Fe1—N21 | 90.75 (4)  |
| N1—Fe1—N21 | 89.25 (4)  |

Symmetry code: (i) x+1, y+1, z+1.

Figure 4
The molecular structure of compound 2 with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (A) 1−x, 1−y, 1−z.]

Figure 5
The packing of compound 1 viewed along the crystallographic b-axis.
Table 3
Hydrogen-bond geometry (Å, °) for 1.

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|--------|------|-----|-----|--------|
| C11—H11⋯N1i | 0.95 | 2.60 | 3.2484 (17) | 126 |
| C15—H15⋯S1ii | 0.95 | 3.00 | 3.5588 (14) | 119 |
| C15—H15⋯N1 | 0.95 | 2.52 | 3.1535 (17) | 125 |

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

Table 4
Hydrogen-bond geometry (Å, °) for 2.

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|--------|------|-----|-----|--------|
| C11—H11⋯N1i | 0.95 | 2.54 | 3.1688 (16) | 124 |
| C15—H15⋯S1ii | 0.95 | 3.00 | 3.5523 (13) | 119 |
| C15—H15⋯N1i | 0.95 | 2.48 | 3.0961 (16) | 123 |

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

4. Database survey

In the Cambridge Structure Database (CSD, version 5.43, last update November 2021; Groom et al., 2016) no Fe(NCS)2-based compounds with 3-methylpyridine as a coligand are reported. With Mn(NCS)2 there is only the mixed-metal based compounds with 3-methylpyridine as a coligand are known (MEGCEH; Taniguchi et al., 1984, 1986; Pang et al., 1990, 1992). Moreover, one compound with the composition Mn(NCS)2(3-methylpyridine)2(H2O)2 (EYAREC), Co(NCS)2(3-methylpyridine)2, isotypic to the title compounds (EYAROM and EYAROM01) as well as Co(NCS)2(3-methylpyridine)2 (EYARIG) are reported, in which the MnII cations are octahedrally coordinated by two 3-methylpyridine-N-oxide ligands and two N-bonding μ-1,3-bridging thiocyanate anions and are linked to HgII cations via the thiocyanate S-atoms (Malecki, 2017a). The HgII cations act as tetrahedral nodes, connecting the MnII cations into a three-dimensional network.

However, several thiocyanate compounds with other transition-metal cations and 3-methylpyridine as coligand are found in the CSD. With cobalt, three different discrete complexes with the composition Co(NCS)2(3-methylpyridine)2(H2O)2 (EYAREC), Co(NCS)2(3-methylpyridine)2, isotypic to the title compounds (EYAROM and EYAROM01) as well as Co(NCS)2(3-methylpyridine)2 (EYARIG) are reported, in which the CoII cations are octahedrally or tetrahedrally coordinated (Boeckmann et al., 2011a; Malecki et al., 2012). Discrete complexes, in which NiII cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and two 3-methylpyridine coligands are also known (CIVIEW, CIVIEW10, JICMIR, LAYLAY, LAYLEC, LAYLIG, LAYLON and LAYLUS) but in their structures cavities are formed, in which additional solvent molecules are embedded (Nassimbeni et al., 1984, 1986; Pang et al., 1990, 1992). Moreover, one compound with the composition Ni(NCS)2(3-methylpyridine)2(H2O)2 is also reported (MEGCEH; Tan et al., 2006).

With CuII, the discrete complexes Cu(NCS)2(3-methylpyridine)2 (ABOTET) and Cu(NCS)2(3-methylpyridine)2 (VEPBAT) with fourfold and fivefold coordinations, respectively, and the chain compound Cu(NCS)2(3-methylpyridine)2 (CUHBEM) are reported (Handy et al., 2017; Healy et al., 1984; Kabešová & Kožíšková, 1989). With Zn(NCS)2, the discrete tetrahedral complex Zn(NCS)2(3-methylpyridine)2 (ETUSAO) is reported (Boeckmann & Näther, 2011b), which is isotypic to the corresponding Co(NCS)2 compound.

With Cd(NCS)2, one compound with the composition Cd(NCS)2(3-methylpyridine)2 (FIYGUP) is observed in which the CdII cations are linked by pairs of thiocyanate anions into chains (Taniuchi et al., 1987). This corresponds exactly to the structural motif in which we are interested and for which many paramagnetic compounds are known with pyridine-based ligands (Werner et al., 2014, 2015b). Finally, two compounds with mercury are also found, viz. catena-[tetrakis(thiocyanato)bis(3-methylpyridine)manganese] (NAQYOW; Malecki, 2017a) mentioned above and the isotypic compound where MnII is replaced by ZnII (QAMSIJ; Malecki, 2017b).

5. Synthesis and crystallization

Synthesis

Ba(SCN)2·3H2O and 3-picoline were purchased from Alfa Aesar. MnSO4·H2O was purchased from Merck. A reaction of equimolar amounts of Ba(SCN)2·3H2O with MnSO4·H2O in deionized water was performed. After that, the precipitate of BaSO4 was filtered off. The filtrate was dried in a rotary evaporator and as a result, a powder of Mn(NCS)2 was obtained.

Mn(NCS)2(3-methylpyridine)2: 0.25 mmol of Mn(NCS)2 (42.8 mg) were dissolved in 0.5 ml of water and then 1.0 mmol of 3-methylpyridine (97.3 µl) were added. The mixture was then heated to 333 K and left at this temperature for 2 d. Afterwards, some colorless crystals were obtained that were suitable for single-crystal X-ray analysis. To obtain powder samples, 0.5 mmol of Mn(NCS)2 (85.6 mg) were dissolved in 1.0 ml of ethanol and then 2.0 mmol of 3-methylpyridine (194.6 µl) were added. The reaction mixture was stirred for 1 d and the colorless powder was filtered off and dried in the air.

Fe(NCS)2(3-methylpyridine)2: A mixture of 0.25 mmol of FeCl3·4H2O (49.7 mg) and 0.5 mmol of KSCN (48.6 mg) was dissolved in a mixture of 0.5 ml of water and 0.5 ml of ether. Afterwards, 1.25 mmol of 3-methylpyridine (121.6 µl) were added. The mixture was left for 3 d at room temperature, leading to some yellow crystals suitable for single-crystal X-ray diffraction measurements. To obtain powder samples, a mixture of 0.5 mmol of FeCl3·4H2O (98.6 mg) and 1.0 mmol of KSCN (97.2 µg) was dissolved in 0.5 ml of water. Afterwards, 2.0 mmol of 3-methylpyridine (194.6 µl) were added and the reaction mixture was stirred for 1 d. The yellow-colored powder was filtered off and dried in the air.

Experimental details

The data collection for single-crystal structure analysis was performed using an XtaLAB Synergy, Dualflex, HyPix diffractometer from Rigaku with Cu Kα radiation.

The IR spectrum was measured using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Mattson.

The PXRD measurement was performed with Cu Kα radiation (λ = 1.540598 Å) using a Stoe Transmission Powder Diffraction System (STADI P) that is equipped with a
|       | 1                                           | 2                                           |
|-------|---------------------------------------------|---------------------------------------------|
|       | Crystal data                                | Crystal data                                |
|       | Chemical formula                            | Chemical formula                            |
|       | $\text{[Mn(NCS)}_2\text{(C}_6\text{H}_7\text{N)}_4\text{]}$ | $\text{[Fe(NCS)}_2\text{(C}_6\text{H}_7\text{N)}_4\text{]}$ |
| $M_r$ | 543.60                                      | 544.51                                      |
| Crystal system, space group | Orthorhombic, $Pbcn$ | Orthorhombic, $Pbcn$ |
| Temperature (K) | 100                                         | 100                                         |
| $a$, $b$, $c$ ($\text{Å}$) | $17.4811(10)$, $8.93570(6)$, $17.36177(10)$ | $17.3733(1)$, $8.94119(5)$, $17.24862(10)$ |
| $V$ ($\text{Å}^3$) | 2711.55 (3)                                 | 2679.37 (3)                                 |
| $Z$ | 4                                           | 4                                           |
| Radiation type | Cu $K\alpha$                               | Cu $K\alpha$                               |
| $\mu$ ($\text{mm}^{-1}$) | 5.60                                        | 6.17                                        |
| Crystal size (mm) | $0.18 \times 0.15 \times 0.1$               | $0.16 \times 0.15 \times 0.15$              |
| Data collection | XtaLAB Synergy, Dualflex, HyPix              | Multi-scan (CrysAlis PRO; Rigaku OD, 2021) |
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2021) | Multi-scan (CrysAlis PRO; Rigaku OD, 2021) |
| $T_{\text{min}}$ - $T_{\text{max}}$ | 0.786, 1.000                                | 0.555, 1.000                                |
| No. of measured, independent and observed $| I > 2\sigma (I) |$ reflections | 23041, 2918, 2841 | 22225, 2875, 2804 |
| $R_{\text{int}}$ | 0.021                                        | 0.020                                        |
| ($\sin \theta/\lambda_{\text{max}}$ (Å$^{-1}$)) | 0.638                                        | 0.638                                        |
| Refinement |                                           |                                             |
| $\bar{R}(F^2 > 2\sigma(F^2))$, $wR(F^2)$, $S$ | 0.028, 0.078, 1.07                      | 0.026, 0.073, 1.06                        |
| No. of reflections | 2918                                         | 2875                                         |
| No. of parameters | 162                                          | 163                                          |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta \rho_{\text{max}}$, $\Delta \rho_{\text{min}}$ ($\text{e} \text{Å}^{-3}$) | 0.45, $-0.35$                               | 0.39, $-0.28$                               |

Computer programs: CrysAlis PRO (Rigaku OD, 2021), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2016/6 (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 1999) and pubICIF (Westrup, 2010).

MYTHEN 1K detector and a Johannson-type Ge(111) monochromator.

Thermogravimetry and differential thermoanalysis (TG–DTA) measurements were performed in a dynamic nitrogen atmosphere in $\text{Al}_2\text{O}_3$ crucibles using a STA-PT 1000 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (1.5 for methyl H atoms) using a riding model.

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Syntheses, crystal structures and properties of tetrakis(3-methylpyridine-κN)bis(isothiocyanato-κN)manganese(II) and tetrakis(3-methylpyridine-κN)bis(isothiocyanato-κN)iron(II)

Magdalena Ceglarska, Christoph Krebs and Christian Näther

Computing details

For both 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).

Tetrakis(3-methylpyridine-κN)bis(isothiocyanato-κN)manganese(II) (1)

Crystal data

\[\text{[Mn(NCS)₂(C₆H₇N)₄]}\]

Mr = 543.60

Orthorhombic, Pbcn

\[a = 17.47811 (10) \, \text{Å}\]

\[b = 8.93570 (6) \, \text{Å}\]

\[c = 17.36177 (10) \, \text{Å}\]

\[V = 2711.55 (3) \, \text{Å}^3\]

\[Z = 4\]

\[F(000) = 1132\]

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

(CrystalisPro; Rigaku OD, 2021)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.028\)

\(wR(F^2) = 0.078\)

\(S = 1.07\)

2918 reflections

162 parameters

\(D_x = 1.332 \, \text{Mg m}^{-3}\)

Cu Kα radiation, \(\lambda = 1.54184 \, \text{Å}\)

Cell parameters from 12231 reflections

\(\theta = 5.1^\circ - 79.2^\circ\)

\(\mu = 5.60 \, \text{mm}^{-1}\)

\(T = 100 \, \text{K}\)

Block, intense colourless

0.18 \times 0.15 \times 0.1 \, \text{mm}

\(T_{\text{min}} = 0.786, \, T_{\text{max}} = 1.000\)

23041 measured reflections

2918 independent reflections

2841 reflections with \(I > 2\sigma(I)\)

\(R_{	ext{int}} = 0.021\)

\(\theta_{\text{max}} = 79.8^\circ, \, \theta_{\text{min}} = 5.1^\circ\)

\(h = -16\rightarrow22\)

\(k = -10\rightarrow11\)

\(l = -22\rightarrow22\)

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\(w = 1/\left[\sigma^2(F_o^2) + (0.0428P)^2 + 1.4595P\right]\)

where \(P = (F_o^2 + 2F_c^2)/3\)
(Δ/σ)\textsubscript{max} = 0.001
Δρ\textsubscript{max} = 0.45 e Å\textsuperscript{−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\textsuperscript{2})

|     | x     | y     | z     | U\textsubscript{eq}/*U\textsubscript{eq} |
|-----|-------|-------|-------|--------------------------------|
| Mn1 | 0.500000 | 0.500000 | 0.500000 | 0.01493 (10) |
| S1  | 0.37925 (2) | 0.28776 (4) | 0.72629 (2) | 0.02871 (11) |
| C1  | 0.43007 (7) | 0.32513 (14) | 0.65000 (8) | 0.0197 (3) |
| N1  | 0.46439 (6) | 0.35374 (13) | 0.59412 (6) | 0.0213 (2) |
| N11 | 0.62368 (6) | 0.40622 (13) | 0.51371 (6) | 0.0187 (2) |
| C11 | 0.68099 (7) | 0.45625 (15) | 0.46930 (8) | 0.0211 (3) |
| H11 | 0.668777 | 0.523569 | 0.428777 | 0.025* |
| C12 | 0.75732 (8) | 0.41561 (15) | 0.47890 (8) | 0.0230 (3) |
| C13 | 0.77419 (8) | 0.31480 (16) | 0.53720 (9) | 0.0260 (3) |
| H13 | 0.825438 | 0.283210 | 0.545420 | 0.031* |
| C14 | 0.71595 (8) | 0.26057 (16) | 0.58327 (8) | 0.0262 (3) |
| H14 | 0.726560 | 0.191037 | 0.623264 | 0.031* |
| C15 | 0.64179 (8) | 0.30937 (15) | 0.57014 (8) | 0.0210 (3) |
| H15 | 0.602055 | 0.272809 | 0.602382 | 0.025* |
| C16 | 0.81796 (9) | 0.48323 (18) | 0.42866 (10) | 0.0328 (3) |
| H16A| 0.805388 | 0.465065 | 0.374453 | 0.049* |
| H16B| 0.867527 | 0.437548 | 0.440654 | 0.049* |
| H16C| 0.820602 | 0.591251 | 0.438045 | 0.049* |
| N21 | 0.52897 (6) | 0.68274 (12) | 0.58746 (6) | 0.0188 (2) |
| C21 | 0.56837 (7) | 0.65317 (14) | 0.65216 (7) | 0.0198 (3) |
| H21 | 0.579930 | 0.551668 | 0.663532 | 0.024* |
| C22 | 0.59328 (8) | 0.76267 (16) | 0.70361 (8) | 0.0228 (3) |
| C23 | 0.57305 (8) | 0.91022 (16) | 0.68741 (8) | 0.0264 (3) |
| H23 | 0.588277 | 0.988617 | 0.721038 | 0.032* |
| C24 | 0.53606 (8) | 0.94200 (15) | 0.62205 (9) | 0.0260 (3) |
| H24 | 0.515523 | 1.041791 | 0.610919 | 0.031* |
| C25 | 0.51069 (8) | 0.82605 (15) | 0.57323 (8) | 0.0220 (3) |
| H25 | 0.482864 | 0.848780 | 0.527706 | 0.026* |
| C26 | 0.63924 (10) | 0.72132 (18) | 0.77362 (9) | 0.0320 (3) |
| H26A| 0.688861 | 0.772265 | 0.771841 | 0.048* |
| H26B| 0.647277 | 0.612794 | 0.774556 | 0.048* |
| H26C| 0.611546 | 0.751935 | 0.820100 | 0.048* |

Atomic displacement parameters (Å\textsuperscript{2})

|    | U\textsubscript{11} | U\textsubscript{22} | U\textsubscript{33} | U\textsubscript{12} | U\textsubscript{13} | U\textsubscript{23} |
|----|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Mn1| 0.01338 (16) | 0.01517 (16) | 0.01624 (17) | -0.00031 (10) | -0.00030 (9) | 0.00049 (9) |

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### Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°)  |
|-----------------------|--------------|------------|
| Mn1—N1                | 2.3307 (11)  | 90.0       |
| Mn1—N11               | 2.3306 (11)  | 90.0       |
| Mn1—N21               | 2.2866 (11)  | 90.0       |
| Mn1—N21i              | 2.2866 (11)  | 90.0       |
| S1—C1                | 1.6293 (14)  | 90.0       |
| C1—N1                | 1.1690 (18)  | 90.0       |
| C1—C21               | 1.3945 (18)  | 90.0       |
| N11—C11              | 1.3408 (17)  | 90.0       |
| N11—C15              | 1.3450 (17)  | 90.0       |
| C11—H11              | 0.9500       | 90.0       |
| C11—C12              | 1.3926 (18)  | 90.0       |
| C12—C13              | 1.387 (2)    | 90.0       |
| C12—C16              | 1.500 (2)    | 90.0       |
| C13—H13              | 0.9500       | 90.0       |
| C13—C14              | 1.382 (2)    | 90.0       |
| C14—H14              | 0.9500       | 90.0       |
| C14—C15              | 1.3864 (19)  | 90.0       |

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**Supporting Information**

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N11—Mn1—N11 180.00 (5) C25—N21—Mn1 120.41 (9)
N21—Mn1—N11 89.06 (4) C25—N21—C21 117.59 (11)
N21—Mn1—N11i 90.94 (4) N21—C21—H21 118.1
N21—Mn1—N11i 90.94 (4) C25—N21—C21 117.59 (11)
N21i—Mn1—N11i 89.06 (4) N21—C21—H21 118.1
N1—C21—S1 177.78 (12) C23—C22—C21 117.08 (13)
C1—N1—Mn1 153.96 (10) C23—C22—C26 122.10 (13)
C11—N11—Mn1 120.95 (9) C22—C23—C22 119.68 (12)
C11—N11—C15 117.23 (11) C22—C23—H23 120.2
C15—N11—Mn1 121.61 (9) C24—C23—C22 119.58 (13)
N11—C11—H11 118.0 C24—C23—H23 120.5
N11—C11—C12 124.05 (13) C25—C24—C23 118.92 (13)
C12—C11—H11 118.0 C25—C24—H24 120.5
C12—C11—H11 118.0 C25—C24—H24 120.5
C13—C12—C16 120.16 (13) N21—C25—C24 122.79 (13)
C13—C12—C11 117.41 (13) N21—C25—H25 119.68 (12)
C13—C12—C16 122.41 (13) C24—C25—H25 118.6
C12—C13—H13 120.2 C22—C26—H26A 109.5
C14—C13—C12 119.58 (12) C22—C26—H26B 109.5
C14—C13—H13 120.2 C22—C26—H26C 109.5
C13—C14—H14 120.6 H26A—C26—H26B 109.5
C13—C14—C15 118.88 (13) H26A—C26—H26C 109.5
C15—C14—H14 120.6 H26B—C26—H26C 109.5
N11—C15—C14 122.84 (13)

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C11—H11···N1i | 0.95 | 2.60 | 3.2484 (17) | 126 |
| C15—H15···S1ii | 0.95 | 3.00 | 3.5588 (14) | 119 |
| C15—H15···N1i | 0.95 | 2.52 | 3.1535 (17) | 125 |

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

Tetrakis(3-methylpyridine-κN)bis(isothiocyanato-κN)iron(II) (2)

Crystal data

[Fe(NCS)2(C6H7N)4]
Mr = 544.51
Orthorhombic, Pbcn
a = 17.3733 (1) Å
b = 8.94119 (5) Å
c = 17.24862 (10) Å
V = 2679.37 (3) Å³
Z = 4
F(000) = 1136

D = 1.350 Mg m⁻³
Cu Kα radiation, λ = 1.54184 Å
θ = 2.6–79.3°
µ = 6.17 mm⁻¹
T = 100 K
Prism, intense colourless
0.16 × 0.15 × 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\(^{-1}\)

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2021)

\(T_{\text{min}} = 0.555, T_{\text{max}} = 1.000\)

22225 measured reflections

2875 independent reflections

2804 reflections with \(I > 2\sigma(I)\)

\(\theta_{\text{max}} = 79.8^\circ, \theta_{\text{min}} = 5.1^\circ\)

\(h = -22\rightarrow22\)

\(k = -11\rightarrow7\)

\(l = -22\rightarrow20\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.026\)

\(wR(F^2) = 0.073\)

\(S = 1.06\)

2875 reflections

163 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\(w = 1/([\sigma(F_c^2) + (0.0401P)^2 + 1.5203P]/3\)

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

\(\Delta\rho_{\text{max}} = 0.39 \text{ e Å}^{-3}\)

\(\Delta\rho_{\text{min}} = -0.28 \text{ e Å}^{-3}\)

Extinction correction: SHELXL2016/6

(Scheldrick 2015b),

\(Fc^* = kFc[1 + 0.001xFc^2/\sin(2\theta)]^{1/4}\)

Extinction coefficient: 0.00049 (7)

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\(^2\))

|      | x   | y   | z   | \(U_{iso}^*/U_{eq}\) |
|------|-----|-----|-----|----------------------|
| Fe1  | 0.500000 | 0.500000 | 0.500000 | 0.01130 (10) |
| S1   | 0.38206 (2) | 0.28452 (4) | 0.72572 (2) | 0.02425 (11) |
| C1   | 0.43143 (7) | 0.32807 (13) | 0.64874 (7) | 0.0156 (2) |
| N1   | 0.46454 (6) | 0.36130 (12) | 0.59232 (6) | 0.0167 (2) |
| N11  | 0.62142 (6) | 0.40757 (12) | 0.51376 (6) | 0.0149 (2) |
| C11  | 0.67967 (7) | 0.45813 (14) | 0.46972 (7) | 0.0177 (2) |
| H11  | 0.667825 | 0.526986 | 0.429511 | 0.021* |
| C12  | 0.75625 (7) | 0.41613 (15) | 0.47922 (8) | 0.0191 (3) |
| C13  | 0.77283 (7) | 0.31360 (15) | 0.53734 (8) | 0.0219 (3) |
| H13  | 0.824265 | 0.281211 | 0.545588 | 0.026* |
| C14  | 0.71377 (8) | 0.25904 (15) | 0.58315 (8) | 0.0220 (3) |
| H14  | 0.724078 | 0.188658 | 0.623079 | 0.026* |
| C15  | 0.63926 (7) | 0.30874 (14) | 0.56985 (7) | 0.0175 (2) |
| H15  | 0.590047 | 0.271369 | 0.601743 | 0.021* |
| C16  | 0.81754 (8) | 0.48373 (17) | 0.42911 (10) | 0.0285 (3) |
| H16A | 0.806439 | 0.461886 | 0.374566 | 0.043* |
| H16B | 0.867663 | 0.441242 | 0.443056 | 0.043* |
| H16C | 0.818606 | 0.592272 | 0.436935 | 0.043* |
| N21  | 0.52872 (6) | 0.67812 (12) | 0.58534 (6) | 0.0151 (2) |
C21  0.56858 (7)  0.64878 (14)  0.65039 (7)  0.0162 (2)  
H21  0.580676  0.547467  0.661651  0.019*  
C22  0.59325 (8)  0.75852 (15)  0.70240 (7)  0.0188 (3)  
C23  0.57244 (8)  0.90588 (15)  0.68632 (8)  0.0222 (3)  
H23  0.584287  0.720223  0.670712  0.0182 (3)  
C24  0.52958 (8)  0.93723 (14)  0.62059 (8)  0.0215 (3)  
H24  0.536811  0.609476  0.622615  0.026*  
C25  0.50971 (7)  0.82099 (14)  0.57126 (8)  0.0182 (3)  
H25  0.481440  0.843481  0.525582  0.022*  
C26  0.63958 (9)  0.71736 (17)  0.77282 (8)  0.0274 (3)  
H26A  0.689042  0.769994  0.771510  0.041*  
H26B  0.648640  0.609178  0.773221  0.041*  
H26C  0.611273  0.746064  0.819661  0.041*  

Atomic displacement parameters (Å²)

|     | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|-----|-----|-----|-----|-----|-----|-----|
| Fe1 | 0.01186 (15) | 0.01149 (16) | 0.01054 (16) | −0.00048 (9) | 0.00004 (9) | 0.00100 (9) |
| S1  | 0.03164 (19) | 0.02224 (18) | 0.01886 (17) | −0.00132 (13) | 0.00886 (13) | 0.00403 (12) |
| C1  | 0.0169 (6) | 0.0121 (5) | 0.0178 (6) | 0.0006 (4) | −0.0026 (4) | −0.0002 (4) |
| N1  | 0.0174 (5) | 0.0168 (5) | 0.0159 (5) | −0.0005 (4) | 0.0002 (4) | 0.0032 (4) |
| N11 | 0.0149 (5) | 0.0147 (5) | 0.0151 (5) | 0.0006 (4) | −0.0013 (4) | −0.0015 (4) |
| C11 | 0.0176 (6) | 0.0168 (6) | 0.0185 (6) | 0.0003 (5) | −0.0004 (5) | 0.0002 (5) |
| C12 | 0.0157 (6) | 0.0190 (6) | 0.0227 (6) | −0.0008 (5) | 0.0006 (5) | −0.0026 (5) |
| C13 | 0.0153 (6) | 0.0228 (6) | 0.0276 (7) | 0.0027 (5) | −0.0050 (5) | −0.0014 (5) |
| C14 | 0.0217 (6) | 0.0218 (6) | 0.0224 (6) | 0.0039 (5) | −0.0045 (5) | 0.0036 (5) |
| C15 | 0.0185 (6) | 0.0171 (6) | 0.0168 (6) | −0.0001 (5) | −0.0012 (5) | 0.0003 (5) |
| C16 | 0.0209 (7) | 0.0325 (8) | 0.0319 (8) | −0.0001 (6) | 0.0060 (6) | 0.0019 (6) |
| N21 | 0.0153 (5) | 0.0147 (5) | 0.0155 (5) | −0.0007 (4) | 0.0012 (4) | −0.0012 (4) |
| C21 | 0.0174 (6) | 0.0160 (6) | 0.0151 (6) | −0.0011 (5) | 0.0006 (4) | −0.0010 (4) |
| C22 | 0.0209 (6) | 0.0194 (6) | 0.0161 (6) | −0.0036 (5) | 0.0019 (5) | −0.0031 (5) |
| C23 | 0.0265 (6) | 0.0178 (6) | 0.0222 (6) | −0.0051 (5) | 0.0041 (5) | −0.0060 (5) |
| C24 | 0.0241 (6) | 0.0130 (6) | 0.0275 (7) | −0.0004 (5) | 0.0042 (5) | −0.0008 (5) |
| C25 | 0.0174 (6) | 0.0166 (6) | 0.0205 (6) | 0.0008 (5) | 0.0008 (5) | 0.0013 (5) |
| C26 | 0.0352 (8) | 0.0273 (8) | 0.0198 (7) | −0.0040 (6) | −0.0065 (6) | −0.0044 (5) |

Geometric parameters (Å, °)

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| Fe1 | N1i | 2.1103 (10) | C15—H15 | 0.9500 |
| Fe1 | N1  | 2.1103 (10) | C16—H16A | 0.9800 |
| Fe1 | N11 | 2.2780 (10) | C16—H16B | 0.9800 |
| Fe1 | N11 | 2.2779 (10) | C16—H16C | 0.9800 |
| Fe1 | N21 | 2.2253 (10) | N21—C21 | 1.3444 (16) |
| Fe1 | N21 | 2.2253 (10) | N21—C25 | 1.3416 (16) |
| S1  | C1  | 1.6279 (13) | C21—H21 | 0.9500 |
| C1  | N1  | 1.1688 (17) | C21—C22 | 1.3968 (17) |
| N11 | C11 | 1.3436 (16) | C22—C23 | 1.3942 (19) |
| N11 | C15 | 1.3464 (16) | C22—C26 | 1.5030 (19) |
| Bond               | Length (Å) | Bond               | Length (Å) |
|--------------------|------------|--------------------|------------|
| C11—H11            | 0.9500     | C23—H23            | 0.9500     |
| C11—C12            | 1.3922 (18)| C23—C24            | 1.385 (2)  |
| C12—C13            | 1.3887 (19)| C24—H24            | 0.9500     |
| C12—C16            | 1.4987 (19)| C24—C25            | 1.3868 (18)|
| C13—H13            | 0.9500     | C25—H25            | 0.9500     |
| C13—C14            | 1.3838 (19)| C26—H26A           | 0.9800     |
| C14—H14            | 0.9500     | C26—H26B           | 0.9800     |
| C14—C15            | 1.3878 (18)| C26—H26C           | 0.9800     |

| Bond               | Angle (°)  |
|--------------------|------------|
| N1i—Fe1—N1        | 180.0      |
| N1—Fe1—N11        | 91.23 (4)  |
| N1—Fe1—N11i       | 88.77 (4)  |
| N1i—Fe1—N11i      | 91.23 (4)  |
| N1—Fe1—N11i       | 88.77 (4)  |
| N1i—Fe1—N11       | 91.23 (4)  |
| N1—Fe1—N21        | 90.75 (4)  |
| N1i—Fe1—N21i      | 90.75 (4)  |
| N1—Fe1—N21i       | 89.25 (4)  |
| N1—Fe1—N21        | 89.25 (4)  |
| N11—Fe1—N1        | 180.00 (5) |
| N21—Fe1—N11       | 89.03 (4)  |
| N21—Fe1—N11i      | 90.97 (4)  |
| N21—Fe1—N11i      | 90.97 (4)  |
| N21—Fe1—N21i      | 89.03 (4)  |
| N21—Fe1—N21       | 180.00 (4) |
| N1—C1—S1          | 177.62 (12)|
| C1—N1—Fe1         | 157.12 (10)|
| C11—N11—Fe1       | 121.10 (8) |
| C11—N11—C15       | 116.97 (11)|
| C15—N11—Fe1       | 121.75 (8) |
| N11—C11—H11       | 117.9      |
| N11—C11—C12       | 124.24 (12)|
| C12—C11—H11       | 117.9      |
| C12—C12—C16       | 120.16 (12)|
| C13—C12—C16       | 117.46 (12)|
| C13—C12—C11       | 117.46 (12)|
| C12—C13—H13       | 120.3      |
| C14—C13—C12       | 119.41 (12)|
| C14—C13—H13       | 120.3      |
| C13—C14—H14       | 120.5      |
| C13—C14—C15       | 118.97 (12)|
| C15—C14—H14       | 120.5      |
| N11—C15—C14       | 122.94 (12)|

Symmetry code: (i) −x+1, −y+1, −z+1.

**Hydrogen-bond geometry (Å, °)**

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|----------|------|-------|--------|--------|
| C11—H11···N1i | 0.95 | 2.54  | 3.1668 (16) | 124 |

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| Bond          | d (Å) | r (Å)  | D (Å)   | ϕ (°) |
|--------------|-------|--------|---------|-------|
| C15—H15···S1   | 0.95  | 3.00   | 3.5523 (13) | 119   |
| C15—H15···N1   | 0.95  | 2.48   | 3.0961 (16)  | 123   |

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