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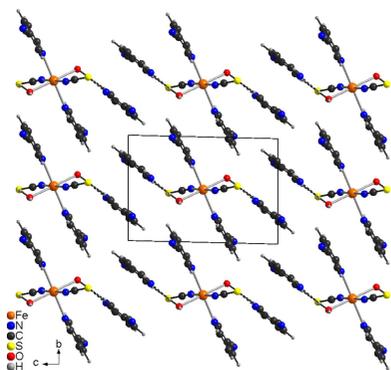
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Aberdeen, United Kingdom**Keywords:** crystal structure; iron thiocyanate; 3-  
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# Synthesis, crystal structure and properties of tetrakis(pyridine-3-carbonitrile)dithiocyanatoiron(II) and of diaquabis(pyridine-3-carbonitrile)-dithiocyanatoiron(II) pyridine-3-carbonitrile monosolvate

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The reaction of iron thiocyanate with 3-cyanopyridine ( $C_6H_4N_2$ ) leads to the formation of two compounds with the composition  $[Fe(NCS)_2(C_6H_4N_2)_4]$  (**1**) and  $[Fe(NCS)_2(C_6H_4N_2)_2(H_2O)_2] \cdot 2C_6H_4N_2$  (**2**). The asymmetric unit of **1** consists of one iron cation, two thiocyanate anions and four 3-cyanopyridine ligands in general positions. The iron cation is octahedrally coordinated by two N-bonded thiocyanate anions and four 3-cyanopyridine ligands. The complexes are arranged in columns along the crystallographic *c*-axis direction and are linked by weak C—H...N interactions. In **2**, the asymmetric unit consists of one iron cation on a center of inversion as well as one thiocyanate anion, one 3-cyanopyridine ligand, one water ligand and one 3-cyanopyridine solvate molecule in general positions. The iron cation is octahedrally coordinated by two N-bonded thiocyanate anions, two cyanopyridine ligands and two water ligands. O—H...N and C—H...S hydrogen bonding is observed between the water ligands and the solvent 3-cyanopyridine molecules. In the crystal structure, alternating layers of the iron complexes and the solvated 3-cyanopyridine molecules are observed. Powder X-ray (PXRD) investigations reveal that both compounds were obtained as pure phases and from IR spectroscopic measurements conclusions on the coordination mode of the thiocyanate anions and the cyanogroup were made. Thermogravimetric (TG) and differential thermoanalysis (DTA) of **1** indicate the formation of a compound with the composition  $\{[Fe(NCS)_2]_3(C_6H_4N_2)_4\}_n$  that is isotopic to the corresponding Cd compound already reported in the literature. TG/DTA of **2** show several mass losses. The first mass loss corresponds to the removal of the two water ligands leading to the formation of **1**, which transforms into  $\{[Fe(NCS)_2]_3(C_6H_4N_2)_4\}_n$ , upon further heating.



## 1. Chemical context

For several years, we and others have been interested in the synthesis, structures and physical properties of coordination compounds based on transition-metal thiocyanates with additional neutral organic coligands. In such compounds, the anionic ligands can be terminally coordinated to the metal cations or they can act as bridging ligands, leading to the formation of networks (Kabešová & Gažo, 1980). The latter compounds are of special interest because different magnetic phenomena can be observed (González *et al.*, 2012; Werner *et al.*, 2014; Palion-Gazda *et al.*, 2015; Mautner *et al.*, 2018; Rams *et al.*, 2020). Unfortunately, the compounds with a bridging coordination are sometimes difficult to prepare with metal cations such as Mn, Fe, Co or Ni, because these cations are less chalcophilic, which means that a terminal coordination is

preferred. In such cases, an alternative synthetic approach can be used based on thermal treatment of suitable precursor compounds, which we developed many years ago for the synthesis of copper(I) halide coordination polymers (Näther *et al.*, 2001; Näther & Jess, 2004). For the synthesis of thiocyanate coordination polymers, these precursors consist of compounds in which the metal cations are octahedrally coordinated by two terminally N-bonding thiocyanate anions and four coligands that in most cases consist of pyridine derivatives. If such compounds are heated, the coligands are frequently stepwise removed and the empty coordination sites at the metal centers are completed by the S atoms of the anionic ligands that in the complex do not participate in the metal coordination, which enforces a bridging coordination of the thiocyanate anions. Major advantages of this approach are the fact that this reaction is irreversible, that the products are formed in quantitative yields, and that in several cases, polymorphic or isomeric modifications can be prepared (Werner *et al.*, 2015). However, following this approach, only microcrystalline powders are observed that cannot be investigated by single crystal X-ray diffraction. In this case, the corresponding Cd(NCS)<sub>2</sub> compounds can be prepared, which also prefer an octahedral coordination. Because cadmium is more chalcophilic than the cations mentioned above, the synthesis of compounds with a bridging coordination is easier and, in most cases, they can easily be crystallized and characterized by single-crystal structure analysis (Wöhlert *et al.*, 2013). In several cases they are isotypic with the Mn, Fe, Co or Ni compounds, allowing the structural identification of the latter. Moreover, with Cd(NCS)<sub>2</sub> and one definite ligand, usually several compounds with a different, in part unusual ratio between Cd(NCS)<sub>2</sub> and the coligands can be obtained. If such compounds are detected, one can determine whether they are also available with other metal cations.

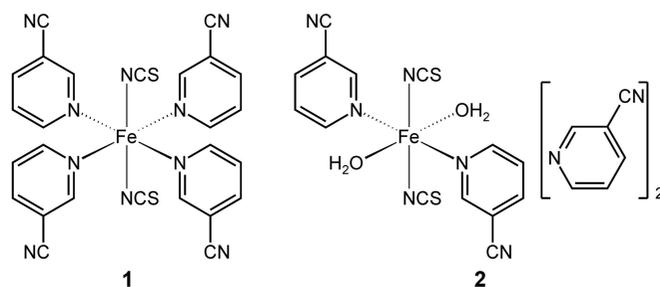
In this context, we have reported new thiocyanate coordination compounds based on Cd(NCS)<sub>2</sub> and 3-cyanopyridine as ligand, where five different compounds were detected (Jochim *et al.*, 2020). This includes two solvates with the composition [Cd(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]<sub>n</sub>·C<sub>6</sub>H<sub>4</sub>N<sub>2</sub> and [Cd(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]<sub>n</sub>·1/3C<sub>6</sub>H<sub>4</sub>N<sub>2</sub> (C<sub>6</sub>H<sub>4</sub>N<sub>2</sub> = 3-cyanopyridine) and one further compound with a similar structure with the composition [Cd(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]<sub>n</sub>. In all of these compounds, the Cd cations are octahedrally coordinated by two thiocyanate anions and four 3-cyanopyridine coligands and are linked by pairs of  $\mu$ -1,3-bridging thiocyanate anions into chains, which is a common motif in thiocyanate coordination polymers. Two additional 3-cyanopyridine deficient compounds with an unusual ratio between Cd(NCS)<sub>2</sub> and 3-cyanopyridine were also characterized. In {[Cd(NCS)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>3</sub>]<sub>n</sub> and {[Cd(NCS)<sub>2</sub>]<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]<sub>n</sub> the cations are also octahedrally coordinated and linked into chains, but some of the 3-cyanopyridine ligands act as bridging ligands and connect the chains into layers.

In further work, corresponding compounds with Ni(NCS)<sub>2</sub> were investigated. With this cation, discrete complexes with the composition Ni(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub> have already been reported in the literature (Kilkenny & Nassimbeni, 2001),

Ni(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, Ni(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub> and Ni(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> were prepared in which the metal cations are always octahedrally coordinated (Krebs *et al.*, 2021). All of these complexes transform into a new compound with the composition Ni(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub> upon heating, which can also be prepared from solution. In this compound, the metal cations are linked by pairs of  $\mu$ -1,3-bridging thiocyanate anions into dinuclear units that are further connected by single anionic ligands into layers. Therefore, the structures of the Ni(NCS)<sub>2</sub> compounds are completely different from those of the Cd(NCS)<sub>2</sub> compounds.

Compounds with Mn(NCS)<sub>2</sub> and 3-cyanopyridine were prepared because Mn<sup>II</sup> compounds frequently behave similar to Cd(NCS)<sub>2</sub> compounds (Krebs *et al.*, 2023). With Mn(NCS)<sub>2</sub> compounds with the composition Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>, Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·bis(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>) solvate and Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)(H<sub>2</sub>O) and Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> were obtained, but the latter compound cannot be prepared as a pure phase. Most compounds consist of discrete complexes but in Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)(H<sub>2</sub>O) the Mn cations are linked by single  $\mu$ -1,3-bridging thiocyanates into chains, which are further connected into layers by the 3-cyanopyridine coligands. Thermoanalytical investigations reveal that the discrete complex Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub> transforms into a new compound with the composition [(Mn(NCS)<sub>2</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]<sub>n</sub> that is isotypic to the corresponding Cd compound mentioned above. When Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·bis(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>) solvate is heated, it transforms into [(Mn(NCS)<sub>2</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]<sub>n</sub> via the discrete complex Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub> as an intermediate. Therefore, the structural behavior and the thermal reactivity is much more similar to that of the Cd(NCS)<sub>2</sub> compounds with 3-cyanopyridine as coligand.

Based on all these findings, we decided to prepare corresponding compounds based on Fe(NCS)<sub>2</sub> and 3-cyanopyridine to investigate if this cation behaves more similarly to Cd<sup>II</sup>, Mn<sup>II</sup> or Ni<sup>II</sup>. Within this systematic work, only two discrete complexes were obtained, which were investigated for their thermal behavior.



## 2. Structural commentary

The asymmetric unit of Fe(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub> (**1**) consists of one iron cation as well as of two thiocyanate anions and four 3-cyanopyridine coligands in general positions (Fig. 1). The iron cations are octahedrally coordinated by two terminally N-bonded thiocyanate anions and four 3-cyanopyridine coligands that coordinate *via* the pyridine N atom to the metal

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

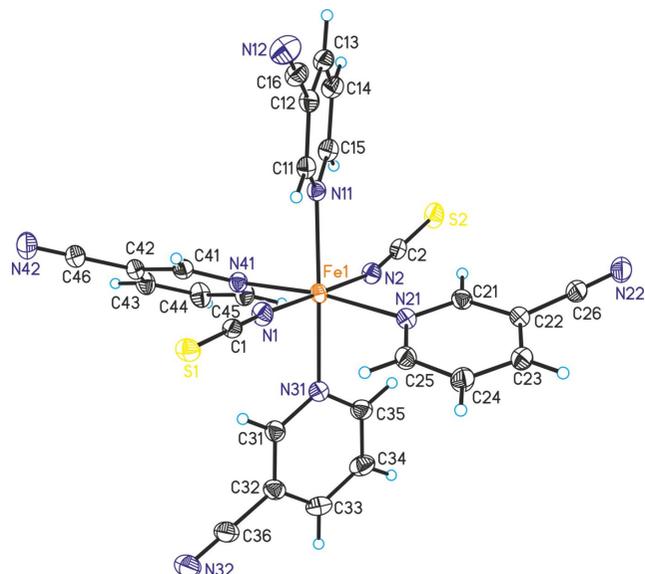
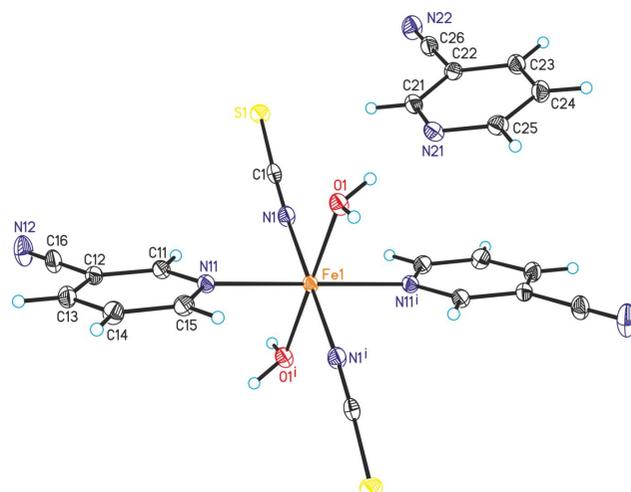
Fe1—N1	2.065 (2)	Fe1—N21	2.273 (2)
Fe1—N2	2.069 (2)	Fe1—N31	2.257 (2)
Fe1—N11	2.2660 (19)	Fe1—N41	2.2339 (19)
N1—Fe1—N2	179.21 (9)	N11—Fe1—N21	97.44 (7)
N1—Fe1—N11	90.70 (8)	N31—Fe1—N11	176.72 (7)
N1—Fe1—N21	90.56 (8)	N31—Fe1—N21	85.31 (7)
N1—Fe1—N31	91.05 (8)	N41—Fe1—N11	90.12 (7)
N1—Fe1—N41	90.15 (9)	N41—Fe1—N21	172.40 (7)
N2—Fe1—N11	88.70 (8)	N41—Fe1—N31	87.11 (7)
N2—Fe1—N21	89.00 (8)	Fe1—N1—C1	175.0 (2)
N2—Fe1—N31	89.57 (8)	Fe1—N2—C2	163.2 (2)
N2—Fe1—N41	90.37 (8)		

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

Fe1—N1	2.1207 (10)	Fe1—N11	2.2358 (10)
Fe1—O1	2.1267 (9)		
N1—Fe1—O1	89.42 (4)	O1 <sup>i</sup> —Fe1—N11	87.62 (3)
N1 <sup>i</sup> —Fe1—O1	90.58 (4)	O1—Fe1—N11	92.38 (3)
N1—Fe1—N11	89.86 (4)	Fe1—N1—C1	167.09 (10)
N1 <sup>i</sup> —Fe1—N11	90.14 (4)		

centers (Fig. 1). This compound is isotopic to Ni(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>, Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub> and Zn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub> already reported in the literature (Kilkenny & Nassimbeni, 2001; Krebs *et al.*, 2021, Krebs *et al.*, 2023; Jochim *et al.*, 2019). Despite differences because of the different ionic radii, the bond lengths are comparable to those in the isotopic compounds (Table 1). From the N—Fe—N bond angles it is obvious that the octahedra are slightly distorted (Table 1).

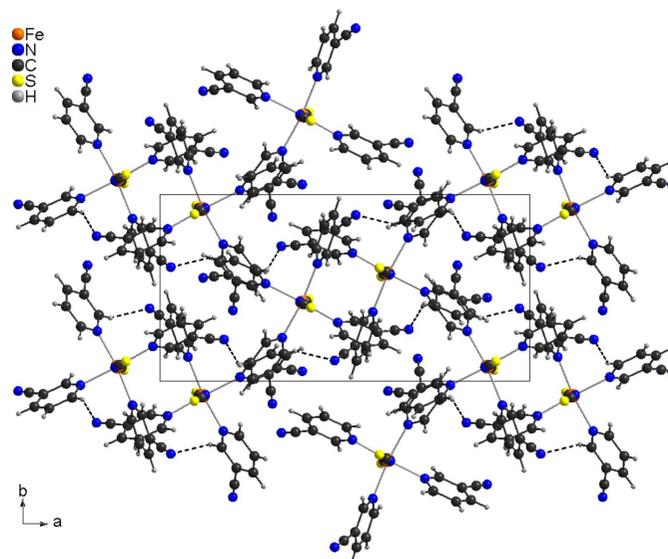
In Fe(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>) (**2**), the asymmetric unit consists of one iron cation that is located on a center of inversion as well as one thiocyanate anion, one 3-cyanopyridine ligand, one water ligand and one 3-cyanopyridine solvate molecule in general positions (Fig. 2). The


**Figure 1**  
 The molecular structure of **1** with displacement ellipsoids drawn at the 50% probability level.

**Figure 2**  
 The molecular structure of **2** with displacement ellipsoids drawn at the 50% probability level. Symmetry codes for the generation of equivalent atoms: (i)  $-x + 1, -y + 1, -z + 1$ .

iron cation is octahedrally coordinated by two 3-cyanopyridine coligands that are connected *via* the pyridine N atom to the Fe<sup>II</sup> cations, two water ligands and two terminally N-bonded thiocyanate anions. This compound is isotopic to Mn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>) and Zn(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>) that are reported in the literature (Krebs *et al.*, 2023; Jochim *et al.*, 2019). The Fe—X (X = N, O) bond lengths are slightly shorter than those in the corresponding Mn compound and the bond angles show that the octahedra are slightly distorted (Table 2).

### 3. Supramolecular features

In compound **1** the discrete complexes are arranged in columns that are oriented along the crystallographic *c*-axis direction (Fig. 3). Within the columns, neighboring 3-cyano-


**Figure 3**  
 Crystal structure of **1** viewed along the crystallographic *c*-axis direction with C—H...N bonds shown as dashed lines.

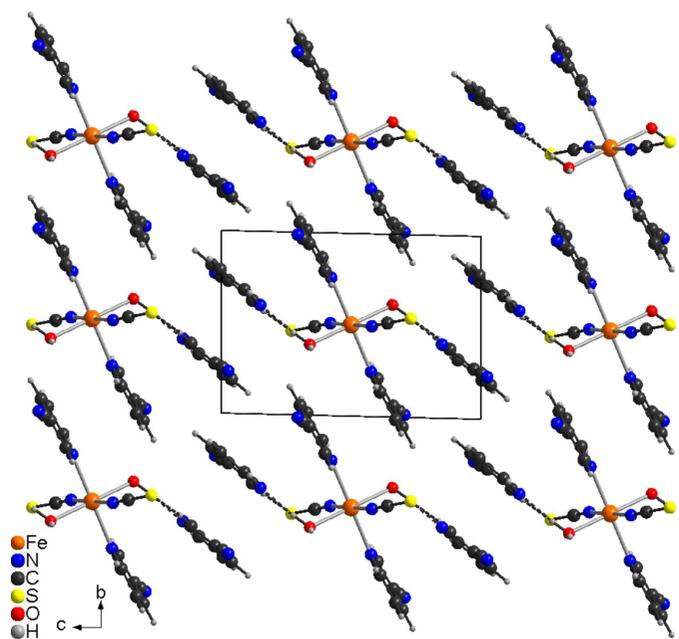
**Table 3**  
Hydrogen-bond geometry (Å, °) for **1**.

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···N1	0.95	2.63	3.190 (3)	118
C15—H15···N2	0.95	2.58	3.113 (3)	115
C21—H21···N2	0.95	2.54	3.108 (3)	118
C24—H24···N2 <sup>i</sup>	0.95	2.67	3.514 (4)	148
C25—H25···N1	0.95	2.61	3.181 (3)	119
C31—H31···N1	0.95	2.67	3.214 (3)	117
C35—H35···N2	0.95	2.53	3.091 (3)	118
C35—H35···N12 <sup>ii</sup>	0.95	2.67	3.538 (4)	151
C41—H41···N22 <sup>iii</sup>	0.95	2.61	3.487 (3)	154
C44—H44···S1 <sup>iv</sup>	0.95	2.82	3.498 (3)	129
C45—H45···N2	0.95	2.55	3.123 (3)	119

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

pyridine rings are not coplanar, with no indication of  $\pi$ - $\pi$  stacking interactions. The complexes are connected *via* weak C—H···N hydrogen bonding but most of these interactions exhibit C—H···N angles far from linearity, indicating that they do not represent strong interactions (Table 3 and Fig. 3)

In compound **2** the discrete complexes are also stacked in columns that proceed along the crystallographic *a*-axis (Fig. 4). These columns are arranged in layers that are parallel to the *ab*-plane. The 3-cyanopyridine solvate molecules are located between these layers and are connected to the complexes *via* C—H···S and O—H···N hydrogen bonding where the pyridine N atom is involved (Table 4 and Fig. 4). There are additional C—H···N interactions, but from the distances and angles it is obvious that they correspond to only very weak interactions. Within the 3-cyanopyridine layers, neighboring 3-cyanopyridine molecules are oriented parallel but shifted relative to each other, preventing  $\pi$ - $\pi$  interactions (Fig. 4).



**Figure 4**  
Crystal structure of **2** viewed along the crystallographic *a*-axis direction with C—H···S and O—H···N hydrogen bonds shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N21	0.89 (2)	1.88 (2)	2.7615 (14)	175 (2)
O1—H1B···S1 <sup>ii</sup>	0.81 (2)	2.62 (2)	3.3184 (9)	145.7 (18)
C11—H11···N1	0.95	2.54	3.1243 (16)	120
C11—H11···S1 <sup>iii</sup>	0.95	3.03	3.6833 (12)	128
C14—H14···S1 <sup>iv</sup>	0.95	2.98	3.7688 (13)	141
C15—H15···N1 <sup>i</sup>	0.95	2.67	3.1894 (16)	115
C21—H21···S1	0.95	2.92	3.8513 (13)	165
C24—H24···N22 <sup>ii</sup>	0.95	2.67	3.3082 (17)	125
C25—H25···S1 <sup>ii</sup>	0.95	3.01	3.8056 (13)	142

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x, -y + 1, -z + 1$ ; (iv)  $-x + 1, -y, -z + 1$ .

#### 4. Database survey

A search in the CSD (version 5.43, last update November 2023; Groom *et al.*, 2016) using *ConQuest* (Bruno *et al.*, 2002) reveals that a number of thiocyanate coordination compounds with 3-cyanopyridine have already been reported in the literature and most of these compounds have already been mentioned in the *Chemical context* section above. This includes discrete complexes with the composition  $M(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_4$  ( $M = \text{Ni}, \text{Zn}$ ) in which the metal cations are octahedrally coordinated by two thiocyanate anions and four 3-cyanopyridine coligands (CSD refcode UDABAC, Kilkenny & Nassimbeni, 2001; UDABAC01, Krebs *et al.*, 2021; LIPZES, Jochim *et al.*, 2019). There are additional complexes with the composition  $M(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_4$  ( $M = \text{Ni}, \text{Co}$ ) that contain solvate molecules (UDABIK, Kilkenny & Nassimbeni, 2001; UDABEG, Kilkenny & Nassimbeni, 2001; OBONOK, Diehr *et al.*, 2011) as well as one complex of composition  $\text{Zn}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2$  that also contains solvate molecules (LIZNOA; Jochim *et al.*, 2019).

Additionally, complexes with the composition  $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2(\text{X})_2$  ( $\text{X} = \text{MeCN}, \text{OCH}_3, \text{H}_2\text{O}, \text{OHCH}_3$ ) are reported, in which the nickel cations are octahedrally coordinated by two thiocyanate anions, two 3-cyanopyridine coligands and two further coligands (YAXDOU, Krebs *et al.*, 2021; YAXDIO, Krebs *et al.*, 2021; YAXCUZ, Krebs *et al.*, 2021). With  $\text{Cu}^{\text{II}}$ , an aqua complex with the composition  $\text{Cu}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2$  is also found (ABOVAR; Handy *et al.*, 2017). One complex of the composition  $\text{Zn}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2$  is reported in which the zinc cations are tetrahedrally coordinated by two thiocyanate anions and two 3-cyanopyridine coligands (LIZNUG; Jochim *et al.*, 2019).

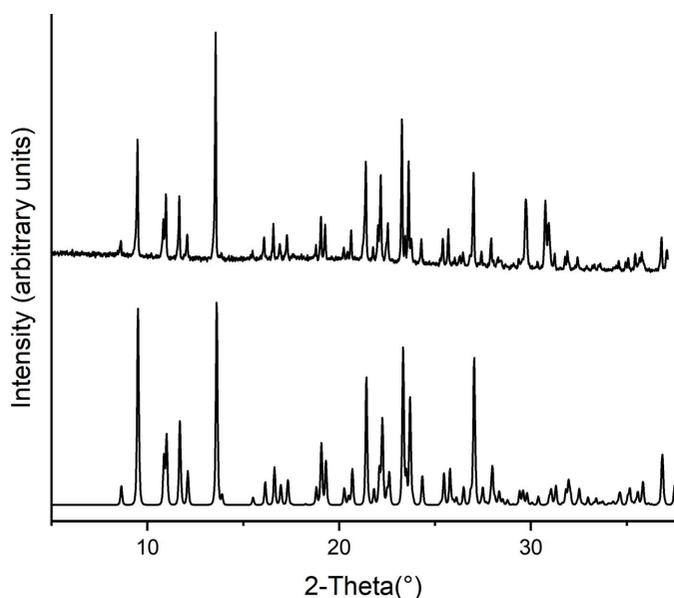
Furthermore, one structure of the composition  $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2$  exists in which nickel cations are octahedrally coordinated by four thiocyanate anions and two 3-cyanopyridine coligands. The nickel cations are linked by pairs of thiocyanate anions into dinuclear units that are further connected into layers by single bridging anionic ligands (YAXDEK; Krebs *et al.*, 2021). In a further compound of the composition  $\text{Cd}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2$ , the cadmium cations are octahedrally coordinated by four thiocyanate anions and two 3-cyanopyridine coligands and are linked through two thiocyanate anions into chains (NURTUS; Jochim *et al.*, 2020). Two additional compounds with similar chain structures are

also listed that contain 3-cyanopyridine solvate molecules (NURTOM, Jochim *et al.*, 2020; NURTIG, Jochim *et al.*, 2020). With  $\text{Cd}(\text{NCS})_2$ , two additional compounds are reported in which  $\text{Cd}(\text{NCS})_2$  chains are linked by some of the 3-cyanopyridine ligands into layers (NURVAA and NURVEE; Jochim *et al.*, 2020). With  $\text{Mn}(\text{NCS})_2$ , the previously mentioned compounds with the composition  $\text{Mn}(\text{NCS})_2 \cdot (\text{C}_6\text{H}_4\text{N}_2)_4$ ,  $\text{Mn}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2 \cdot \text{bis}(\text{C}_6\text{H}_4\text{N}_2)$  solvate and  $\text{Mn}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)(\text{H}_2\text{O})$  and  $\text{Mn}(\text{NCS})_2(\text{C}_6\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2$  have also been reported (Krebs *et al.*, 2023) but these are not yet listed in the CSD.

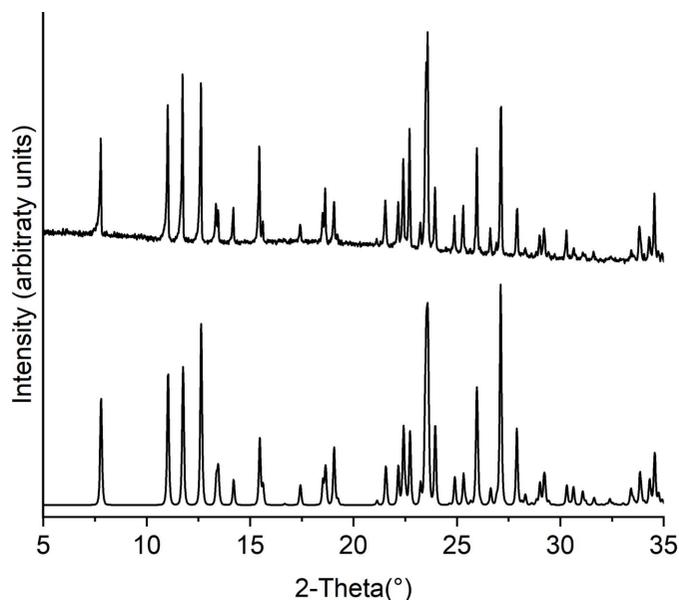
## 5. Physical characterization investigations

Comparison of the experimental powder pattern of **1** and **2** with that calculated from single crystal data shows that both compounds were obtained as pure phases (Figs. 5 and 6). For compound **1**, the CN stretching vibration of the thiocyanate anion is observed at  $2056\text{ cm}^{-1}$  and for the cyanogroup of the 3-cyanopyridine ligand at  $2234\text{ cm}^{-1}$  while for compound **2** these values amount to  $2238\text{ cm}^{-1}$  and  $2080\text{ cm}^{-1}$ , which is in agreement with the fact that the thiocyanate anions are only terminally coordinated and that the cyanogroup is not involved in the metal coordination (Figs. S1 and S2).

The thermal properties of both compounds were investigated by simultaneous thermogravimetry and differential thermoanalysis (TG–DTA). For compound **1** the measurements reveal three mass losses due to heating that are accompanied with two endothermic (first and second mass loss) and one exothermic (third mass loss) events in the DTA curve (Fig. 7 and S3). From the first derivative of the TG curve it is obvious that all mass losses are not well resolved. The first mass loss of 37.3% is slightly higher than that calculated for the removal of two 3-cyanopyridine ligands ( $\Delta m_{\text{calc.}} = 35.4\%$ ). To identify the intermediate formed after the first mass loss we

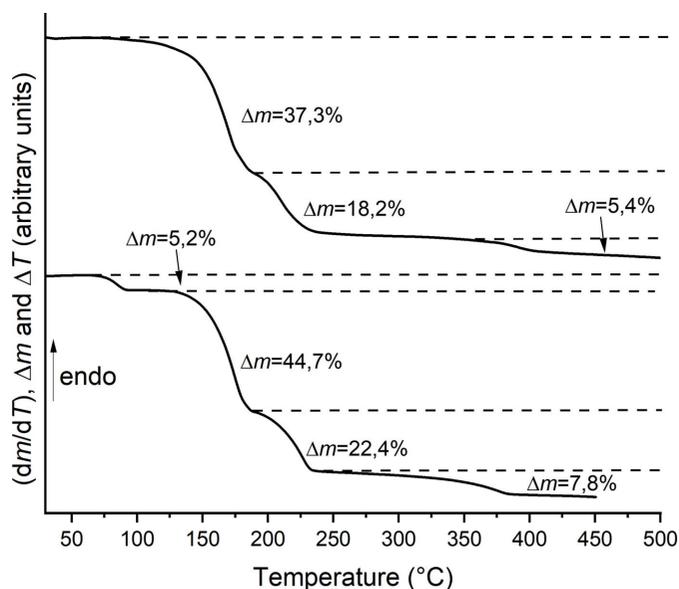


**Figure 5**  
Experimental (top) and calculated PXRD patterns (bottom) of **1**.



**Figure 6**  
Experimental (top) and calculated PXRD patterns (bottom) of **2**.

repeated the TG measurement and isolated the residue after the respective mass loss. The residue was then investigated by IR spectroscopy and powder X-ray diffraction (PXRD). The CN stretching vibrations of the thiocyanate anions are observed at  $2105\text{ cm}^{-1}$  and at  $2078\text{ cm}^{-1}$ , which indicates that  $\mu$ -1,3-bridging anionic ligands are present (Fig. S4). For the cyano group, two different values at  $2248\text{ cm}^{-1}$  and  $2270\text{ cm}^{-1}$  are observed, indicating that some of them are coordinated to the metal center, whereas some others are not (Fig. S4). If the experimental powder pattern is compared with those calculated for all thiocyanate compounds with less 3-cyanopyridine (Fig. S5) that are reported in the literature (see *Database survey*), it is evident that this crystalline phase is isotypic to



**Figure 7**  
TG curves for **1** (top) and **2** (bottom) measured with a  $4\text{ °C min}^{-1}$  heating rate. The mass losses are stated in %.

**Table 5**  
Experimental details.

	1	2
Crystal data		
Chemical formula	[Fe(NCS) <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>4</sub> ]	[Fe(NCS) <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]·2C <sub>6</sub> H <sub>4</sub> N <sub>2</sub>
<i>M<sub>r</sub></i>	588.46	624.49
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.3549 (2), 10.2084 (1), 13.0310 (1)	8.1065 (1), 8.2880 (1), 11.4347 (2)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 90, 90	84.765 (1), 77.787 (1), 70.826 (1)
<i>V</i> (Å <sup>3</sup> )	2707.72 (4)	709.02 (2)
<i>Z</i>	4	1
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	6.21	6.01
Crystal size (mm)	0.10 × 0.08 × 0.06	0.11 × 0.10 × 0.08
Data collection		
Diffractometer	XtaLAB Synergy, Dualflex, HyPix	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2023)	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2023)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.745, 1.000	0.727, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	26794, 5727, 5676	29397, 2999, 2999
<i>R</i> <sub>int</sub>	0.019	0.022
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.639	0.639
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.027, 0.074, 1.06	0.022, 0.060, 1.15
No. of reflections	5727	2999
No. of parameters	352	196
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.24, -0.29	0.29, -0.25
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower	–
Absolute structure parameter	-0.001 (3)	–

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT2014/5* (Sheldrick, 2015b), *SHELXL2016/6* (Sheldrick, 2015a), *DIAMOND* (Brandenburg & Putz, 1999) and *publCIF* (Westrip, 2010).

compounds {[Cd(NCS)<sub>2</sub>]<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]<sub>*n*</sub> (Jochim *et al.*, 2020) and {[Mn(NCS)<sub>2</sub>]<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]<sub>*n*</sub> (Krebs *et al.*, 2023) already reported in the literature (Fig. S5). In this context, it is surprising that two different CN stretching vibrations for the thiocyanate anions are observed, because this structure contains only one crystallographically independent anion, but similar observations were made for the corresponding Mn compound (Krebs *et al.*, 2023). However, in the second mass loss the remaining 3-cyanopyridine ligands are removed and upon further heating Mn(NCS)<sub>2</sub> decomposes.

For compound **2**, four mass losses were observed upon heating that are accompanied with three endothermic and one exothermic events in the DTA curve (Figs. 7 and S6). The first mass loss of 5.2% is in good agreement with the loss of two water ligands ( $\Delta m_{\text{calc.}} = 5.8\%$ ). This indicates that compound **1** has been formed. To prove this assumption, a second TG measurement was performed in which the residue formed after the first mass loss was isolated and investigated by IR spectroscopy and PXRD. The IR spectra is very similar to that of compound **1** (compare Figs. S1 and S7) and comparison of the experimental pattern with that calculated for **1** proves that this compound was obtained (Fig. S8). The second mass loss of 44.7% is in excellent agreement with the loss of 2.67 3-cyanopyridine ligands ( $\Delta m_{\text{calc.}} = 44.5\%$ ), which indicates that after the second mass loss {[Fe(NCS)<sub>2</sub>]<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]<sub>*n*</sub> has been formed. This assumption has been proved through a repetition

of the TG measurement, isolation of the residue after the second mass loss and by IR (Fig. S9) as well as PXRD investigations (Fig. S10).

## 6. Synthesis and crystallization

FeSO<sub>4</sub>·7H<sub>2</sub>O and KSCN were purchased from Sigma-Aldrich and 3-cyanopyridine was purchased from Alfa Aesar.

A microcrystalline powder of **1** was obtained by the reaction of 0.25 mmol of FeSO<sub>4</sub>·7 H<sub>2</sub>O (69.5 mg), 0.5 mmol of KSCN (48.6 mg) and 1 mmol (104.1 mg) of 3-cyanopyridine in 0.5 ml of ethanol. The mixture was stirred for 1 d at room temperature and filtered off. Crystals suitable for single crystal X-ray diffraction were obtained with the same amount of reactants and solvent under hydrothermal conditions (400 K for 1 d) without stirring.

For **2**, a microcrystalline powder was obtained by the reaction of 1 mmol of FeSO<sub>4</sub>·7H<sub>2</sub>O (278 mg), 2 mmol of KSCN (194 mg) and 2 mmol (208.2 mg) of 3-cyanopyridine in 1.5 ml of water. The mixture was filtered off after stirring at room temperature for 2 d. To obtain crystals for single-crystal X-ray diffraction, 0.25 mmol of FeSO<sub>4</sub>·7H<sub>2</sub>O (69.5 mg), 0.5 mmol of KSCN (48.6 mg) and 1 mmol (104.1 mg) of 3-cyanopyridine were mixed in 1.5 ml of water and heated for 2 d at 403 K under hydrothermal conditions.

IR spectra of **1** and **2** can be found in Figs. S1 and S2.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The C-bound H atoms were positioned with idealized geometry and were refined isotropically with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  using a riding model. The water H atoms were located in a difference map and refined isotropically with freely varying coordinates.

## Acknowledgements

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## supporting information

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## Synthesis, crystal structure and properties of tetrakis(pyridine-3-carbonitrile)-dithiocyanatoiron(II) and of diaquabis(pyridine-3-carbonitrile)dithiocyanatoiron(II) pyridine-3-carbonitrile monosolvate

Christian Näther, Asmus Müller-Meinhard and Inke Jess

### Computing details

Data collection: *CrysAlis PRO* 1.171.42.90a (Rigaku OD, 2023) for (1); *CrysAlis PRO* 1.171.42.100a (Rigaku OD, 2023) for (2). Cell refinement: *CrysAlis PRO* 1.171.42.90a (Rigaku OD, 2023) for (1); *CrysAlis PRO* 1.171.42.100a (Rigaku OD, 2023) for (2). Data reduction: *CrysAlis PRO* 1.171.42.90a (Rigaku OD, 2023) for (1); *CrysAlis PRO* 1.171.42.100a (Rigaku OD, 2023) for (2). For both structures, program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015b); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015a); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Tetrakis(pyridine-3-carbonitrile)dithiocyanatoiron(II) (1)

#### Crystal data

[Fe(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]

*M<sub>r</sub>* = 588.46

Orthorhombic, *Pna*2<sub>1</sub>

*a* = 20.3549 (2) Å

*b* = 10.2084 (1) Å

*c* = 13.0310 (1) Å

*V* = 2707.72 (4) Å<sup>3</sup>

*Z* = 4

*F*(000) = 1200

*D<sub>x</sub>* = 1.444 Mg m<sup>-3</sup>

Cu *Kα* radiation, λ = 1.54178 Å

Cell parameters from 22008 reflections

θ = 4.3–79.7°

μ = 6.21 mm<sup>-1</sup>

*T* = 100 K

Block, yellow

0.10 × 0.08 × 0.06 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<sup>-1</sup>

ω scans

Absorption correction: multi-scan  
(CrysAlisPro; Rigaku OD, 2023)

*T<sub>min</sub>* = 0.745, *T<sub>max</sub>* = 1.000

26794 measured reflections

5727 independent reflections

5676 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.019

θ<sub>max</sub> = 80.1°, θ<sub>min</sub> = 4.3°

*h* = -25→24

*k* = -13→13

*l* = -16→15

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.027

*wR*(*F*<sup>2</sup>) = 0.074

*S* = 1.06

5727 reflections

352 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.7383P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Classical Flack method preferred over Parsons because s.u. lower  
 Absolute structure parameter:  $-0.001$  (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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.61644 (2)	0.57715 (4)	0.50208 (3)	0.01625 (10)
N1	0.60947 (11)	0.5803 (2)	0.34404 (18)	0.0220 (5)
C1	0.60437 (12)	0.5722 (2)	0.2549 (2)	0.0182 (5)
S1	0.59757 (3)	0.56051 (6)	0.13118 (5)	0.02232 (13)
N2	0.62205 (11)	0.5735 (2)	0.66062 (18)	0.0207 (5)
C2	0.61060 (12)	0.5872 (2)	0.7474 (2)	0.0184 (5)
S2	0.59268 (4)	0.60626 (6)	0.86779 (5)	0.02877 (15)
N11	0.51976 (9)	0.68579 (19)	0.51593 (16)	0.0186 (4)
C11	0.47464 (12)	0.6794 (2)	0.44172 (17)	0.0193 (4)
H11	0.485160	0.634024	0.380244	0.023*
C12	0.41249 (12)	0.7369 (2)	0.45077 (19)	0.0203 (5)
C13	0.39634 (12)	0.8027 (2)	0.5405 (2)	0.0218 (5)
H13	0.354112	0.840674	0.549291	0.026*
C14	0.44349 (12)	0.8114 (2)	0.61682 (19)	0.0227 (5)
H14	0.434368	0.856933	0.678783	0.027*
C15	0.50423 (12)	0.7527 (2)	0.60161 (18)	0.0214 (5)
H15	0.536372	0.760156	0.654147	0.026*
C16	0.36587 (13)	0.7271 (2)	0.3681 (2)	0.0233 (5)
N12	0.32775 (12)	0.7231 (2)	0.30298 (19)	0.0312 (5)
N21	0.57491 (9)	0.37054 (19)	0.50576 (17)	0.0190 (4)
C21	0.54990 (11)	0.3198 (2)	0.59197 (19)	0.0198 (4)
H21	0.547628	0.373602	0.651370	0.024*
C22	0.52700 (11)	0.1912 (2)	0.59825 (19)	0.0210 (5)
C23	0.53071 (12)	0.1103 (2)	0.5122 (2)	0.0244 (5)
H23	0.516095	0.021992	0.514719	0.029*
C24	0.55633 (13)	0.1629 (2)	0.4232 (2)	0.0258 (5)
H24	0.559409	0.111195	0.362787	0.031*
C25	0.57755 (13)	0.2922 (2)	0.4227 (2)	0.0231 (5)
H25	0.594798	0.327145	0.360763	0.028*
C26	0.49712 (13)	0.1461 (3)	0.6918 (2)	0.0250 (5)
N22	0.47136 (13)	0.1104 (2)	0.7652 (2)	0.0325 (5)
N31	0.71545 (9)	0.4783 (2)	0.49342 (16)	0.0208 (4)
C31	0.75413 (12)	0.4869 (2)	0.4104 (2)	0.0219 (5)

H31	0.738616	0.533481	0.352142	0.026*
C32	0.81617 (13)	0.4300 (2)	0.4066 (2)	0.0237 (5)
C33	0.84021 (12)	0.3634 (3)	0.4921 (2)	0.0275 (5)
H33	0.882745	0.325046	0.491573	0.033*
C34	0.80029 (14)	0.3547 (3)	0.5778 (2)	0.0293 (5)
H34	0.815036	0.310288	0.637584	0.035*
C35	0.73825 (13)	0.4119 (2)	0.5752 (2)	0.0248 (5)
H35	0.710769	0.403611	0.633745	0.030*
C36	0.85443 (14)	0.4395 (3)	0.3136 (2)	0.0285 (6)
N32	0.88400 (12)	0.4469 (3)	0.2389 (2)	0.0368 (6)
N41	0.67037 (9)	0.76769 (19)	0.49903 (17)	0.0190 (4)
C41	0.66633 (11)	0.8538 (2)	0.42188 (19)	0.0212 (4)
H41	0.635285	0.838771	0.368733	0.025*
C42	0.70611 (12)	0.9649 (3)	0.4167 (2)	0.0220 (5)
C43	0.75141 (12)	0.9892 (3)	0.4943 (2)	0.0263 (5)
H43	0.779162	1.064013	0.492090	0.032*
C44	0.75473 (13)	0.9008 (3)	0.5748 (2)	0.0273 (5)
H44	0.784604	0.914585	0.629764	0.033*
C45	0.71398 (12)	0.7922 (3)	0.5742 (2)	0.0229 (5)
H45	0.716965	0.731957	0.629611	0.027*
C46	0.70086 (13)	1.0523 (3)	0.3298 (2)	0.0260 (5)
N42	0.69645 (12)	1.1210 (3)	0.2610 (2)	0.0350 (6)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Fe1	0.01820 (17)	0.01806 (17)	0.01250 (17)	-0.00105 (13)	0.00061 (15)	0.00084 (13)
N1	0.0273 (11)	0.0241 (11)	0.0147 (12)	0.0001 (8)	-0.0005 (8)	0.0004 (7)
C1	0.0154 (10)	0.0165 (11)	0.0225 (15)	0.0006 (8)	0.0018 (9)	0.0016 (9)
S1	0.0246 (3)	0.0278 (3)	0.0145 (3)	0.0040 (2)	-0.0001 (2)	-0.0018 (2)
N2	0.0233 (10)	0.0220 (11)	0.0167 (11)	-0.0001 (8)	-0.0013 (7)	0.0010 (7)
C2	0.0208 (11)	0.0159 (11)	0.0185 (14)	-0.0020 (8)	-0.0029 (9)	0.0024 (9)
S2	0.0467 (4)	0.0235 (3)	0.0162 (3)	-0.0019 (3)	0.0055 (3)	-0.0007 (3)
N11	0.0195 (8)	0.0169 (9)	0.0196 (10)	-0.0021 (7)	0.0008 (7)	0.0002 (7)
C11	0.0222 (11)	0.0183 (10)	0.0175 (11)	-0.0019 (8)	0.0008 (8)	0.0011 (8)
C12	0.0210 (11)	0.0187 (11)	0.0210 (12)	-0.0023 (8)	-0.0002 (9)	0.0008 (9)
C13	0.0233 (11)	0.0177 (11)	0.0243 (12)	-0.0001 (9)	0.0002 (9)	0.0006 (9)
C14	0.0286 (12)	0.0189 (11)	0.0206 (12)	0.0012 (9)	-0.0004 (9)	-0.0040 (9)
C15	0.0251 (11)	0.0193 (10)	0.0199 (11)	-0.0022 (9)	-0.0021 (9)	-0.0013 (9)
C16	0.0260 (12)	0.0195 (11)	0.0245 (12)	0.0018 (9)	-0.0002 (10)	0.0001 (10)
N12	0.0324 (12)	0.0298 (11)	0.0314 (13)	0.0020 (10)	-0.0101 (10)	-0.0030 (9)
N21	0.0187 (8)	0.0200 (9)	0.0182 (9)	-0.0009 (7)	0.0006 (7)	0.0000 (8)
C21	0.0197 (10)	0.0197 (11)	0.0201 (11)	-0.0005 (8)	0.0015 (8)	-0.0020 (9)
C22	0.0197 (10)	0.0203 (11)	0.0230 (12)	0.0006 (8)	0.0039 (9)	0.0018 (9)
C23	0.0264 (11)	0.0193 (11)	0.0276 (13)	-0.0010 (9)	0.0038 (10)	-0.0011 (10)
C24	0.0327 (13)	0.0204 (12)	0.0244 (12)	-0.0013 (10)	0.0036 (10)	-0.0037 (10)
C25	0.0284 (12)	0.0219 (12)	0.0191 (11)	0.0001 (9)	0.0037 (9)	0.0001 (9)
C26	0.0284 (12)	0.0185 (11)	0.0280 (13)	-0.0004 (9)	0.0060 (10)	-0.0019 (10)

N22	0.0417 (14)	0.0225 (11)	0.0333 (13)	-0.0015 (9)	0.0141 (10)	0.0011 (9)
N31	0.0208 (9)	0.0207 (9)	0.0210 (10)	0.0006 (7)	0.0005 (8)	0.0005 (8)
C31	0.0219 (11)	0.0206 (11)	0.0232 (11)	-0.0020 (9)	0.0021 (9)	-0.0010 (9)
C32	0.0223 (12)	0.0216 (12)	0.0274 (14)	-0.0017 (9)	0.0038 (10)	-0.0050 (9)
C33	0.0246 (11)	0.0255 (11)	0.0324 (14)	0.0068 (10)	-0.0025 (10)	-0.0063 (10)
C34	0.0328 (13)	0.0287 (13)	0.0263 (13)	0.0102 (11)	-0.0037 (10)	-0.0002 (11)
C35	0.0278 (12)	0.0248 (11)	0.0219 (12)	0.0048 (10)	0.0026 (10)	-0.0001 (10)
C36	0.0234 (13)	0.0257 (12)	0.0363 (15)	0.0005 (9)	0.0058 (11)	-0.0049 (11)
N32	0.0333 (13)	0.0315 (12)	0.0456 (16)	0.0010 (9)	0.0146 (11)	-0.0031 (11)
N41	0.0182 (8)	0.0193 (9)	0.0196 (8)	-0.0012 (7)	-0.0011 (8)	0.0018 (8)
C41	0.0195 (10)	0.0224 (11)	0.0217 (11)	0.0011 (9)	-0.0003 (9)	0.0011 (10)
C42	0.0212 (10)	0.0228 (11)	0.0221 (12)	0.0003 (9)	0.0037 (9)	0.0042 (10)
C43	0.0231 (11)	0.0271 (12)	0.0288 (13)	-0.0069 (9)	0.0007 (10)	0.0023 (10)
C44	0.0240 (12)	0.0329 (13)	0.0250 (13)	-0.0080 (10)	-0.0047 (10)	0.0025 (11)
C45	0.0230 (11)	0.0242 (11)	0.0215 (11)	-0.0018 (9)	-0.0030 (9)	0.0028 (10)
C46	0.0241 (12)	0.0241 (12)	0.0297 (14)	-0.0011 (9)	0.0041 (10)	0.0039 (11)
N42	0.0339 (12)	0.0356 (13)	0.0356 (14)	-0.0006 (10)	0.0048 (10)	0.0130 (11)

*Geometric parameters (Å, °)*

Fe1—N1	2.065 (2)	C23—C24	1.380 (4)
Fe1—N2	2.069 (2)	C24—H24	0.9500
Fe1—N11	2.2660 (19)	C24—C25	1.389 (4)
Fe1—N21	2.273 (2)	C25—H25	0.9500
Fe1—N31	2.257 (2)	C26—N22	1.149 (4)
Fe1—N41	2.2339 (19)	N31—C31	1.341 (3)
N1—C1	1.169 (4)	N31—C35	1.346 (3)
C1—S1	1.622 (3)	C31—H31	0.9500
N2—C2	1.163 (4)	C31—C32	1.391 (4)
C2—S2	1.622 (3)	C32—C33	1.394 (4)
N11—C11	1.335 (3)	C32—C36	1.444 (4)
N11—C15	1.347 (3)	C33—H33	0.9500
C11—H11	0.9500	C33—C34	1.384 (4)
C11—C12	1.399 (3)	C34—H34	0.9500
C12—C13	1.388 (3)	C34—C35	1.392 (4)
C12—C16	1.439 (3)	C35—H35	0.9500
C13—H13	0.9500	C36—N32	1.146 (4)
C13—C14	1.385 (4)	N41—C41	1.338 (3)
C14—H14	0.9500	N41—C45	1.345 (3)
C14—C15	1.388 (3)	C41—H41	0.9500
C15—H15	0.9500	C41—C42	1.395 (4)
C16—N12	1.151 (4)	C42—C43	1.390 (4)
N21—C21	1.338 (3)	C42—C46	1.447 (4)
N21—C25	1.346 (3)	C43—H43	0.9500
C21—H21	0.9500	C43—C44	1.386 (4)
C21—C22	1.396 (3)	C44—H44	0.9500
C22—C23	1.395 (3)	C44—C45	1.385 (4)
C22—C26	1.438 (3)	C45—H45	0.9500

C23—H23	0.9500	C46—N42	1.141 (4)
N1—Fe1—N2	179.21 (9)	C24—C23—C22	117.7 (2)
N1—Fe1—N11	90.70 (8)	C24—C23—H23	121.1
N1—Fe1—N21	90.56 (8)	C23—C24—H24	120.3
N1—Fe1—N31	91.05 (8)	C23—C24—C25	119.4 (2)
N1—Fe1—N41	90.15 (9)	C25—C24—H24	120.3
N2—Fe1—N11	88.70 (8)	N21—C25—C24	123.3 (2)
N2—Fe1—N21	89.00 (8)	N21—C25—H25	118.4
N2—Fe1—N31	89.57 (8)	C24—C25—H25	118.4
N2—Fe1—N41	90.37 (8)	N22—C26—C22	177.9 (3)
N11—Fe1—N21	97.44 (7)	C31—N31—Fe1	122.38 (17)
N31—Fe1—N11	176.72 (7)	C31—N31—C35	118.0 (2)
N31—Fe1—N21	85.31 (7)	C35—N31—Fe1	119.59 (17)
N41—Fe1—N11	90.12 (7)	N31—C31—H31	118.8
N41—Fe1—N21	172.40 (7)	N31—C31—C32	122.3 (2)
N41—Fe1—N31	87.11 (7)	C32—C31—H31	118.8
Fe1—N1—C1	175.0 (2)	C31—C32—C33	119.6 (2)
N1—C1—S1	179.7 (3)	C31—C32—C36	119.4 (3)
Fe1—N2—C2	163.2 (2)	C33—C32—C36	121.0 (2)
N2—C2—S2	178.6 (2)	C32—C33—H33	121.0
C11—N11—Fe1	121.06 (16)	C34—C33—C32	118.0 (2)
C11—N11—C15	117.6 (2)	C34—C33—H33	121.0
C15—N11—Fe1	121.22 (16)	C33—C34—H34	120.5
N11—C11—H11	118.6	C33—C34—C35	119.1 (3)
N11—C11—C12	122.7 (2)	C35—C34—H34	120.5
C12—C11—H11	118.6	N31—C35—C34	122.9 (3)
C11—C12—C16	120.3 (2)	N31—C35—H35	118.5
C13—C12—C11	119.2 (2)	C34—C35—H35	118.5
C13—C12—C16	120.5 (2)	N32—C36—C32	179.0 (3)
C12—C13—H13	120.9	C41—N41—Fe1	123.72 (16)
C14—C13—C12	118.2 (2)	C41—N41—C45	117.8 (2)
C14—C13—H13	120.9	C45—N41—Fe1	118.22 (16)
C13—C14—H14	120.4	N41—C41—H41	118.8
C13—C14—C15	119.1 (2)	N41—C41—C42	122.3 (2)
C15—C14—H14	120.4	C42—C41—H41	118.8
N11—C15—C14	123.1 (2)	C41—C42—C46	119.7 (2)
N11—C15—H15	118.4	C43—C42—C41	119.7 (2)
C14—C15—H15	118.4	C43—C42—C46	120.5 (2)
N12—C16—C12	177.8 (3)	C42—C43—H43	121.1
C21—N21—Fe1	121.22 (16)	C44—C43—C42	117.8 (2)
C21—N21—C25	117.4 (2)	C44—C43—H43	121.1
C25—N21—Fe1	121.28 (17)	C43—C44—H44	120.4
N21—C21—H21	118.6	C45—C44—C43	119.2 (2)
N21—C21—C22	122.7 (2)	C45—C44—H44	120.4
C22—C21—H21	118.6	N41—C45—C44	123.2 (2)
C21—C22—C26	119.5 (2)	N41—C45—H45	118.4
C23—C22—C21	119.5 (2)	C44—C45—H45	118.4

C23—C22—C26	121.0 (2)	N42—C46—C42	179.7 (3)
C22—C23—H23	121.1		

*Hydrogen-bond geometry* (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C11—H11...N1	0.95	2.63	3.190 (3)	118
C15—H15...N2	0.95	2.58	3.113 (3)	115
C21—H21...N2	0.95	2.54	3.108 (3)	118
C24—H24...N22 <sup>i</sup>	0.95	2.67	3.514 (4)	148
C25—H25...N1	0.95	2.61	3.181 (3)	119
C31—H31...N1	0.95	2.67	3.214 (3)	117
C35—H35...N2	0.95	2.53	3.091 (3)	118
C35—H35...N12 <sup>ii</sup>	0.95	2.67	3.538 (4)	151
C41—H41...N22 <sup>iii</sup>	0.95	2.61	3.487 (3)	154
C44—H44...S1 <sup>iv</sup>	0.95	2.82	3.498 (3)	129
C45—H45...N2	0.95	2.55	3.123 (3)	119

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

**Diaquabis(pyridine-3-carbonitrile)dithiocyanatoiron(II) pyridine-3-carbonitrile monosolvate (2)***Crystal data*

[Fe(NCS)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>

*M<sub>r</sub>* = 624.49

Triclinic, *P* $\bar{1}$

*a* = 8.1065 (1) Å

*b* = 8.2880 (1) Å

*c* = 11.4347 (2) Å

$\alpha$  = 84.765 (1)°

$\beta$  = 77.787 (1)°

$\gamma$  = 70.826 (1)°

*V* = 709.02 (2) Å<sup>3</sup>

*Z* = 1

*F*(000) = 320

*D<sub>x</sub>* = 1.463 Mg m<sup>-3</sup>

Cu *K*α radiation,  $\lambda$  = 1.54184 Å

Cell parameters from 25131 reflections

$\theta$  = 4.0–79.7°

$\mu$  = 6.01 mm<sup>-1</sup>

*T* = 100 K

Block, yellow

0.11 × 0.10 × 0.08 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<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(CrysalisPro; Rigaku OD, 2023)

*T<sub>min</sub>* = 0.727, *T<sub>max</sub>* = 1.000

29397 measured reflections

2999 independent reflections

2999 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.022

$\theta_{\max}$  = 80.4°,  $\theta_{\min}$  = 4.0°

*h* = -10→10

*k* = -10→10

*l* = -11→14

*Refinement*

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.022

*wR*(*F*<sup>2</sup>) = 0.060

*S* = 1.15

2999 reflections

196 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0302*P*)<sup>2</sup> + 0.2457*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.29 e Å<sup>-3</sup>

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2016/6  
(Sheldrick 2016),  
 $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.0036 (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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.500000	0.500000	0.500000	0.01216 (8)
N1	0.23749 (14)	0.50517 (14)	0.58058 (10)	0.0175 (2)
C1	0.10930 (16)	0.48617 (15)	0.64015 (11)	0.0145 (2)
S1	-0.06651 (4)	0.45890 (4)	0.72985 (3)	0.01772 (9)
O1	0.58744 (12)	0.38660 (11)	0.65983 (8)	0.01684 (18)
N11	0.55002 (13)	0.24567 (12)	0.42347 (9)	0.0137 (2)
C11	0.41230 (15)	0.20838 (15)	0.39913 (10)	0.0144 (2)
H11	0.295430	0.284514	0.423936	0.017*
C12	0.43436 (16)	0.06162 (15)	0.33861 (11)	0.0151 (2)
C13	0.60473 (17)	-0.05288 (15)	0.30294 (11)	0.0179 (2)
H13	0.622799	-0.154127	0.262362	0.022*
C14	0.74656 (16)	-0.01402 (16)	0.32865 (12)	0.0183 (2)
H14	0.864668	-0.088837	0.306060	0.022*
C15	0.71430 (16)	0.13553 (15)	0.38781 (11)	0.0163 (2)
H15	0.812998	0.161414	0.403931	0.020*
C16	0.27896 (17)	0.03358 (16)	0.31361 (12)	0.0195 (3)
N12	0.15470 (16)	0.01357 (16)	0.29369 (12)	0.0292 (3)
N21	0.40361 (14)	0.59653 (13)	0.85071 (9)	0.0177 (2)
C21	0.22852 (17)	0.62145 (16)	0.88138 (11)	0.0176 (2)
H21	0.176535	0.564393	0.838477	0.021*
C22	0.11976 (16)	0.72784 (15)	0.97378 (11)	0.0160 (2)
C23	0.19423 (17)	0.81232 (16)	1.03776 (11)	0.0177 (2)
H23	0.122870	0.885180	1.101462	0.021*
C24	0.37532 (17)	0.78663 (16)	1.00549 (12)	0.0190 (3)
H24	0.430907	0.842236	1.046636	0.023*
C25	0.47433 (16)	0.67873 (16)	0.91238 (11)	0.0177 (2)
H25	0.598501	0.661992	0.891042	0.021*
C26	-0.06797 (17)	0.74885 (16)	1.00254 (11)	0.0191 (3)
N22	-0.21762 (15)	0.76797 (16)	1.02557 (11)	0.0256 (3)
H1A	0.531 (3)	0.450 (3)	0.724 (2)	0.045 (6)*
H1B	0.693 (3)	0.369 (3)	0.6554 (18)	0.042 (6)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Fe1	0.01011 (13)	0.01477 (14)	0.01245 (14)	-0.00513 (10)	-0.00059 (9)	-0.00395 (9)
N1	0.0134 (5)	0.0216 (5)	0.0188 (5)	-0.0079 (4)	0.0004 (4)	-0.0065 (4)
C1	0.0146 (5)	0.0146 (5)	0.0155 (6)	-0.0034 (4)	-0.0054 (4)	-0.0043 (4)
S1	0.01226 (14)	0.02427 (16)	0.01741 (16)	-0.00805 (11)	-0.00037 (10)	-0.00184 (11)
O1	0.0146 (4)	0.0193 (4)	0.0166 (4)	-0.0046 (3)	-0.0025 (3)	-0.0045 (3)
N11	0.0132 (5)	0.0148 (5)	0.0131 (5)	-0.0048 (4)	-0.0013 (4)	-0.0020 (4)
C11	0.0134 (5)	0.0162 (5)	0.0137 (6)	-0.0048 (4)	-0.0023 (4)	-0.0018 (4)
C12	0.0159 (6)	0.0173 (5)	0.0141 (6)	-0.0077 (5)	-0.0025 (4)	-0.0018 (4)
C13	0.0188 (6)	0.0160 (6)	0.0190 (6)	-0.0064 (5)	-0.0004 (5)	-0.0046 (5)
C14	0.0141 (5)	0.0161 (6)	0.0223 (6)	-0.0029 (4)	0.0000 (5)	-0.0038 (5)
C15	0.0132 (5)	0.0192 (6)	0.0172 (6)	-0.0066 (5)	-0.0019 (4)	-0.0013 (5)
C16	0.0188 (6)	0.0182 (6)	0.0217 (6)	-0.0058 (5)	-0.0019 (5)	-0.0074 (5)
N12	0.0209 (6)	0.0302 (6)	0.0397 (7)	-0.0088 (5)	-0.0059 (5)	-0.0151 (5)
N21	0.0180 (5)	0.0207 (5)	0.0139 (5)	-0.0057 (4)	-0.0024 (4)	-0.0019 (4)
C21	0.0191 (6)	0.0207 (6)	0.0153 (6)	-0.0084 (5)	-0.0041 (5)	-0.0019 (5)
C22	0.0152 (6)	0.0189 (6)	0.0152 (6)	-0.0073 (5)	-0.0034 (4)	0.0005 (4)
C23	0.0181 (6)	0.0193 (6)	0.0162 (6)	-0.0068 (5)	-0.0015 (5)	-0.0040 (5)
C24	0.0183 (6)	0.0225 (6)	0.0194 (6)	-0.0097 (5)	-0.0045 (5)	-0.0029 (5)
C25	0.0147 (5)	0.0213 (6)	0.0172 (6)	-0.0066 (5)	-0.0026 (4)	0.0006 (5)
C26	0.0198 (6)	0.0216 (6)	0.0180 (6)	-0.0084 (5)	-0.0037 (5)	-0.0031 (5)
N22	0.0188 (6)	0.0314 (6)	0.0290 (6)	-0.0103 (5)	-0.0041 (5)	-0.0055 (5)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Fe1—N1 <sup>i</sup>	2.1207 (10)	C13—C14	1.3841 (17)
Fe1—N1	2.1207 (10)	C14—H14	0.9500
Fe1—O1 <sup>i</sup>	2.1267 (9)	C14—C15	1.3883 (17)
Fe1—O1	2.1267 (9)	C15—H15	0.9500
Fe1—N11	2.2358 (10)	C16—N12	1.1435 (18)
Fe1—N11 <sup>i</sup>	2.2358 (10)	N21—C21	1.3380 (16)
N1—C1	1.1649 (17)	N21—C25	1.3436 (16)
C1—S1	1.6387 (12)	C21—H21	0.9500
O1—H1A	0.89 (2)	C21—C22	1.3916 (18)
O1—H1B	0.81 (2)	C22—C23	1.3956 (17)
N11—C11	1.3390 (15)	C22—C26	1.4419 (17)
N11—C15	1.3463 (15)	C23—H23	0.9500
C11—H11	0.9500	C23—C24	1.3844 (17)
C11—C12	1.3960 (16)	C24—H24	0.9500
C12—C13	1.3949 (17)	C24—C25	1.3850 (18)
C12—C16	1.4421 (17)	C25—H25	0.9500
C13—H13	0.9500	C26—N22	1.1456 (17)
N1 <sup>i</sup> —Fe1—N1	180.0	C13—C12—C16	121.70 (11)
N1—Fe1—O1	89.42 (4)	C12—C13—H13	121.1
N1 <sup>i</sup> —Fe1—O1	90.58 (4)	C14—C13—C12	117.77 (11)

N1—Fe1—O1 <sup>i</sup>	90.58 (4)	C14—C13—H13	121.1
N1 <sup>i</sup> —Fe1—O1 <sup>i</sup>	89.42 (4)	C13—C14—H14	120.4
N1—Fe1—N11	89.86 (4)	C13—C14—C15	119.26 (11)
N1 <sup>i</sup> —Fe1—N11	90.14 (4)	C15—C14—H14	120.4
N1 <sup>i</sup> —Fe1—N11 <sup>i</sup>	89.86 (4)	N11—C15—C14	123.23 (11)
N1—Fe1—N11 <sup>i</sup>	90.14 (4)	N11—C15—H15	118.4
O1 <sup>i</sup> —Fe1—O1	180.0	C14—C15—H15	118.4
O1 <sup>i</sup> —Fe1—N11	87.62 (3)	N12—C16—C12	179.12 (14)
O1 <sup>i</sup> —Fe1—N11 <sup>i</sup>	92.38 (3)	C21—N21—C25	117.81 (11)
O1—Fe1—N11	92.38 (3)	N21—C21—H21	118.8
O1—Fe1—N11 <sup>i</sup>	87.62 (3)	N21—C21—C22	122.43 (11)
N11—Fe1—N11 <sup>i</sup>	180.0	C22—C21—H21	118.8
Fe1—N1—C1	167.09 (10)	C21—C22—C23	119.45 (11)
N1—C1—S1	177.12 (11)	C21—C22—C26	119.67 (11)
Fe1—O1—H1A	113.2 (14)	C23—C22—C26	120.87 (11)
Fe1—O1—H1B	112.3 (14)	C22—C23—H23	121.0
H1A—O1—H1B	106.9 (19)	C24—C23—C22	117.93 (12)
C11—N11—Fe1	118.64 (8)	C24—C23—H23	121.0
C11—N11—C15	117.74 (10)	C23—C24—H24	120.5
C15—N11—Fe1	123.18 (8)	C23—C24—C25	119.07 (11)
N11—C11—H11	118.8	C25—C24—H24	120.5
N11—C11—C12	122.34 (11)	N21—C25—C24	123.30 (11)
C12—C11—H11	118.8	N21—C25—H25	118.3
C11—C12—C16	118.64 (11)	C24—C25—H25	118.3
C13—C12—C11	119.66 (11)	N22—C26—C22	179.03 (14)
Fe1—N11—C11—C12	172.36 (9)	C16—C12—C13—C14	178.74 (12)
Fe1—N11—C15—C14	-172.87 (9)	N21—C21—C22—C23	-0.10 (19)
N11—C11—C12—C13	0.88 (18)	N21—C21—C22—C26	-179.84 (11)
N11—C11—C12—C16	-178.52 (11)	C21—N21—C25—C24	0.17 (18)
C11—N11—C15—C14	-0.63 (18)	C21—C22—C23—C24	0.31 (18)
C11—C12—C13—C14	-0.64 (18)	C22—C23—C24—C25	-0.28 (19)
C12—C13—C14—C15	-0.17 (18)	C23—C24—C25—N21	0.04 (19)
C13—C14—C15—N11	0.84 (19)	C25—N21—C21—C22	-0.14 (18)
C15—N11—C11—C12	-0.24 (17)	C26—C22—C23—C24	-179.96 (12)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A $\cdots$ N21	0.89 (2)	1.88 (2)	2.7615 (14)	175 (2)
O1—H1B $\cdots$ S1 <sup>ii</sup>	0.81 (2)	2.62 (2)	3.3184 (9)	145.7 (18)
C11—H11 $\cdots$ N1	0.95	2.54	3.1243 (16)	120
C11—H11 $\cdots$ S1 <sup>iii</sup>	0.95	3.03	3.6833 (12)	128
C14—H14 $\cdots$ S1 <sup>iv</sup>	0.95	2.98	3.7688 (13)	141
C15—H15 $\cdots$ N1 <sup>i</sup>	0.95	2.67	3.1894 (16)	115
C21—H21 $\cdots$ S1	0.95	2.92	3.8513 (13)	165

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C24—H24···N22 <sup>ii</sup>	0.95	2.67	3.3082 (17)	125
C25—H25···S1 <sup>ii</sup>	0.95	3.01	3.8056 (13)	142

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Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x+1, y, z$ ; (iii)  $-x, -y+1, -z+1$ ; (iv)  $-x+1, -y, -z+1$ .