# Bis(ethanol-$\kappa O$)bis(pyridine-3-carbaldehyde-$\kappa N$ thiosemicarbazone)bis(thiocyanato-$\kappa N$)iron(II)–pyridine-3-carbaldehyde thiosemicarbazone (1/2)

## Shao-Mei Wang

College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang, Henan 455000, People's Republic of China

Correspondence e-mail: wang_shaomei@yahoo.cn

The crystal structure of the title $Fe^{II}$ complex, $[Fe(NCS)_2(C_7H_8N_4S)_2(CH_3CH_2OH)_2]\cdot 2C_7H_8N_4S$, based on the Schiff base ligand pyridine-3-carbaldehyde thiosemicarbazone (pct), results from the cocrystallization of an $Fe^{II}$ coordination compound together with two of the pct ligands. The complex unit is mononuclear, with the central $Fe^{II}$ ion located on a crystallographic centre of inversion and coordinated by four N atoms from two pct ligands and two thiocyanate anions. The slightly distorted octahedral coordination is completed by two O atoms from ethanol molecules. The crystal packing is accomplished intermolecular N—H···S hydrogen bonds.

## Related literature

For the structures of metal complexes of Schiff base ligands synthesized by condensation of pyridine-3-carbaldehyde and amino compounds, see: Brook *et al.* (2000); Deng *et al.* (2007); Garbelini *et al.* (2008); Kowol *et al.* (2007); Zhong *et al.* (2007). For the corresponding Mn(II) complex of pyridine-3-carbaldehyde thiosemicarbazone, see: Li *et al.* (2006).
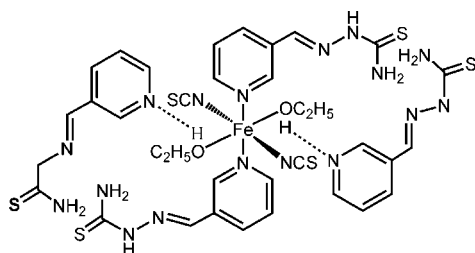


## Experimental

### Crystal data

| | |
|---|---|
| $[Fe(NCS)_2(C_7H_8N_4S)_2(C_2H_6O)_2]\cdot$ $2C_7H_8N_4S$ | $\beta = 88.191\ (8)°$ |
| $M_r = 985.08$ | $\gamma = 69.604\ (8)°$ |
| Triclinic, $P\bar{1}$ | $V = 1160\ (1)$ Å$^3$ |
| $a = 8.916\ (4)$ Å | $Z = 1$ |
| $b = 9.556\ (5)$ Å | Mo $K\alpha$ radiation |
| $c = 14.538\ (7)$ Å | $\mu = 0.65$ mm$^{-1}$ |
| $\alpha = 87.341\ (8)°$ | $T = 173$ K |
| | $0.32 \times 0.26 \times 0.22$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 8300 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.819$, $T_{max} = 0.871$ | 4037 independent reflections 2953 reflections with $I > 2\sigma(I)$ $R_{int} = 0.022$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.134$ | |
| $S = 1.01$ | |
| 4037 reflections | $\Delta\rho_{max} = 0.43$ e Å$^{-3}$ |
| 282 parameters | $\Delta\rho_{min} = -0.24$ e Å$^{-3}$ |
| 1 restraint | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N9—H9$B$···S3$^i$ | 0.88 | 2.67 | 3.533 (3) | 165 |
| N4—H4$B$···S1$^{ii}$ | 0.88 | 2.52 | 3.373 (3) | 164 |
| N4—H4$A$···S2 | 0.88 | 2.80 | 3.360 (3) | 123 |
| N3—H3···S3$^{iii}$ | 0.88 | 2.59 | 3.414 (3) | 156 |

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

## References

Brook, D.-J.-R., Fornell, S., Stevens, J.-E., Noll, B., Koch, T.-H. & Eisfeld, W. (2000). *Inorg. Chem.* **39**, 562–567.

Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Deng, J.-H., Guo, G.-Q. & Zhong, D.-C. (2007). *Acta Cryst.* E**63**, m2696–m2697.

Garbelini, E.-R., Horner, M., Behm, M.-B., Evans, D.-J. & Nunes, F.-S. (2008). *Z. Anorg. Allg. Chem.* **634**, 1801–1806.

Kowol, C.-R., Eichinger, R., Jakupec, M.-A., Galanski, M., Arion, V.-B. & Keppler, B.-K. (2007). *J. Inorg. Biochem.* **101**, 1946–1957.

Li, M.-X., Zhou, J., Wang, J.-P. & Wang, Z.-L. (2006). *Chin. J. Struct. Chem.* **25**, 1275–1279.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Zhong, D.-C., Guo, G.-Q. & Deng, J.-H. (2007). *Acta Cryst.* E**63**, m1747.

**supplementary materials**

# Bis(ethanol-*κO*)bis(pyridine-3-carbaldehyde-*κN* thiosemicarbazone)bis(thiocyanato-*κN*)iron(II)-pyridine-3-carbaldehyde thiosemicarbazone (1/2)

## S.-M. Wang

## Comment

Several crystal structures of metal complexes based on Schiff base ligands being synthesized by condensation of pyridine-3-carbaldehyde and amino compounds have been previously reported (Brook *et al.*, 2000; Deng *et al.*, 2007; Garbelini *et al.*, 2008; Kowol *et al.*, 2007; Zhong *et al.*, 2007). However, with regard to pyridine-3-carbaldehyde thiosemicarbazone (pct), only the corresponding Mn(II) complex has been documented (Li *et al.*, 2006). Herein, we report the synthesis and crystal crystal structure of its Fe$^{II}$ complex.

The structure of the title compound, (I), consists of discrete [Fe($C_7H_8N_4S$)$_2$(SCN)$_2$($C_2H_5OH$)$_2$] neutral units and un-coordinated pct molecules. The two semicarbazone ligands are planar, and each binds to Fe$^{II}$ via the pyridine N atom. Therefore, pct acts as a monodentate ligand with the sulphur and nitrogen atoms of the semicarbazone subunit remaining uncoordinated. In addition to pct, the central Fe$^{II}$ is coordinated by two SCN$^-$ anions and two $C_2H_5OH$ molecules via the N and O atoms, respectively. (Fig. 1)

The molecules are held together by intermolecular hydrogen bonding interactions. The imino nitrogen N3 acts as a hydrogen donor site towards S3 of the uncoordinated pct molecule forming intermolecular N3—H3···S3 hydrogen bonds. S3 also accepts a hydrogen bond from N9 of a neighboring uncoordinated pct to form N9—H9B···S3 hydrogen bonds. In addition, the SCN$^-$ also is involved in the construction of the hydrogen bond network by establishing an interaction between the terminal S atoms accept and the hydrogen atom at N4 to form N4—H4A···S2 and N4—H4B···S1 hydrogen bonds (Table 1, Fig. 2).

## Experimental

A mixture of 0.5 mmol FeCl$_2$ × 6 H$_2$O, 1.0 mmol of (NH$_4$)SCN and 10 ml water-ethanol (1:2 *v/v*) was stirred for *ca.* 2 hrs at 343 K. Then 1.0 mmol pct in 10 ml water-ethanol mixture (1:2 *v/v*) was added. The mixture was further stirred for another 2 h, then filtered. The resultant filtrate was left to stand for slow evaporation at room temperature. Dark green single crystals of (**I**) suitable for X-ray structure analysis were obtained after a period of one week (yield 63%).

## Refinement

Hydrogen atoms attached to carbon atoms and nitrogen atoms were positioned geometrically and treated as riding, with C—H = 0.93 Å, N—H = 0.86 Å, and $U_{iso}$(H) = 1.2$U_{eq}$(C or N). The H atom attached to the hydroxy group of the ethanol ligand was located from difference density maps and was refined with distance restraints of O–H = 0.82 (1) Å.
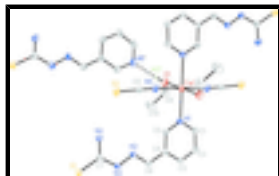
# supplementary materials

**Figures**



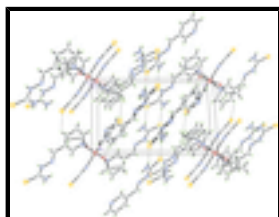Fig. 1. The structure of (**I**) × pct, symmetry code: (i) -*x* + 2, -*y*, -*z* + 1.



Fig. 2. Three-dimensional supramolecular network constructed by hydrogen bonding interactions (dashed lines).

**Bis(ethanol-κ*O*)bis(pyridine-3-carbaldehyde-κ*N* thiosemicarbazone-κ*N*)bis(thiocyanato)iron(II)– pyridine-3-carbaldehyde thiosemicarbazone (1/2)**

*Crystal data*

| | |
|---|---|
| $[Fe(NCS)_2(C_7H_8N_4S)_2(C_2H_6O)_2] \cdot 2C_7H_8N_4S$ | $Z = 1$ |
| $M_r = 985.08$ | $F_{000} = 512$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.411$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 8.916$ (4) Å | Cell parameters from 3773 reflections |
| $b = 9.556$ (5) Å | $\theta = 2.3$–26.9º |
| $c = 14.538$ (7) Å | $\mu = 0.65$ mm$^{-1}$ |
| $\alpha = 87.341$ (8)º | $T = 173$ K |
| $\beta = 88.191$ (8)º | Block, dark green |
| $\gamma = 69.604$ (8)º | $0.32 \times 0.26 \times 0.22$ mm |
| $V = 1160$ (1) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 4037 independent reflections |
| Radiation source: fine-focus sealed tube | 2953 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.022$ |
| $T = 173$ K | $\theta_{max} = 25.0$º |
| φ and ω scans | $\theta_{min} = 1.4$º |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -10\rightarrow10$ |
| $T_{min} = 0.819$, $T_{max} = 0.871$ | $k = -11\rightarrow11$ |
| 8300 measured reflections | $l = -17\rightarrow17$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.042$

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.134$

$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 0.3403P]$
where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.01$

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

4037 reflections

$\Delta\rho_{max} = 0.43$ e Å$^{-3}$

282 parameters

$\Delta\rho_{min} = -0.24$ e Å$^{-3}$

1 restraint

Extinction correction: none

Primary atom site location: structure-invariant direct methods

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

|      | $x$          | $y$           | $z$          | $U_{iso}*/U_{eq}$ |
|------|--------------|---------------|--------------|-------------------|
| Fe1  | 0.5000       | 0.0000        | 0.0000       | 0.0416 (2)        |
| N1   | 0.2848 (3)   | 0.1196 (3)    | 0.09806 (16) | 0.0410 (6)        |
| N2   | 0.1975 (3)   | −0.0995 (3)   | 0.33648 (15) | 0.0389 (6)        |
| N3   | 0.1640 (3)   | −0.1698 (3)   | 0.41443 (16) | 0.0413 (6)        |
| H3   | 0.0676       | −0.1382       | 0.4397       | 0.050*            |
| N4   | 0.4186 (3)   | −0.3344 (3)   | 0.40767 (19) | 0.0659 (9)        |
| H4A  | 0.4316       | −0.2885       | 0.3557       | 0.079*            |
| H4B  | 0.4981       | −0.4112       | 0.4298       | 0.079*            |
| N5   | 0.5606 (3)   | −0.2022 (3)   | 0.08302 (19) | 0.0536 (7)        |
| C12  | 0.7900 (4)   | 0.3134 (4)    | 0.8792 (2)   | 0.0604 (9)        |
| H12  | 0.6944       | 0.3331        | 0.9150       | 0.072*            |
| N7   | 0.8316 (3)   | 0.5754 (3)    | 0.64455 (16) | 0.0424 (6)        |
| N8   | 0.8582 (3)   | 0.6617 (3)    | 0.57213 (17) | 0.0453 (6)        |
| H8   | 0.9546       | 0.6403        | 0.5474       | 0.054*            |
| N9   | 0.5924 (3)   | 0.7961 (3)    | 0.5738 (2)   | 0.0652 (8)        |
| H9A  | 0.5814       | 0.7316        | 0.6163       | 0.078*            |
| H9B  | 0.5080       | 0.8711        | 0.5547       | 0.078*            |
| O1   | 0.6741 (3)   | 0.0634 (3)    | 0.07601 (15) | 0.0541 (6)        |
| S1   | 0.24701 (9)  | −0.36692 (9)  | 0.55347 (5)  | 0.0500 (2)        |
| S2   | 0.64184 (10) | −0.43494 (10) | 0.21504 (7)  | 0.0632 (3)        |

| | | | | |
|---|---|---|---|---|
| S3 | 0.76674 (9) | 0.89666 (9) | 0.45668 (6) | 0.0525 (3) |
| C1 | 0.1770 (4) | 0.2554 (3) | 0.0754 (2) | 0.0457 (7) |
| H1 | 0.1962 | 0.3076 | 0.0218 | 0.055* |
| C2 | 0.0403 (4) | 0.3210 (3) | 0.1271 (2) | 0.0471 (7) |
| H2 | −0.0332 | 0.4165 | 0.1092 | 0.057* |
| C3 | 0.0117 (3) | 0.2462 (3) | 0.20499 (19) | 0.0416 (7) |
| H3A | −0.0815 | 0.2902 | 0.2418 | 0.050* |
| C4 | 0.1196 (3) | 0.1064 (3) | 0.22943 (18) | 0.0354 (6) |
| C5 | 0.2540 (3) | 0.0486 (3) | 0.17329 (19) | 0.0405 (7) |
| H5 | 0.3286 | −0.0473 | 0.1895 | 0.049* |
| C6 | 0.0921 (3) | 0.0255 (3) | 0.3116 (2) | 0.0409 (7) |
| H6 | −0.0039 | 0.0653 | 0.3468 | 0.049* |
| C7 | 0.2808 (3) | −0.2882 (3) | 0.4521 (2) | 0.0424 (7) |
| C8 | 0.5957 (3) | −0.2995 (3) | 0.1376 (2) | 0.0409 (7) |
| C9 | 0.6438 (4) | 0.1960 (4) | 0.1234 (2) | 0.0602 (9) |
| H9C | 0.5507 | 0.2751 | 0.0956 | 0.072* |
| H9D | 0.7375 | 0.2286 | 0.1155 | 0.072* |
| C10 | 0.6107 (5) | 0.1792 (5) | 0.2242 (3) | 0.0809 (13) |
| H10A | 0.5138 | 0.1535 | 0.2327 | 0.121* |
| H10B | 0.5952 | 0.2735 | 0.2538 | 0.121* |
| H10C | 0.7015 | 0.0997 | 0.2521 | 0.121* |
| C11 | 0.9244 (4) | 0.1953 (4) | 0.9025 (2) | 0.0577 (9) |
| H11 | 0.9201 | 0.1350 | 0.9557 | 0.069* |
| N6 | 1.0609 (3) | 0.1611 (3) | 0.85410 (18) | 0.0512 (7) |
| C13 | 1.0645 (4) | 0.2479 (3) | 0.7803 (2) | 0.0457 (7) |
| H13 | 1.1613 | 0.2244 | 0.7453 | 0.055* |
| C14 | 0.9344 (3) | 0.3714 (3) | 0.7514 (2) | 0.0404 (7) |
| C15 | 0.7945 (4) | 0.4035 (4) | 0.8032 (2) | 0.0533 (8) |
| H15 | 0.7026 | 0.4867 | 0.7865 | 0.064* |
| C16 | 0.9506 (3) | 0.4637 (3) | 0.6721 (2) | 0.0419 (7) |
| H16 | 1.0508 | 0.4406 | 0.6406 | 0.050* |
| C17 | 0.7345 (3) | 0.7807 (3) | 0.53873 (19) | 0.0417 (7) |
| H17 | 0.747 (3) | −0.006 (3) | 0.099 (2) | 0.067 (12)* |

*Atomic displacement parameters ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Fe1 | 0.0384 (3) | 0.0424 (4) | 0.0381 (4) | −0.0086 (3) | 0.0034 (2) | 0.0106 (3) |
| N1 | 0.0387 (13) | 0.0410 (14) | 0.0383 (13) | −0.0092 (11) | 0.0062 (10) | 0.0063 (11) |
| N2 | 0.0372 (13) | 0.0431 (14) | 0.0345 (13) | −0.0130 (11) | 0.0060 (10) | 0.0047 (11) |
| N3 | 0.0344 (13) | 0.0445 (14) | 0.0391 (13) | −0.0085 (11) | 0.0080 (10) | 0.0102 (11) |
| N4 | 0.0418 (15) | 0.073 (2) | 0.0584 (18) | 0.0057 (14) | 0.0150 (13) | 0.0275 (15) |
| N5 | 0.0464 (16) | 0.0499 (16) | 0.0545 (16) | −0.0076 (12) | 0.0044 (12) | 0.0220 (14) |
| C12 | 0.0473 (19) | 0.075 (2) | 0.058 (2) | −0.0233 (18) | 0.0052 (16) | 0.0173 (18) |
| N7 | 0.0404 (14) | 0.0469 (15) | 0.0407 (14) | −0.0173 (12) | −0.0005 (11) | 0.0076 (11) |
| N8 | 0.0379 (13) | 0.0464 (15) | 0.0485 (15) | −0.0129 (11) | 0.0044 (11) | 0.0104 (12) |
| N9 | 0.0362 (15) | 0.071 (2) | 0.0734 (19) | −0.0046 (13) | 0.0092 (13) | 0.0306 (16) |
| O1 | 0.0492 (14) | 0.0503 (14) | 0.0551 (14) | −0.0065 (11) | −0.0113 (11) | −0.0028 (11) |

| | | | | | |
|---|---|---|---|---|---|
| S1 | 0.0399 (4) | 0.0577 (5) | 0.0429 (5) | −0.0078 (4) | 0.0058 (3) | 0.0164 (4) |
| S2 | 0.0511 (5) | 0.0507 (5) | 0.0736 (6) | −0.0045 (4) | 0.0042 (4) | 0.0327 (4) |
| S3 | 0.0410 (4) | 0.0548 (5) | 0.0520 (5) | −0.0077 (4) | 0.0059 (4) | 0.0184 (4) |
| C1 | 0.0456 (17) | 0.0447 (17) | 0.0418 (17) | −0.0112 (14) | 0.0055 (13) | 0.0094 (14) |
| C2 | 0.0442 (17) | 0.0364 (16) | 0.0482 (18) | 0.0007 (13) | 0.0010 (14) | 0.0061 (14) |
| C3 | 0.0349 (15) | 0.0430 (17) | 0.0404 (16) | −0.0061 (13) | 0.0061 (12) | −0.0018 (13) |
| C4 | 0.0319 (14) | 0.0388 (15) | 0.0347 (15) | −0.0115 (12) | 0.0024 (11) | −0.0008 (12) |
| C5 | 0.0370 (15) | 0.0333 (15) | 0.0431 (16) | −0.0036 (12) | 0.0037 (12) | 0.0090 (13) |
| C6 | 0.0350 (15) | 0.0429 (17) | 0.0403 (16) | −0.0090 (13) | 0.0086 (12) | 0.0013 (13) |
| C7 | 0.0378 (16) | 0.0458 (17) | 0.0401 (16) | −0.0114 (13) | 0.0033 (13) | 0.0044 (13) |
| C8 | 0.0312 (14) | 0.0402 (17) | 0.0454 (17) | −0.0063 (12) | 0.0083 (12) | 0.0018 (14) |
| C9 | 0.066 (2) | 0.062 (2) | 0.059 (2) | −0.0292 (19) | −0.0024 (17) | −0.0029 (18) |
| C10 | 0.103 (3) | 0.092 (3) | 0.063 (3) | −0.054 (3) | 0.015 (2) | −0.007 (2) |
| C11 | 0.060 (2) | 0.064 (2) | 0.053 (2) | −0.0279 (18) | −0.0082 (17) | 0.0184 (17) |
| N6 | 0.0501 (16) | 0.0493 (16) | 0.0521 (16) | −0.0155 (13) | −0.0111 (13) | 0.0132 (13) |
| C13 | 0.0415 (17) | 0.0480 (18) | 0.0475 (18) | −0.0159 (14) | −0.0004 (13) | 0.0023 (14) |
| C14 | 0.0389 (16) | 0.0409 (17) | 0.0428 (16) | −0.0161 (13) | −0.0033 (13) | 0.0042 (13) |
| C15 | 0.0388 (17) | 0.056 (2) | 0.060 (2) | −0.0117 (15) | −0.0008 (15) | 0.0154 (16) |
| C16 | 0.0389 (16) | 0.0433 (17) | 0.0438 (17) | −0.0157 (14) | 0.0018 (13) | 0.0029 (13) |
| C17 | 0.0406 (16) | 0.0466 (17) | 0.0365 (16) | −0.0139 (13) | 0.0010 (13) | 0.0025 (13) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Fe1—N5$^i$ | 2.140 (3) | S1—C7 | 1.690 (3) |
| Fe1—N5 | 2.140 (3) | S2—C8 | 1.623 (3) |
| Fe1—O1$^i$ | 2.196 (2) | S3—C17 | 1.677 (3) |
| Fe1—O1 | 2.196 (2) | C1—C2 | 1.377 (4) |
| Fe1—N1 | 2.339 (2) | C1—H1 | 0.9500 |
| Fe1—N1$^i$ | 2.339 (2) | C2—C3 | 1.375 (4) |
| N1—C5 | 1.332 (3) | C2—H2 | 0.9500 |
| N1—C1 | 1.352 (4) | C3—C4 | 1.385 (4) |
| N2—C6 | 1.280 (4) | C3—H3A | 0.9500 |
| N2—N3 | 1.368 (3) | C4—C5 | 1.388 (4) |
| N3—C7 | 1.350 (4) | C4—C6 | 1.453 (4) |
| N3—H3 | 0.8800 | C5—H5 | 0.9500 |
| N4—C7 | 1.312 (4) | C6—H6 | 0.9500 |
| N4—H4A | 0.8800 | C9—C10 | 1.498 (5) |
| N4—H4B | 0.8800 | C9—H9C | 0.9900 |
| N5—C8 | 1.156 (4) | C9—H9D | 0.9900 |
| C12—C11 | 1.368 (5) | C10—H10A | 0.9800 |
| C12—C15 | 1.377 (4) | C10—H10B | 0.9800 |
| C12—H12 | 0.9500 | C10—H10C | 0.9800 |
| N7—C16 | 1.274 (4) | C11—N6 | 1.332 (4) |
| N7—N8 | 1.373 (3) | C11—H11 | 0.9500 |
| N8—C17 | 1.361 (4) | N6—C13 | 1.332 (4) |
| N8—H8 | 0.8800 | C13—C14 | 1.395 (4) |
| N9—C17 | 1.312 (4) | C13—H13 | 0.9500 |
| N9—H9A | 0.8800 | C14—C15 | 1.383 (4) |

| | | | |
|---|---|---|---|
| N9—H9B | 0.8800 | C14—C16 | 1.453 (4) |
| O1—C9 | 1.408 (4) | C15—H15 | 0.9500 |
| O1—H17 | 0.816 (10) | C16—H16 | 0.9500 |
| N5$^i$—Fe1—N5 | 180.00 (14) | C2—C3—H3A | 120.2 |
| N5$^i$—Fe1—O1$^i$ | 88.99 (10) | C4—C3—H3A | 120.2 |
| N5—Fe1—O1$^i$ | 91.01 (10) | C3—C4—C5 | 117.5 (2) |
| N5$^i$—Fe1—O1 | 91.01 (10) | C3—C4—C6 | 120.6 (2) |
| N5—Fe1—O1 | 88.99 (10) | C5—C4—C6 | 121.9 (3) |
| O1$^i$—Fe1—O1 | 180.00 (14) | N1—C5—C4 | 123.9 (3) |
| N5$^i$—Fe1—N1 | 88.53 (9) | N1—C5—H5 | 118.0 |
| N5—Fe1—N1 | 91.47 (9) | C4—C5—H5 | 118.0 |
| O1$^i$—Fe1—N1 | 85.58 (9) | N2—C6—C4 | 119.9 (2) |
| O1—Fe1—N1 | 94.42 (9) | N2—C6—H6 | 120.0 |
| N5$^i$—Fe1—N1$^i$ | 91.47 (9) | C4—C6—H6 | 120.0 |
| N5—Fe1—N1$^i$ | 88.53 (9) | N4—C7—N3 | 116.9 (3) |
| O1$^i$—Fe1—N1$^i$ | 94.42 (9) | N4—C7—S1 | 123.1 (2) |
| O1—Fe1—N1$^i$ | 85.58 (9) | N3—C7—S1 | 119.9 (2) |
| N1—Fe1—N1$^i$ | 180.00 (12) | N5—C8—S2 | 179.0 (3) |
| C5—N1—C1 | 117.4 (2) | O1—C9—C10 | 113.3 (3) |
| C5—N1—Fe1 | 120.69 (18) | O1—C9—H9C | 108.9 |
| C1—N1—Fe1 | 121.52 (18) | C10—C9—H9C | 108.9 |
| C6—N2—N3 | 116.9 (2) | O1—C9—H9D | 108.9 |
| C7—N3—N2 | 119.2 (2) | C10—C9—H9D | 108.9 |
| C7—N3—H3 | 120.4 | H9C—C9—H9D | 107.7 |
| N2—N3—H3 | 120.4 | C9—C10—H10A | 109.5 |
| C7—N4—H4A | 120.0 | C9—C10—H10B | 109.5 |
| C7—N4—H4B | 120.0 | H10A—C10—H10B | 109.5 |
| H4A—N4—H4B | 120.0 | C9—C10—H10C | 109.5 |
| C8—N5—Fe1 | 170.5 (3) | H10A—C10—H10C | 109.5 |
| C11—C12—C15 | 119.4 (3) | H10B—C10—H10C | 109.5 |
| C11—C12—H12 | 120.3 | N6—C11—C12 | 122.9 (3) |
| C15—C12—H12 | 120.3 | N6—C11—H11 | 118.5 |
| C16—N7—N8 | 117.2 (2) | C12—C11—H11 | 118.5 |
| C17—N8—N7 | 119.6 (2) | C11—N6—C13 | 117.4 (3) |
| C17—N8—H8 | 120.2 | N6—C13—C14 | 123.9 (3) |
| N7—N8—H8 | 120.2 | N6—C13—H13 | 118.1 |
| C17—N9—H9A | 120.0 | C14—C13—H13 | 118.1 |
| C17—N9—H9B | 120.0 | C15—C14—C13 | 117.1 (3) |
| H9A—N9—H9B | 120.0 | C15—C14—C16 | 122.6 (3) |
| C9—O1—Fe1 | 126.7 (2) | C13—C14—C16 | 120.3 (3) |
| C9—O1—H17 | 112 (3) | C12—C15—C14 | 119.2 (3) |
| Fe1—O1—H17 | 115 (3) | C12—C15—H15 | 120.4 |
| N1—C1—C2 | 122.6 (3) | C14—C15—H15 | 120.4 |
| N1—C1—H1 | 118.7 | N7—C16—C14 | 120.5 (3) |
| C2—C1—H1 | 118.7 | N7—C16—H16 | 119.7 |
| C3—C2—C1 | 119.1 (3) | C14—C16—H16 | 119.7 |

| | | | |
|---|---|---|---|
| C3—C2—H2 | 120.5 | N9—C17—N8 | 116.1 (3) |
| C1—C2—H2 | 120.5 | N9—C17—S3 | 123.4 (2) |
| C2—C3—C4 | 119.6 (3) | N8—C17—S3 | 120.5 (2) |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N9—H9B···S3<sup>ii</sup> | 0.88 | 2.67 | 3.533 (3) | 165 |
| N4—H4B···S1<sup>iii</sup> | 0.88 | 2.52 | 3.373 (3) | 164 |
| N4—H4A···S2 | 0.88 | 2.80 | 3.360 (3) | 123 |
| N3—H3···S3<sup>iv</sup> | 0.88 | 2.59 | 3.414 (3) | 156 |

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

**Fig. 1**

**Fig. 2**