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)

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The reaction of $Mn(NCS)_2$ or $Fe(NCS)_2$ with 3-methylpyridine (C_6H_7N) leads to the formation of two isostructural compounds with compositions $[Mn(NCS)_2(C_6H_7N)_4]$ (**1**) and $[Fe(NCS)_2(C_6H_7N)_4]$ (**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 thiocyanate 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 Mn^{II}, Fe^{II}, Co^{II} or Ni^{II} 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).


M = Mn (**1**), Fe (**2**)
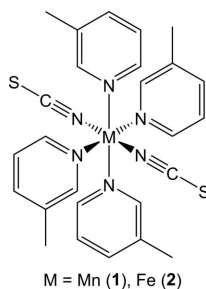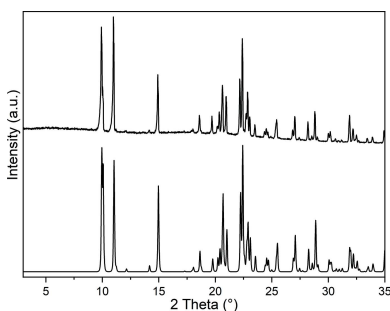
In the past, many such compounds were prepared following this route, using predominantly pyridine-based ligands that are substituted at the 4-position. In the course of our systematic work, we became interested in 3-methylpyridine (3-picoline; C_6H_7N) as a coligand. Some compounds have already been 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 Cu^{II}, Hg^{II} or Cd^{II} (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.*, 2011*a*). 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 Co^{II} 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, 2017*a*) 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). Compound **1** shows a mass loss of 34.8%, which is in reasonable agreement with that calculated for the removal of two 3-methylpyridine ligands. For compound **2**, a poorly resolved TG curve is observed where the sample mass decreases continuously. The residue of **1** isolated after this mass loss was investigated by XRPD, but the pattern could neither be indexed nor assigned to the possibly isotypic phase $Cd(NCS)_2$(3-methylpyridine)$_2$ (Figure S5; Taniguchi *et al.*, 1987).

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.*, 2011*a*) 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
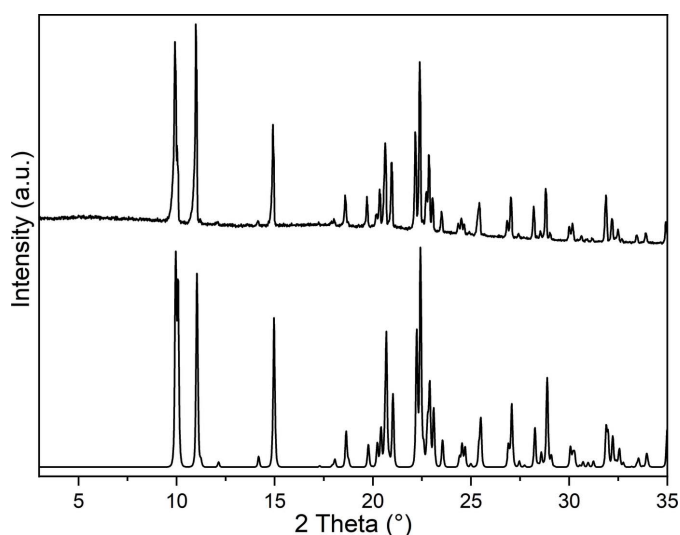
Figure 1
Experimental (top) and calculated (bottom) X-ray powder patterns of compound **1** measured with Cu $K\alpha$ radiation.
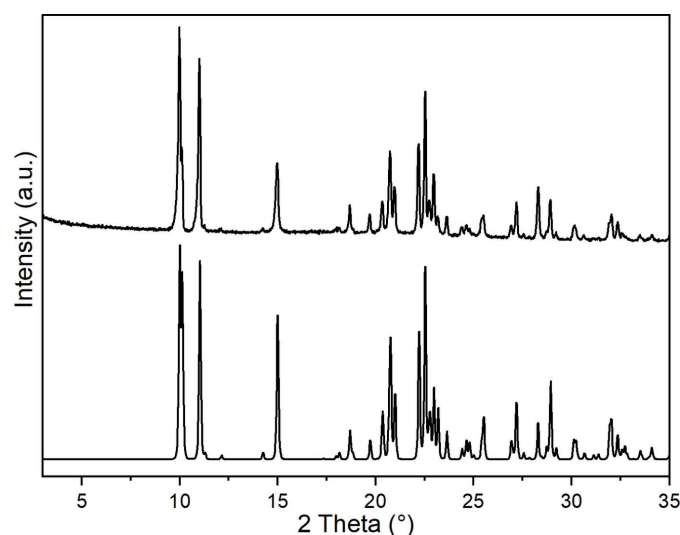
Figure 2
Experimental (top) and calculated (bottom) X-ray powder patterns of compound **2** measured with Cu $K\alpha$ radiation.

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

Mn1—N1	2.1830 (11)	Mn1—N21	2.2866 (11)
Mn1—N11	2.3306 (11)		
N1—Mn1—N11^i	91.56 (4)	N21—Mn1—N11	89.06 (4)
N1—Mn1—N11	88.44 (4)	N21^i—Mn1—N11	90.94 (4)
N1^i—Mn1—N21	90.37 (4)	C1—N1—Mn1	153.96 (10)
N1—Mn1—N21	89.63 (4)		

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

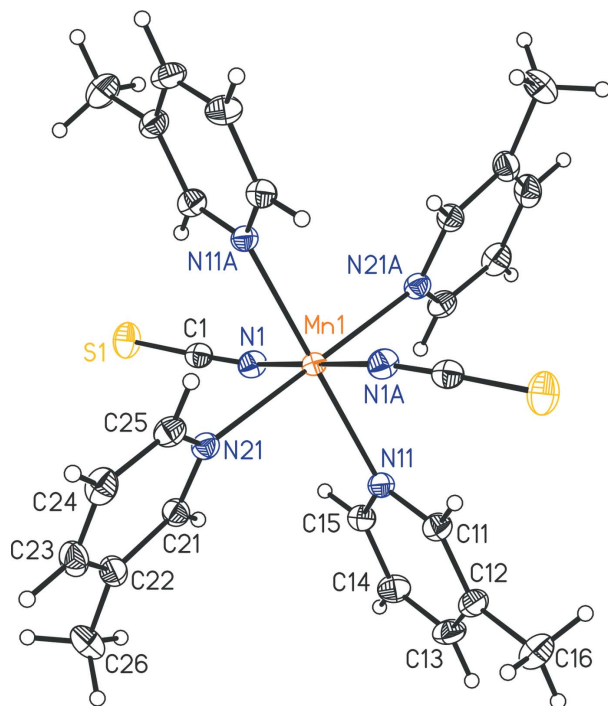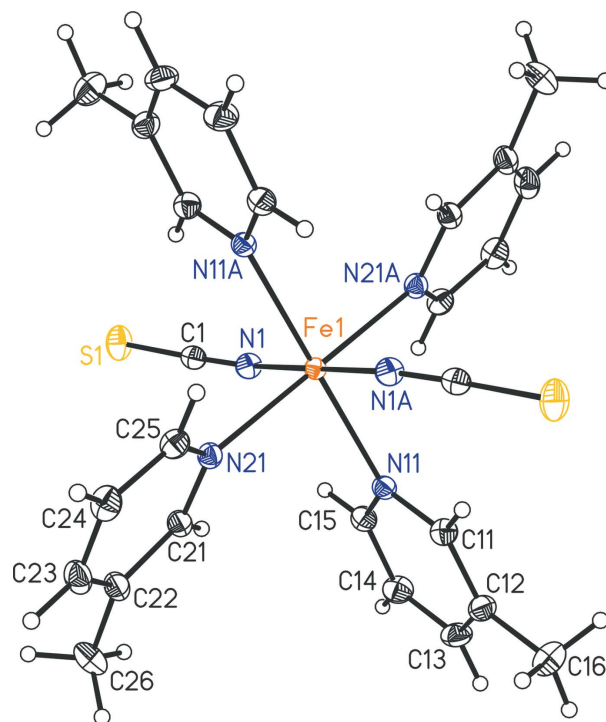**Table 2**
Selected geometric parameters (Å, °) for **2**.

Fe1—N1	2.1103 (10)	Fe1—N21	2.2253 (10)
Fe1—N11	2.2779 (10)		
N1—Fe1—N11^i	91.23 (4)	N21—Fe1—N11	89.03 (4)
N1—Fe1—N11	88.77 (4)	N21^i—Fe1—N11	90.97 (4)
N1^i—Fe1—N21	90.75 (4)	C1—N1—Fe1	157.12 (10)
N1—Fe1—N21	89.25 (4)		

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

(1.0018 for **1** and 1.0023 for **2**) and the octahedral angle variance (1.259$^{\circ 2}$ for **1** and 1.096$^{\circ 2}$ 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

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

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).

Figure 3
The molecular structure of compound **1** with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (A) $1 - x, 1 - y, 1 - z$.]
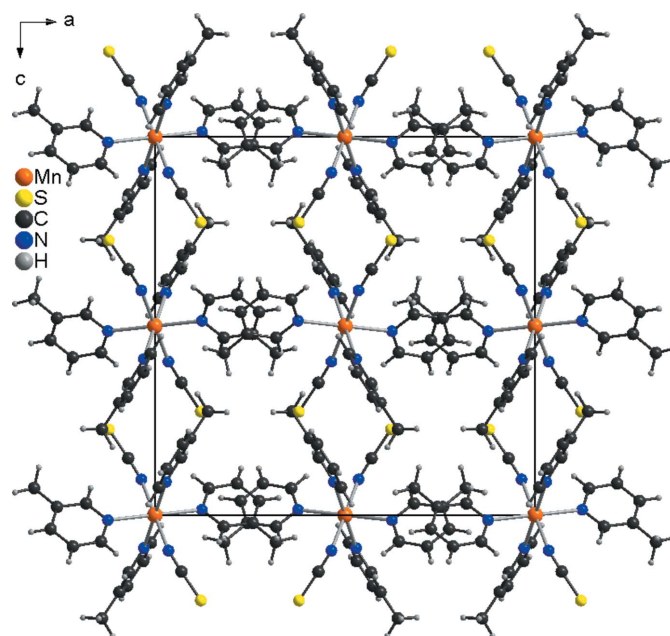
Figure 5
The packing of compound **1** viewed along the crystallographic *b*-axis.

Table 3
Hydrogen-bond geometry (Å, °) for **1**.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H11$\cdots$N1^i	0.95	2.60	3.2484 (17)	126
C15—H15$\cdots$S1^{ii}	0.95	3.00	3.5588 (14)	119
C15—H15$\cdots$N1	0.95	2.52	3.1535 (17)	125

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H11$\cdots$N1^i	0.95	2.54	3.1668 (16)	124
C15—H15$\cdots$S1^{ii}	0.95	3.00	3.5523 (13)	119
C15—H15$\cdots$N1	0.95	2.48	3.0961 (16)	123

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

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 compound *catena*-[tetrakis(thiocyanato)bis(3-methylpyridine)manganesemercury] (refcode NAQYOW), in which the Mn^{II} 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 Hg^{II} cations *via* the thiocyanate S-atoms (Małecki, 2017a). The Hg^{II} cations act as tetrahedral nodes, connecting the Mn^{II} 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)$_2$(H$_2$O)$_2$ (EYAREC), $Co(NCS)_2$(3-methylpyridine)$_4$, isotypic to the title compounds (EYAROM and EYAROM01) as well as $Co(NCS)_2$(3-methylpyridine)$_2$ (EYARIG) are reported, in which the Co^{II} cations are octahedrally or tetrahedrally coordinated (Boeckmann *et al.*, 2011a; Małecki *et al.*, 2012). Discrete complexes, in which Ni^{II} cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and two 3-methylpyridine coligands are also known (CIVJEW, CIVJEW10, JICMIR, LAYLAY, LAYLEC, LAYLIG, LAYLOM 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)$_2$(H$_2$O)$_2$ is also reported (MEGCEH; Tan *et al.*, 2006).

With Cu^{II}, the discrete complexes $Cu(NCS)_2$(3-methylpyridine)$_2$ (ABOTET) and $Cu(NCS)_2$(3-methylpyridine)$_3$ (VEPBAT) with fourfold and fivefold coordinations, respectively, and the chain compound $Cu(NCS)$(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 Cd^{II} cations are linked by pairs of thiocyanate anions into chains (Taniguchi *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)manganesemercury] (NAQYOW; Małecki, 2017a) mentioned above and the isotypic compound where Mn^{II} is replaced by Zn^{II} (QAMSIJ; Małecki, 2017b).

5. Synthesis and crystallization

Synthesis

$Ba(SCN)_2\cdot 3H_2O$ and 3-picoline were purchased from Alfa Aesar. $MnSO_4\cdot H_2O$ was purchased from Merck. A reaction of equimolar amounts of $Ba(SCN)_2\cdot 3H_2O$ with $MnSO_4\cdot H_2O$ in deionized water was performed. After that, the precipitate of $BaSO_4$ 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)$_4$: 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)$_4$: A mixture of 0.25 mmol of $FeCl_2\cdot 4H_2O$ (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 $FeCl_2\cdot 4H_2O$ (98.6 mg) and 1.0 mmol of KSCN (97.2 mg) 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 $K\alpha$ 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 $K\alpha_1$ radiation ($\lambda = 1.540598$ Å) using a Stoe Transmission Powder Diffraction System (STADI P) that is equipped with a

Table 5
Experimental details.

	1	2
Crystal data		
Chemical formula	[Mn(NCS)$_2$(C$_6$H$_7$N)$_4$]	[Fe(NCS)$_2$(C$_6$H$_7$N)$_4$]
M_r	543.60	544.51
Crystal system, space group	Orthorhombic, *Pbcn*	Orthorhombic, *Pbcn*
Temperature (K)	100	100
a, b, c (Å)	17.47811 (10), 8.93570 (6), 17.36177 (10)	17.3733 (1), 8.94119 (5), 17.24862 (10)
V (Å^3)	2711.55 (3)	2679.37 (3)
Z	4	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	5.60	6.17
Crystal size (mm)	0.18 × 0.15 × 0.1	0.16 × 0.15 × 0.15
Data collection		
Diffractometer	XtaLAB Synergy, Dualflex, HyPix	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{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_{int}	0.021	0.020
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.638	0.638
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, 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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e 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 *publCIF* (Westrip, 2010).

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

Thermogravimetry and differential thermoanalysis (TG–DTA) measurements were performed in a dynamic nitrogen atmosphere in Al$_2$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 $U_{iso}(H) = 1.2U_{eq}(C)$ (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)

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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

[Mn(NCS)$_2$(C$_6$H$_7$N)$_4$]	D_x = 1.332 Mg m^{-3}
M_r = 543.60	Cu $K\alpha$ radiation, λ = 1.54184 Å
Orthorhombic, *Pbcn*	Cell parameters from 12231 reflections
a = 17.47811 (10) Å	θ = 5.1–79.2°
b = 8.93570 (6) Å	μ = 5.60 mm^{-1}
c = 17.36177 (10) Å	T = 100 K
V = 2711.55 (3) Å^3	Block, intense colourless
Z = 4	0.18 × 0.15 × 0.1 mm
$F(000)$ = 1132	

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	T_{min} = 0.786, T_{max} = 1.000
	23041 measured reflections
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	2918 independent reflections
	2841 reflections with $I > 2\sigma(I)$
Mirror monochromator	R_{int} = 0.021
Detector resolution: 10.0000 pixels mm^{-1}	θ_{max} = 79.8°, θ_{min} = 5.1°
ω scans	h = −16→22
Absorption correction: multi-scan (CrysalisPro; Rigaku OD, 2021)	k = −10→11
	l = −22→22

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: dual
$R[F^2 > 2\sigma(F^2)]$ = 0.028	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.078	
S = 1.07	H-atom parameters constrained
2918 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 1.4595P]$
162 parameters	where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.45$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ 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)

	x	*y*	*z*	U_{iso}*/U_{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	0.53065 (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 (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01338 (16)	0.01517 (16)	0.01624 (17)	−0.00031 (10)	−0.00030 (9)	0.00049 (9)

S1	0.0353 (2)	0.02628 (19)	0.02457 (18)	−0.00033 (14)	0.00961 (14)	0.00401 (13)
C1	0.0195 (6)	0.0158 (6)	0.0238 (6)	0.0011 (5)	−0.0029 (5)	0.0002 (5)
N1	0.0202 (5)	0.0216 (5)	0.0220 (5)	−0.0006 (4)	0.0010 (4)	0.0034 (4)
N11	0.0166 (5)	0.0185 (5)	0.0209 (5)	0.0003 (4)	−0.0011 (4)	−0.0022 (4)
C11	0.0194 (6)	0.0201 (6)	0.0238 (6)	0.0004 (5)	0.0000 (5)	0.0003 (5)
C12	0.0177 (6)	0.0220 (6)	0.0292 (6)	−0.0003 (5)	0.0015 (5)	−0.0028 (5)
C13	0.0166 (6)	0.0272 (7)	0.0341 (8)	0.0029 (5)	−0.0045 (5)	−0.0007 (6)
C14	0.0235 (7)	0.0268 (7)	0.0282 (7)	0.0034 (5)	−0.0050 (5)	0.0044 (6)
C15	0.0203 (6)	0.0205 (6)	0.0222 (6)	−0.0002 (5)	−0.0016 (5)	0.0000 (5)
C16	0.0231 (7)	0.0369 (8)	0.0384 (9)	−0.0003 (6)	0.0074 (6)	0.0014 (6)
N21	0.0168 (5)	0.0180 (5)	0.0217 (5)	−0.0006 (4)	0.0008 (4)	−0.0008 (4)
C21	0.0199 (6)	0.0190 (6)	0.0206 (6)	−0.0009 (5)	0.0006 (5)	−0.0012 (5)
C22	0.0241 (6)	0.0235 (6)	0.0209 (6)	−0.0037 (5)	0.0024 (5)	−0.0031 (5)
C23	0.0296 (7)	0.0215 (6)	0.0279 (7)	−0.0059 (5)	0.0049 (5)	−0.0073 (5)
C24	0.0272 (7)	0.0163 (6)	0.0343 (7)	−0.0002 (5)	0.0054 (6)	−0.0008 (5)
C25	0.0196 (6)	0.0198 (6)	0.0266 (7)	0.0007 (5)	0.0008 (5)	0.0018 (5)
C26	0.0387 (8)	0.0329 (8)	0.0243 (7)	−0.0053 (7)	−0.0066 (6)	−0.0055 (6)

Geometric parameters (Å, º)

Mn1—N1[i]	2.1830 (11)	C15—H15	0.9500
Mn1—N1	2.1830 (11)	C16—H16A	0.9800
Mn1—N11[i]	2.3307 (11)	C16—H16B	0.9800
Mn1—N11	2.3306 (11)	C16—H16C	0.9800
Mn1—N21	2.2866 (11)	N21—C21	1.3439 (17)
Mn1—N21[i]	2.2866 (11)	N21—C25	1.3427 (17)
S1—C1	1.6293 (14)	C21—H21	0.9500
C1—N1	1.1690 (18)	C21—C22	1.3945 (18)
N11—C11	1.3408 (17)	C22—C23	1.394 (2)
N11—C15	1.3450 (17)	C22—C26	1.503 (2)
C11—H11	0.9500	C23—H23	0.9500
C11—C12	1.3926 (18)	C23—C24	1.385 (2)
C12—C13	1.387 (2)	C24—H24	0.9500
C12—C16	1.500 (2)	C24—C25	1.383 (2)
C13—H13	0.9500	C25—H25	0.9500
C13—C14	1.382 (2)	C26—H26A	0.9800
C14—H14	0.9500	C26—H26B	0.9800
C14—C15	1.3864 (19)	C26—H26C	0.9800
N1[i]—Mn1—N1	180.0	N11—C15—H15	118.6
N1—Mn1—N11[i]	91.56 (4)	C14—C15—H15	118.6
N1—Mn1—N11	88.44 (4)	C12—C16—H16A	109.5
N1[i]—Mn1—N11[i]	88.44 (4)	C12—C16—H16B	109.5
N1[i]—Mn1—N11	91.56 (4)	C12—C16—H16C	109.5
N1[i]—Mn1—N21	90.37 (4)	H16A—C16—H16B	109.5
N1—Mn1—N21[i]	90.37 (4)	H16A—C16—H16C	109.5
N1[i]—Mn1—N21[i]	89.63 (4)	H16B—C16—H16C	109.5
N1—Mn1—N21	89.63 (4)	C21—N21—Mn1	121.88 (8)

N11—Mn1—N11[i]	180.00 (5)	C25—N21—Mn1	120.41 (9)
N21—Mn1—N11	89.06 (4)	C25—N21—C21	117.59 (11)
N21[i]—Mn1—N11	90.94 (4)	N21—C21—H21	118.1
N21—Mn1—N11[i]	90.94 (4)	N21—C21—C22	123.88 (12)
N21[i]—Mn1—N11[i]	89.06 (4)	C22—C21—H21	118.1
N21—Mn1—N21[i]	180.0	C21—C22—C26	120.82 (13)
N1—C1—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—H23	120.2
C11—N11—C15	117.23 (11)	C24—C23—C22	119.68 (12)
C15—N11—Mn1	121.61 (9)	C24—C23—H23	120.2
N11—C11—H11	118.0	C23—C24—H24	120.5
N11—C11—C12	124.05 (13)	C25—C24—C23	118.92 (13)
C12—C11—H11	118.0	C25—C24—H24	120.5
C11—C12—C16	120.16 (13)	N21—C25—C24	122.79 (13)
C13—C12—C11	117.41 (13)	N21—C25—H25	118.6
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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···N1[i]	0.95	2.60	3.2484 (17)	126
C15—H15···S1[ii]	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*+3/2.

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

Crystal data

[Fe(NCS)₂(C₆H₇N)₄]	D_x = 1.350 Mg m⁻³
M_r = 544.51	Cu *Kα* radiation, λ = 1.54184 Å
Orthorhombic, *Pbcn*	Cell parameters from 17643 reflections
a = 17.3733 (1) Å	θ = 2.6–79.3°
b = 8.94119 (5) Å	μ = 6.17 mm⁻¹
c = 17.24862 (10) Å	*T* = 100 K
V = 2679.37 (3) Å³	Prism, intense colourless
Z = 4	0.16 × 0.15 × 0.15 mm
F(000) = 1136	

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	$T_{min} = 0.555$, $T_{max} = 1.000$
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	22225 measured reflections
	2875 independent reflections
Mirror monochromator	2804 reflections with $I > 2\sigma(I)$
Detector resolution: 10.0000 pixels mm^{-1}	$R_{int} = 0.020$
ω scans	$\theta_{max} = 79.8°$, $\theta_{min} = 5.1°$
Absorption correction: multi-scan (CrysalisPro; Rigaku OD, 2021)	$h = -22 \rightarrow 22$
	$k = -11 \rightarrow 7$
	$l = -22 \rightarrow 20$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 1.5203P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
2875 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}
163 parameters	Extinction correction: SHELXL2016/6 (Sheldrick 2015b),
0 restraints	$Fc^* = kFc[1 + 0.001 \times Fc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: dual	Extinction coefficient: 0.00049 (7)
Hydrogen site location: inferred from neighbouring sites	

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	0.599047	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	0.587559	0.984287	0.720223	0.027*
C24	0.52958 (8)	0.93723 (14)	0.62059 (8)	0.0215 (3)
H24	0.514030	1.036811	0.609476	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)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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, º)

Fe1—N1^i	2.1103 (10)	C15—H15	0.9500
Fe1—N1	2.1103 (10)	C16—H16A	0.9800
Fe1—N11^i	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^i	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)

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
N1^i—Fe1—N1	180.0	N11—C15—H15	118.5
N1—Fe1—N11^i	91.23 (4)	C14—C15—H15	118.5
N1—Fe1—N11	88.77 (4)	C12—C16—H16A	109.5
N1^i—Fe1—N11^i	88.77 (4)	C12—C16—H16B	109.5
N1^i—Fe1—N11	91.23 (4)	C12—C16—H16C	109.5
N1^i—Fe1—N21	90.75 (4)	H16A—C16—H16B	109.5
N1—Fe1—N21^i	90.75 (4)	H16A—C16—H16C	109.5
N1^i—Fe1—N21^i	89.25 (4)	H16B—C16—H16C	109.5
N1—Fe1—N21	89.25 (4)	C21—N21—Fe1	121.87 (8)
N11—Fe1—N11^i	180.00 (5)	C25—N21—Fe1	120.44 (9)
N21—Fe1—N11	89.03 (4)	C25—N21—C21	117.62 (11)
N21^i—Fe1—N11	90.97 (4)	N21—C21—H21	118.1
N21—Fe1—N11^i	90.97 (4)	N21—C21—C22	123.85 (12)
N21^i—Fe1—N11^i	89.03 (4)	C22—C21—H21	118.1
N21—Fe1—N21^i	180.00 (4)	C21—C22—C26	120.76 (12)
N1—C1—S1	177.62 (12)	C23—C22—C21	117.16 (12)
C1—N1—Fe1	157.12 (10)	C23—C22—C26	122.08 (12)
C11—N11—Fe1	121.10 (8)	C22—C23—H23	120.2
C11—N11—C15	116.97 (11)	C24—C23—C22	119.58 (12)
C15—N11—Fe1	121.75 (8)	C24—C23—H23	120.2
N11—C11—H11	117.9	C23—C24—H24	120.5
N11—C11—C12	124.24 (12)	C23—C24—C25	118.97 (12)
C12—C11—H11	117.9	C25—C24—H24	120.5
C11—C12—C16	120.16 (12)	N21—C25—C24	122.77 (12)
C13—C12—C11	117.46 (12)	N21—C25—H25	118.6
C13—C12—C16	122.36 (12)	C24—C25—H25	118.6
C12—C13—H13	120.3	C22—C26—H26A	109.5
C14—C13—C12	119.41 (12)	C22—C26—H26B	109.5
C14—C13—H13	120.3	C22—C26—H26C	109.5
C13—C14—H14	120.5	H26A—C26—H26B	109.5
C13—C14—C15	118.97 (12)	H26A—C26—H26C	109.5
C15—C14—H14	120.5	H26B—C26—H26C	109.5
N11—C15—C14	122.94 (12)		

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···N1^i	0.95	2.54	3.1668 (16)	124

C15—H15···S1ⁱⁱ	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.