

Di- μ -aqua-bis[di-aquabis(thiocyanato- κ N)iron(II)] 4-(4-chlorophenyl)-1,2,4-triazole hexasolvate

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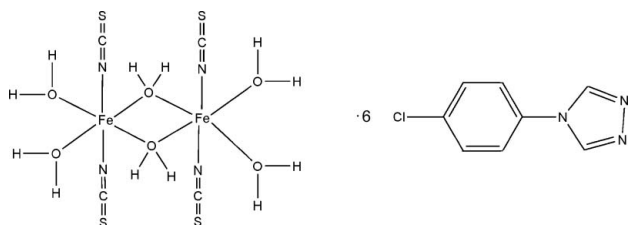
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.044; wR factor = 0.077; data-to-parameter ratio = 13.0.

The title complex, $[\text{Fe}_2(\text{NCS})_4(\text{H}_2\text{O})_6] \cdot 6\text{C}_8\text{H}_6\text{ClN}_3$, comprises two distorted octahedral iron(II) centers straddling a crystallographic inversion center and bridged by two aqua O atoms to form a quadrilateral core. The aqua O atom of the core is involved in hydrogen bonds with the triazole N atoms of the solvent molecules, generating one-dimensional ladder motifs, and three intermolecular $\text{C}-\text{H} \cdots \text{S}$ hydrogen bonds, forming a three-dimensional hydrogen-bonding network.

Related literature

For related literature, see: Hsu *et al.* (1999); MacMurdo *et al.* (2000); Nordlund & Eklund (1993); Sazinsky *et al.* (2004); Stubbe & Van der Donk (1998); Yoon *et al.* (2004); Zheng *et al.* (1999).



Experimental

Crystal data

 $[\text{Fe}_2(\text{NCS})_4(\text{H}_2\text{O})_6] \cdot 6\text{C}_8\text{H}_6\text{ClN}_3$
 $M_r = 1529.76$

 Triclinic, $P\bar{1}$
 $a = 7.944$ (3) Å

 $b = 11.085$ (5) Å

 $c = 19.912$ (10) Å

 $\alpha = 105.613$ (10)°

 $\beta = 97.750$ (10)°

 $\gamma = 97.932$ (7)°

 $V = 1645.1$ (12) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 0.88$ mm⁻¹
 $T = 298$ (2) K

 $0.25 \times 0.21 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

 $T_{\min} = 0.810$, $T_{\max} = 0.865$

8642 measured reflections

5705 independent reflections

 2903 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.076$
 $S = 0.77$

5705 reflections

439 parameters

9 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³
Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------------------|-------------|--------------------------|------------|
| Fe1—N1 | 2.086 (3) | Fe1—N2 | 2.107 (3) |
| Fe1—O2 | 2.100 (2) | Fe1—O1 ⁱ | 2.264 (3) |
| Fe1—O3 | 2.102 (3) | Fe1—O1 | 2.281 (2) |
| N1—Fe1—O2 | 90.22 (11) | O3—Fe1—O1 ⁱ | 169.95 (9) |
| N1—Fe1—O3 | 89.68 (12) | N2—Fe1—O1 ⁱ | 91.32 (11) |
| O2—Fe1—O3 | 101.01 (10) | O1 ⁱ —Fe1—O1 | 78.36 (9) |
| N1—Fe1—N2 | 178.33 (12) | Fe1 ⁱ —O1—Fe1 | 101.64 (9) |
| O2—Fe1—O1 ⁱ | 89.04 (10) | | |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|----------|--------------|--------------|----------------|
| O1—H1 ⁱ \cdots N10 ⁱⁱ | 0.87 (3) | 1.97 (3) | 2.827 (4) | 170 (3) |
| O1—H2 ⁱ \cdots N9 | 0.88 (3) | 1.94 (3) | 2.819 (4) | 173 (3) |
| O2—H3 ⁱ \cdots N7 ⁱⁱⁱ | 0.88 (3) | 1.98 (3) | 2.866 (5) | 178 (3) |
| O2—H4 ⁱ \cdots N4 ^{iv} | 0.88 (2) | 1.97 (3) | 2.853 (4) | 175 (3) |
| O3—H5 ⁱ \cdots N6 | 0.88 (3) | 1.92 (3) | 2.802 (4) | 174 (3) |
| O3—H6 ⁱ \cdots N3 ^v | 0.88 (2) | 1.93 (2) | 2.803 (4) | 172 (3) |
| C3—H7 ⁱ \cdots S2 ^{vi} | 0.93 | 2.72 | 3.624 (5) | 165 |
| C22—H21 ⁱ \cdots S2 ⁱⁱ | 0.93 | 2.87 | 3.736 (5) | 156 |
| C11—H13 ⁱ \cdots S1 ^{vii} | 0.93 | 2.87 | 3.783 (5) | 167 |

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

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* and *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2093).

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supplementary materials

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Comment

The diiron unit, with a carboxylate-rich coordination environment, continue to attract considerable attention due to the enzyme catalysis activity, which occur in related multicomponent dioxygen dependent enzymes, including toluene monooxygenase (Sazinsky *et al.*, 2004), the R2 subunit of ribonucleotide reductase (Stubbe & Van der Donk, 1998; Nordlund & Eklund, 1993). With the development of compounds that contained the diiron center, the structure of a series of Fe₂(II,II) (MacMurdo *et al.*, 2000), Fe₂(III,III) (Zheng *et al.*, 1999) and Fe₂(III,IV) (Hsu *et al.*, 1999) complexes with a central 2Fe₂O quadrilateral have been currently obtained. Compared with the chelating to the iron atoms with the carboxylic oxygen atoms, it is rarely reported that the quadrilateral center includes both aqueous oxygen atoms. In order to explore the further details of the coordinated environment of the diiron system, the title complex was synthesized. As shown in Fig. 1, the complex structure comprises two distorted octahedron iron(II) centers straddling a crystallographic inversion center bridged by two aqueous oxygen atoms to form a quadrilateral core. The separation between the iron atoms is 3.523 (2) Å, which is remarkably different from that 3.0430 (7) Å reported previously, owing to the absence of two carboxylate ligands (Yoon *et al.*, 2004). Moreover, the distance of Fe—Fe is comparatively distinguished from that diiron containing the other higher valence of iron (MacMurdo *et al.*, 2000; Zheng *et al.*, 1999; Hsu *et al.*, 1999). The bond lengths of Fe—O1 and Fe—O1a are 2.264 (3) and 2.281 (2) Å, and the angles of O1—Fe—O1a and Fe1a—O1—Fe are 78.36 (9)° and 101.64 (9)°. Each Fe(II) center resides in a six-coordinated octahedron of N₂O₄. On the equator plane, the center is bridged by two symmetrical O1 (water) to form the quadrilateral core with the mean distance of 2.272 (2) Å, and is connected with O2 and O3 offered by different waters as the terminal ligands with the bond lengths 2.102 (3) Å and 2.100 (2) Å. The axial positions are occupied by two N atoms from the NCS⁻ anions with the distances 2.086 (3) Å and 2.107 (3) Å to the iron core. Selected bonds and angles are listed in Table 1. As indicated in Fig.2, the classic intermolecular O—H...N H-bonds are formed between the triazol nitrogen atom supplied by the uncoordinated organic ligand 1,2,4-triazol-chloro-benzene and aqueous oxygen atoms supplied by the bridging and terminal water ligands to generate a one-dimension ladder structure with the N...O separation ranged from 2.803 (2) Å to 2.866 (4) Å. Moreover, there are three weak intermolecular hydrogen bonding contacts C—H...S that form a three-dimensional network with the C...S distances between 3.624 (5) Å and 3.783 (5) Å. The details of the hydrogen bonds are shown in Table 2.

Experimental

The compound was synthesized under hydrothermal conditions. A mixture of *L* (*L*=1,2,4-triazol-chloro-benzene) (0.3 mmol, 0.0538 g), FeSO₄·7H₂O (0.1 mmol, 0.028 g), KSCN (0.2 mmol, 0.019 g) and water (10 mL) was placed in a 25 mL acid digestion bomb and heated at 433 K for two days, then equally cooled to room temperature for three days. After washed by 5 ml water for twice, green block crystals of the compound were obtained.

Refinement

The water H atoms were located in a Fourier difference map and refined subject to an O—H restraint 0.88 (1) Å and an H···H restraint of 1.42 (2) Å. Other H atoms were allowed to ride on their parent atoms with C—H distances of 0.93 Å ($U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$). All of the non-hydrogen atoms were refined anisotropically.

Figures

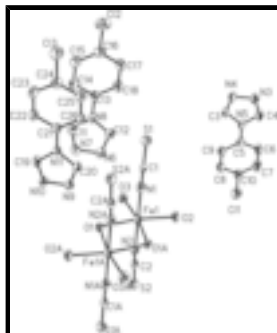


Fig. 1. The structure of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering schemes. H atoms have been omitted for clarity. Atoms of the inversion-related half-complex are indicated with A, symmetry code: $(-x + 1, -y, -z + 1)$.

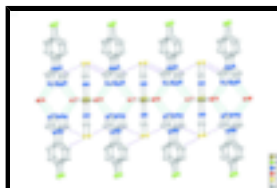


Fig. 2. The three-dimensional structure of the title complex, the chains were drawn in different colors. Dashed lines indicate hydrogen bonds.

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Crystal data

$[\text{Fe}_2(\text{NCS})_4(\text{H}_2\text{O})_6] \cdot 6\text{C}_8\text{H}_6\text{ClN}_3$

$M_r = 1529.76$

Triclinic, $P\bar{1}$

$a = 7.944$ (3) Å

$b = 11.085$ (5) Å

$c = 19.912$ (10) Å

$\alpha = 105.613$ (10)°

$\beta = 97.750$ (10)°

$\gamma = 97.932$ (7)°

$V = 1645.1$ (12) Å³

$Z = 1$

$F_{000} = 780$

$D_x = 1.544$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1471 reflections

$\theta = 2.5\text{--}22.0^\circ$

$\mu = 0.88$ mm⁻¹

$T = 298$ (2) K

Block, green

$0.25 \times 0.21 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

5705 independent reflections

2903 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$T = 298(2)$ K $\theta_{\max} = 25.0^\circ$
 φ and ω scans $\theta_{\min} = 2.4^\circ$
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996) $h = -9 \rightarrow 9$
 $T_{\min} = 0.811$, $T_{\max} = 0.865$ $k = -11 \rightarrow 13$
 8642 measured reflections $l = -21 \rightarrow 23$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.044$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.076$ $w = 1/[\sigma^2(F_o^2) + (0.0191P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 0.77$ $(\Delta/\sigma)_{\max} = 0.002$
 5705 reflections $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 439 parameters $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$
 9 restraints 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Fe1 | 0.53640 (6) | 0.12392 (5) | 0.46090 (2) | 0.04255 (16) |
| Cl1 | 0.81665 (15) | 0.70325 (12) | -0.09593 (6) | 0.0942 (4) |
| Cl2 | 0.41822 (16) | 0.88209 (11) | 0.91545 (5) | 0.0932 (4) |
| Cl3 | 0.28229 (14) | 0.59403 (11) | 1.00137 (5) | 0.0879 (4) |
| N1 | 0.5944 (4) | 0.2571 (3) | 0.56111 (15) | 0.0518 (9) |
| N2 | 0.4754 (3) | -0.0065 (3) | 0.35844 (15) | 0.0493 (8) |
| N3 | 1.0886 (4) | 1.1192 (3) | 0.31387 (16) | 0.0633 (10) |
| N4 | 0.9153 (4) | 1.0935 (3) | 0.31608 (16) | 0.0545 (9) |
| N5 | 0.9562 (4) | 0.9986 (3) | 0.20814 (15) | 0.0469 (8) |
| N6 | 0.2192 (4) | 0.4095 (3) | 0.51909 (16) | 0.0575 (9) |

supplementary materials

| | | | | |
|-----|--------------|---------------|---------------|-------------|
| N7 | 0.0498 (4) | 0.3852 (3) | 0.53051 (17) | 0.0575 (9) |
| N8 | 0.2018 (4) | 0.5377 (3) | 0.62253 (16) | 0.0447 (8) |
| N9 | 0.1490 (4) | 0.1463 (3) | 0.59896 (14) | 0.0468 (8) |
| N10 | -0.0244 (4) | 0.1290 (3) | 0.60322 (15) | 0.0461 (8) |
| N11 | 0.1199 (3) | 0.2618 (3) | 0.70379 (14) | 0.0395 (7) |
| O1 | 0.3213 (3) | 0.0112 (2) | 0.49662 (13) | 0.0402 (6) |
| O2 | 0.7680 (3) | 0.2021 (3) | 0.43624 (14) | 0.0524 (7) |
| O3 | 0.3662 (3) | 0.2333 (3) | 0.42643 (14) | 0.0517 (7) |
| S1 | 0.67311 (13) | 0.44880 (10) | 0.69114 (5) | 0.0643 (3) |
| S2 | 0.40098 (12) | -0.15078 (10) | 0.21581 (5) | 0.0616 (3) |
| C1 | 0.6275 (4) | 0.3375 (3) | 0.61526 (19) | 0.0414 (9) |
| C2 | 0.4443 (4) | -0.0668 (3) | 0.29919 (19) | 0.0432 (10) |
| C3 | 0.8410 (5) | 1.0220 (4) | 0.2526 (2) | 0.0539 (11) |
| H7 | 0.7229 | 0.9906 | 0.2394 | 0.065* |
| C4 | 1.1071 (5) | 1.0625 (4) | 0.2506 (2) | 0.0658 (13) |
| H8 | 1.2132 | 1.0651 | 0.2357 | 0.079* |
| C5 | 0.9232 (5) | 0.9260 (4) | 0.13488 (19) | 0.0478 (10) |
| C6 | 1.0521 (5) | 0.9321 (4) | 0.0947 (2) | 0.0678 (13) |
| H9 | 1.1598 | 0.9828 | 0.1154 | 0.081* |
| C7 | 1.0201 (5) | 0.8626 (4) | 0.0238 (2) | 0.0769 (14) |
| H10 | 1.1065 | 0.8654 | -0.0032 | 0.092* |
| C8 | 0.8611 (5) | 0.7902 (4) | -0.00595 (19) | 0.0603 (11) |
| C9 | 0.7322 (5) | 0.7823 (4) | 0.0331 (2) | 0.0647 (12) |
| H11 | 0.6246 | 0.7318 | 0.0120 | 0.078* |
| C10 | 0.7645 (5) | 0.8500 (4) | 0.1036 (2) | 0.0633 (12) |
| H12 | 0.6784 | 0.8446 | 0.1305 | 0.076* |
| C11 | 0.0450 (5) | 0.4635 (4) | 0.5915 (2) | 0.0558 (11) |
| H13 | -0.0540 | 0.4683 | 0.6115 | 0.067* |
| C12 | 0.3038 (5) | 0.5010 (4) | 0.5745 (2) | 0.0594 (11) |
| H14 | 0.4198 | 0.5364 | 0.5802 | 0.071* |
| C13 | 0.2501 (5) | 0.6260 (3) | 0.69190 (19) | 0.0439 (9) |
| C14 | 0.1375 (5) | 0.6350 (4) | 0.7392 (2) | 0.0592 (11) |
| H15 | 0.0265 | 0.5867 | 0.7250 | 0.071* |
| C15 | 0.1885 (5) | 0.7152 (4) | 0.8074 (2) | 0.0665 (12) |
| H16 | 0.1112 | 0.7220 | 0.8389 | 0.080* |
| C16 | 0.3512 (6) | 0.7843 (4) | 0.82879 (19) | 0.0579 (11) |
| C17 | 0.4632 (5) | 0.7791 (4) | 0.7819 (2) | 0.0668 (13) |
| H17 | 0.5730 | 0.8292 | 0.7963 | 0.080* |
| C18 | 0.4138 (5) | 0.7001 (4) | 0.7134 (2) | 0.0657 (12) |
| H18 | 0.4902 | 0.6966 | 0.6817 | 0.079* |
| C19 | -0.0374 (4) | 0.1979 (3) | 0.66556 (19) | 0.0474 (10) |
| H19 | -0.1410 | 0.2029 | 0.6821 | 0.057* |
| C20 | 0.2307 (5) | 0.2255 (3) | 0.65901 (19) | 0.0497 (10) |
| H20 | 0.3497 | 0.2536 | 0.6699 | 0.060* |
| C21 | 0.1591 (4) | 0.3441 (3) | 0.77494 (18) | 0.0412 (9) |
| C22 | 0.0297 (4) | 0.3605 (3) | 0.81508 (19) | 0.0527 (11) |
| H21 | -0.0833 | 0.3191 | 0.7954 | 0.063* |
| C23 | 0.0681 (5) | 0.4380 (4) | 0.8839 (2) | 0.0591 (11) |
| H22 | -0.0194 | 0.4500 | 0.9104 | 0.071* |

| | | | | |
|-----|------------|------------|--------------|-------------|
| C24 | 0.2350 (5) | 0.4975 (4) | 0.91359 (19) | 0.0560 (11) |
| C25 | 0.3640 (5) | 0.4839 (4) | 0.8742 (2) | 0.0591 (11) |
| H23 | 0.4763 | 0.5268 | 0.8941 | 0.071* |
| C26 | 0.3268 (4) | 0.4065 (3) | 0.80535 (19) | 0.0524 (10) |
| H24 | 0.4147 | 0.3961 | 0.7790 | 0.063* |
| H1 | 0.237 (3) | -0.039 (3) | 0.4646 (12) | 0.094 (15)* |
| H2 | 0.276 (4) | 0.058 (3) | 0.5303 (14) | 0.108 (18)* |
| H3 | 0.854 (3) | 0.260 (3) | 0.4649 (14) | 0.108 (18)* |
| H4 | 0.809 (4) | 0.170 (3) | 0.3975 (10) | 0.078 (15)* |
| H5 | 0.323 (4) | 0.287 (3) | 0.4580 (14) | 0.100 (17)* |
| H6 | 0.279 (3) | 0.192 (3) | 0.3924 (12) | 0.085 (15)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|-------------|
| Fe1 | 0.0324 (3) | 0.0523 (3) | 0.0402 (3) | 0.0071 (3) | 0.0074 (2) | 0.0088 (3) |
| Cl1 | 0.0811 (9) | 0.1224 (11) | 0.0619 (7) | 0.0147 (8) | 0.0189 (6) | -0.0027 (7) |
| Cl2 | 0.1116 (11) | 0.0920 (9) | 0.0594 (7) | 0.0173 (8) | 0.0104 (7) | -0.0025 (6) |
| Cl3 | 0.0801 (8) | 0.1053 (10) | 0.0563 (7) | -0.0014 (7) | 0.0202 (6) | -0.0076 (7) |
| N1 | 0.043 (2) | 0.057 (2) | 0.050 (2) | 0.0085 (17) | 0.0069 (16) | 0.0060 (17) |
| N2 | 0.0364 (19) | 0.060 (2) | 0.050 (2) | 0.0120 (16) | 0.0093 (16) | 0.0124 (18) |
| N3 | 0.046 (2) | 0.089 (3) | 0.051 (2) | 0.0173 (19) | 0.0071 (18) | 0.012 (2) |
| N4 | 0.040 (2) | 0.072 (2) | 0.052 (2) | 0.0103 (18) | 0.0118 (17) | 0.0165 (18) |
| N5 | 0.0368 (19) | 0.060 (2) | 0.048 (2) | 0.0127 (17) | 0.0119 (17) | 0.0190 (17) |
| N6 | 0.050 (2) | 0.057 (2) | 0.059 (2) | 0.0136 (18) | 0.0077 (18) | 0.0059 (18) |
| N7 | 0.047 (2) | 0.057 (2) | 0.062 (2) | 0.0009 (18) | 0.0069 (18) | 0.0117 (19) |
| N8 | 0.0355 (19) | 0.046 (2) | 0.051 (2) | 0.0050 (16) | 0.0086 (16) | 0.0118 (16) |
| N9 | 0.0387 (19) | 0.052 (2) | 0.046 (2) | 0.0069 (16) | 0.0086 (16) | 0.0082 (17) |
| N10 | 0.0346 (19) | 0.054 (2) | 0.0464 (19) | 0.0113 (16) | 0.0056 (15) | 0.0086 (17) |
| N11 | 0.0306 (18) | 0.0447 (19) | 0.0417 (18) | 0.0053 (15) | 0.0082 (15) | 0.0103 (15) |
| O1 | 0.0296 (14) | 0.0511 (17) | 0.0322 (14) | 0.0038 (13) | 0.0064 (12) | 0.0007 (12) |
| O2 | 0.0385 (16) | 0.0649 (19) | 0.0454 (17) | -0.0036 (15) | 0.0167 (14) | 0.0044 (15) |
| O3 | 0.0391 (16) | 0.0647 (19) | 0.0468 (17) | 0.0134 (15) | 0.0049 (15) | 0.0081 (15) |
| S1 | 0.0502 (7) | 0.0720 (8) | 0.0539 (6) | 0.0008 (6) | 0.0134 (5) | -0.0062 (6) |
| S2 | 0.0481 (7) | 0.0740 (8) | 0.0474 (6) | -0.0018 (6) | 0.0103 (5) | -0.0020 (6) |
| C1 | 0.024 (2) | 0.050 (3) | 0.052 (2) | 0.0080 (18) | 0.0129 (18) | 0.014 (2) |
| C2 | 0.026 (2) | 0.048 (3) | 0.051 (2) | 0.0037 (18) | 0.0081 (19) | 0.009 (2) |
| C3 | 0.037 (2) | 0.066 (3) | 0.060 (3) | 0.005 (2) | 0.014 (2) | 0.022 (2) |
| C4 | 0.036 (3) | 0.095 (4) | 0.060 (3) | 0.004 (2) | 0.005 (2) | 0.019 (3) |
| C5 | 0.042 (2) | 0.060 (3) | 0.046 (2) | 0.014 (2) | 0.011 (2) | 0.019 (2) |
| C6 | 0.049 (3) | 0.092 (3) | 0.055 (3) | -0.002 (2) | 0.013 (2) | 0.015 (3) |
| C7 | 0.055 (3) | 0.116 (4) | 0.056 (3) | 0.007 (3) | 0.020 (2) | 0.017 (3) |
| C8 | 0.060 (3) | 0.068 (3) | 0.053 (3) | 0.016 (2) | 0.016 (2) | 0.013 (2) |
| C9 | 0.048 (3) | 0.075 (3) | 0.062 (3) | -0.002 (2) | 0.014 (2) | 0.008 (2) |
| C10 | 0.046 (3) | 0.077 (3) | 0.060 (3) | 0.002 (2) | 0.016 (2) | 0.012 (2) |
| C11 | 0.038 (3) | 0.060 (3) | 0.065 (3) | 0.001 (2) | 0.013 (2) | 0.014 (2) |
| C12 | 0.043 (2) | 0.066 (3) | 0.064 (3) | 0.012 (2) | 0.015 (2) | 0.006 (2) |
| C13 | 0.042 (2) | 0.046 (2) | 0.047 (2) | 0.010 (2) | 0.011 (2) | 0.018 (2) |

supplementary materials

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|-----|-----------|-----------|-----------|-------------|-------------|-------------|
| C14 | 0.048 (3) | 0.062 (3) | 0.070 (3) | 0.008 (2) | 0.019 (2) | 0.021 (2) |
| C15 | 0.070 (3) | 0.072 (3) | 0.057 (3) | 0.013 (3) | 0.024 (2) | 0.012 (2) |
| C16 | 0.070 (3) | 0.054 (3) | 0.045 (3) | 0.011 (2) | 0.008 (2) | 0.009 (2) |
| C17 | 0.059 (3) | 0.069 (3) | 0.057 (3) | -0.008 (2) | 0.009 (2) | 0.002 (2) |
| C18 | 0.056 (3) | 0.077 (3) | 0.060 (3) | -0.002 (2) | 0.022 (2) | 0.015 (2) |
| C19 | 0.027 (2) | 0.062 (3) | 0.052 (2) | 0.004 (2) | 0.0068 (19) | 0.016 (2) |
| C20 | 0.034 (2) | 0.060 (3) | 0.055 (3) | 0.010 (2) | 0.018 (2) | 0.010 (2) |
| C21 | 0.034 (2) | 0.046 (2) | 0.045 (2) | 0.0076 (18) | 0.0099 (18) | 0.0128 (19) |
| C22 | 0.035 (2) | 0.066 (3) | 0.050 (3) | 0.002 (2) | 0.011 (2) | 0.008 (2) |
| C23 | 0.047 (3) | 0.072 (3) | 0.059 (3) | 0.012 (2) | 0.023 (2) | 0.013 (2) |
| C24 | 0.063 (3) | 0.055 (3) | 0.046 (3) | 0.007 (2) | 0.013 (2) | 0.007 (2) |
| C25 | 0.044 (3) | 0.068 (3) | 0.054 (3) | 0.001 (2) | 0.011 (2) | 0.003 (2) |
| C26 | 0.036 (2) | 0.065 (3) | 0.053 (3) | 0.009 (2) | 0.016 (2) | 0.008 (2) |

Geometric parameters (Å, °)

| | | | |
|---------------------|------------|---------|-----------|
| Fe1—N1 | 2.086 (3) | S2—C2 | 1.633 (4) |
| Fe1—O2 | 2.100 (2) | C3—H7 | 0.9300 |
| Fe1—O3 | 2.102 (3) | C4—H8 | 0.9300 |
| Fe1—N2 | 2.107 (3) | C5—C10 | 1.378 (4) |
| Fe1—O1 ⁱ | 2.264 (3) | C5—C6 | 1.387 (4) |
| Fe1—O1 | 2.281 (2) | C6—C7 | 1.383 (5) |
| C11—C8 | 1.752 (4) | C6—H9 | 0.9300 |
| C12—C16 | 1.738 (4) | C7—C8 | 1.362 (5) |
| C13—C24 | 1.745 (4) | C7—H10 | 0.9300 |
| N1—C1 | 1.169 (4) | C8—C9 | 1.373 (4) |
| N2—C2 | 1.162 (4) | C9—C10 | 1.372 (4) |
| N3—C4 | 1.285 (4) | C9—H11 | 0.9300 |
| N3—N4 | 1.376 (4) | C10—H12 | 0.9300 |
| N4—C3 | 1.305 (4) | C11—H13 | 0.9300 |
| N5—C4 | 1.351 (4) | C12—H14 | 0.9300 |
| N5—C3 | 1.360 (4) | C13—C14 | 1.377 (4) |
| N5—C5 | 1.432 (4) | C13—C18 | 1.384 (4) |
| N6—C12 | 1.306 (4) | C14—C15 | 1.380 (4) |
| N6—N7 | 1.397 (4) | C14—H15 | 0.9300 |
| N7—C11 | 1.298 (4) | C15—C16 | 1.357 (5) |
| N8—C12 | 1.352 (4) | C15—H16 | 0.9300 |
| N8—C11 | 1.359 (4) | C16—C17 | 1.370 (4) |
| N8—C13 | 1.428 (4) | C17—C18 | 1.378 (4) |
| N9—C20 | 1.300 (4) | C17—H17 | 0.9300 |
| N9—N10 | 1.381 (3) | C18—H18 | 0.9300 |
| N10—C19 | 1.296 (4) | C19—H19 | 0.9300 |
| N11—C19 | 1.361 (4) | C20—H20 | 0.9300 |
| N11—C20 | 1.359 (4) | C21—C26 | 1.387 (4) |
| N11—C21 | 1.429 (4) | C21—C22 | 1.387 (4) |
| O1—Fe1 ⁱ | 2.264 (3) | C22—C23 | 1.374 (4) |
| O1—H1 | 0.869 (10) | C22—H21 | 0.9300 |
| O1—H2 | 0.880 (10) | C23—C24 | 1.371 (4) |
| O2—H3 | 0.884 (10) | C23—H22 | 0.9300 |

| | | | |
|--------------------------|-------------|-------------|-----------|
| O2—H4 | 0.881 (10) | C24—C25 | 1.372 (4) |
| O3—H5 | 0.885 (10) | C25—C26 | 1.375 (4) |
| O3—H6 | 0.875 (10) | C25—H23 | 0.9300 |
| S1—C1 | 1.632 (4) | C26—H24 | 0.9300 |
| N1—Fe1—O2 | 90.22 (11) | C8—C7—H10 | 120.3 |
| N1—Fe1—O3 | 89.68 (12) | C6—C7—H10 | 120.3 |
| O2—Fe1—O3 | 101.01 (10) | C7—C8—C9 | 121.6 (4) |
| N1—Fe1—N2 | 178.33 (12) | C7—C8—C11 | 120.2 (3) |
| O2—Fe1—N2 | 89.47 (11) | C9—C8—C11 | 118.2 (3) |
| O3—Fe1—N2 | 88.76 (11) | C8—C9—C10 | 119.0 (4) |
| N1—Fe1—O1 ⁱ | 90.32 (11) | C8—C9—H11 | 120.5 |
| O2—Fe1—O1 ⁱ | 89.04 (10) | C10—C9—H11 | 120.5 |
| O3—Fe1—O1 ⁱ | 169.95 (9) | C9—C10—C5 | 120.7 (4) |
| N2—Fe1—O1 ⁱ | 91.32 (11) | C9—C10—H12 | 119.6 |
| N1—Fe1—O1 | 89.79 (10) | C5—C10—H12 | 119.6 |
| O2—Fe1—O1 | 167.40 (10) | N7—C11—N8 | 111.9 (3) |
| O3—Fe1—O1 | 91.59 (10) | N7—C11—H13 | 124.0 |
| N2—Fe1—O1 | 90.87 (10) | N8—C11—H13 | 124.0 |
| O1 ⁱ —Fe1—O1 | 78.36 (9) | N6—C12—N8 | 111.7 (3) |
| C1—N1—Fe1 | 175.9 (3) | N6—C12—H14 | 124.2 |
| C2—N2—Fe1 | 172.4 (3) | N8—C12—H14 | 124.2 |
| C4—N3—N4 | 107.0 (3) | C14—C13—C18 | 119.2 (4) |
| C3—N4—N3 | 105.8 (3) | C14—C13—N8 | 120.7 (3) |
| C4—N5—C3 | 102.1 (3) | C18—C13—N8 | 120.1 (3) |
| C4—N5—C5 | 129.6 (3) | C15—C14—C13 | 120.4 (4) |
| C3—N5—C5 | 128.4 (3) | C15—C14—H15 | 119.8 |
| C12—N6—N7 | 106.4 (3) | C13—C14—H15 | 119.8 |
| C11—N7—N6 | 106.3 (3) | C16—C15—C14 | 120.1 (4) |
| C12—N8—C11 | 103.7 (3) | C16—C15—H16 | 120.0 |
| C12—N8—C13 | 128.3 (3) | C14—C15—H16 | 120.0 |
| C11—N8—C13 | 127.9 (3) | C15—C16—C17 | 120.2 (4) |
| C20—N9—N10 | 106.8 (3) | C15—C16—C12 | 120.3 (3) |
| C19—N10—N9 | 106.9 (3) | C17—C16—C12 | 119.4 (3) |
| C19—N11—C20 | 103.5 (3) | C16—C17—C18 | 120.3 (4) |
| C19—N11—C21 | 128.0 (3) | C16—C17—H17 | 119.8 |
| C20—N11—C21 | 128.5 (3) | C18—C17—H17 | 119.8 |
| Fe1 ⁱ —O1—Fe1 | 101.64 (9) | C17—C18—C13 | 119.7 (4) |
| Fe1 ⁱ —O1—H1 | 104 (3) | C17—C18—H18 | 120.1 |
| Fe1—O1—H1 | 119 (2) | C13—C18—H18 | 120.1 |
| Fe1 ⁱ —O1—H2 | 110 (3) | N10—C19—N11 | 111.4 (3) |
| Fe1—O1—H2 | 114 (2) | N10—C19—H19 | 124.3 |
| H1—O1—H2 | 108 (2) | N11—C19—H19 | 124.3 |
| Fe1—O2—H3 | 128 (2) | N9—C20—N11 | 111.3 (3) |
| Fe1—O2—H4 | 125 (2) | N9—C20—H20 | 124.3 |
| H3—O2—H4 | 106 (2) | N11—C20—H20 | 124.3 |
| Fe1—O3—H5 | 119 (3) | C26—C21—C22 | 119.0 (3) |
| Fe1—O3—H6 | 117 (2) | C26—C21—N11 | 120.8 (3) |

supplementary materials

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| H5—O3—H6 | 106 (2) | C22—C21—N11 | 120.2 (3) |
| N1—C1—S1 | 179.6 (3) | C23—C22—C21 | 120.1 (3) |
| N2—C2—S2 | 179.7 (3) | C23—C22—H21 | 119.9 |
| N4—C3—N5 | 112.2 (3) | C21—C22—H21 | 119.9 |
| N4—C3—H7 | 123.9 | C24—C23—C22 | 120.2 (4) |
| N5—C3—H7 | 123.9 | C24—C23—H22 | 119.9 |
| N3—C4—N5 | 112.9 (4) | C22—C23—H22 | 119.9 |
| N3—C4—H8 | 123.6 | C25—C24—C23 | 120.4 (4) |
| N5—C4—H8 | 123.6 | C25—C24—C13 | 119.9 (3) |
| C10—C5—C6 | 119.4 (4) | C23—C24—C13 | 119.7 (3) |
| C10—C5—N5 | 120.8 (3) | C24—C25—C26 | 119.8 (4) |
| C6—C5—N5 | 119.8 (3) | C24—C25—H23 | 120.1 |
| C5—C6—C7 | 119.9 (4) | C26—C25—H23 | 120.1 |
| C5—C6—H9 | 120.1 | C25—C26—C21 | 120.4 (3) |
| C7—C6—H9 | 120.1 | C25—C26—H24 | 119.8 |
| C8—C7—C6 | 119.4 (4) | C21—C26—H24 | 119.8 |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| O1—H1 \cdots N10 ⁱⁱ | 0.87 (3) | 1.97 (3) | 2.827 (4) | 170 (3) |
| O1—H2 \cdots N9 | 0.88 (3) | 1.94 (3) | 2.819 (4) | 173 (3) |
| O2—H3 \cdots N7 ⁱⁱⁱ | 0.88 (3) | 1.98 (3) | 2.866 (5) | 178 (3) |
| O2—H4 \cdots N4 ^{iv} | 0.88 (2) | 1.97 (3) | 2.853 (4) | 175 (3) |
| O3—H5 \cdots N6 | 0.88 (3) | 1.92 (3) | 2.802 (4) | 174 (3) |
| O3—H6 \cdots N3 ^v | 0.88 (2) | 1.93 (2) | 2.803 (4) | 172 (3) |
| C3—H7 \cdots S2 ^{vi} | 0.93 | 2.72 | 3.624 (5) | 165 |
| C22—H21 \cdots S2 ⁱⁱ | 0.93 | 2.87 | 3.736 (5) | 156 |
| C11—H13 \cdots S1 ^{vii} | 0.93 | 2.87 | 3.783 (5) | 167 |

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

Fig. 1

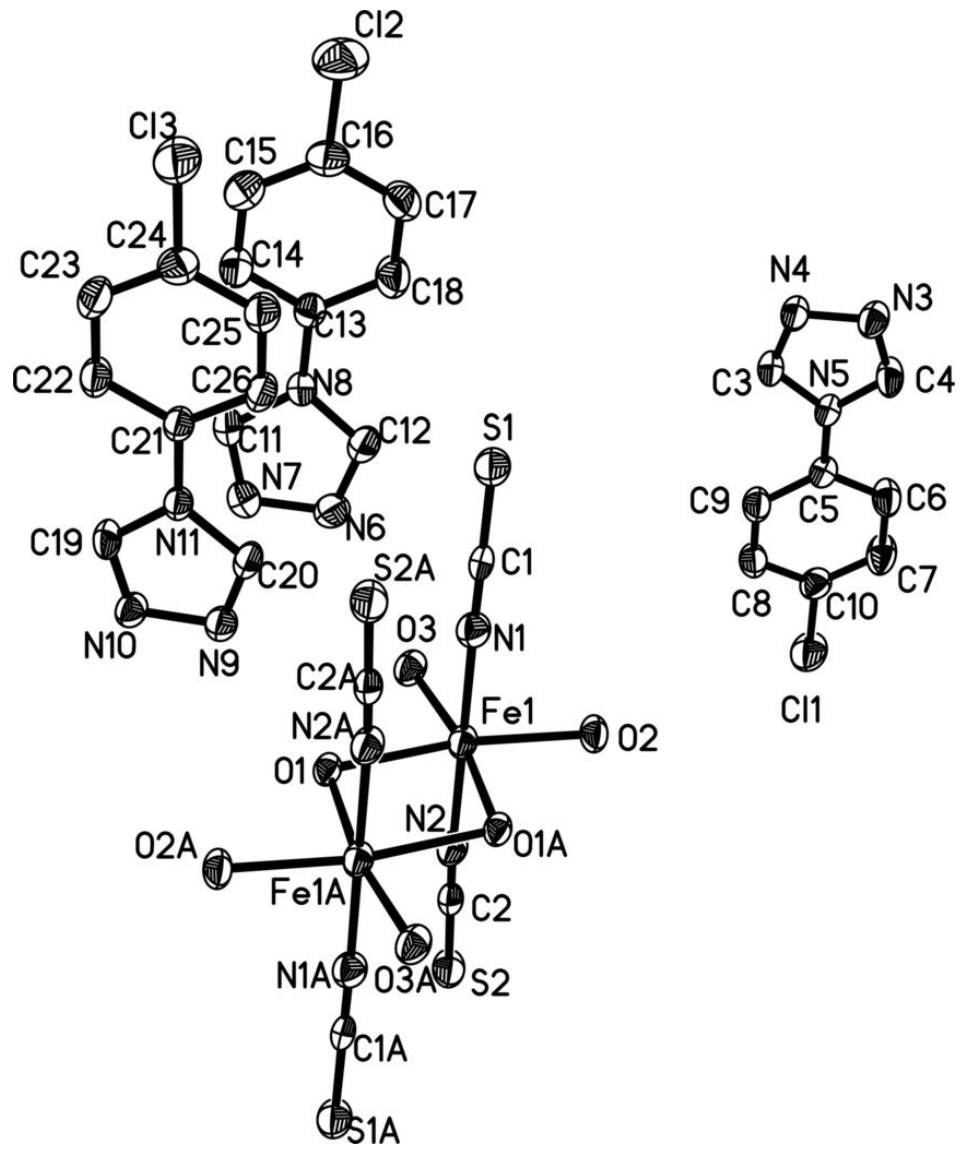


Fig. 2

