

Bis(triethylammonium) bis(μ -pyrazine-2,3-dithiolato)bis(pyrazine-2,3-dithiolato)diferrate(III) methanol disolvate

Toshiki Yamaguchi, Shigeyuki Masaoka and Ken Sakai*

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan

Correspondence e-mail: ksakai@chem.kyushu-univ.jp

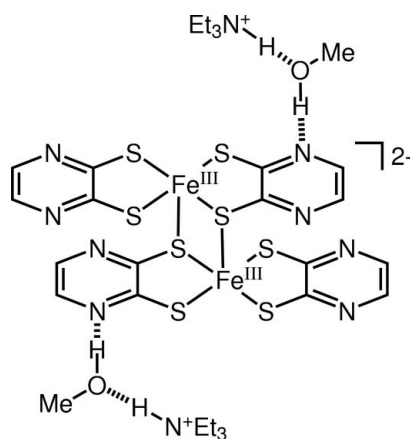
Received 1 December 2008; accepted 10 December 2008

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.021; wR factor = 0.054; data-to-parameter ratio = 16.9.

In the title compound, $(\text{C}_6\text{H}_{16}\text{N})_2[\text{Fe}_2(\text{C}_4\text{H}_2\text{N}_2\text{S}_2)_4]\cdot 2\text{CH}_4\text{O}$, the $[\text{Fe}^{\text{III}}(\text{pdt})_2]^-$ anion (pdt is pyrazine-2,3-dithiolate) forms a centrosymmetric dimer supported by two $\text{Fe}^{\text{III}}-\text{S}$ bonds [$\text{Fe}-\text{S} = 2.4787(4)$ Å]. In the crystal structure, dimers form a one-dimensional stack along the b axis via $\pi-\pi$ stacking interactions, the interplanar separation between adjacent dimers being $3.51(2)$ Å. The methanol solvent molecule is involved in two hydrogen bonds in which the hydroxyl group acts as a hydrogen-bond donor to the N atom of a pdt ligand and the O atom acts as an acceptor for the NH group of the triethylammonium cation.

Related literature

For background information, see: Adams (1990); Frey (2002); Georgakaki *et al.* (2003); Gloaguen *et al.* (2001); Liu *et al.* (2005); Nicolet *et al.* (1999); Peters *et al.* (1998); Sakata (2000); Sun *et al.* (2005); Trasatti (1972); Yamaguchi *et al.* (2008). For other iron(III)-dithiolene complexes, see: Simao *et al.* (2006); Yamaguchi *et al.* (2008). For the synthesis, see: Ribas *et al.* (2004).



Experimental

Crystal data

$(\text{C}_6\text{H}_{16}\text{N})_2[\text{Fe}_2(\text{C}_4\text{H}_2\text{N}_2\text{S}_2)_4]\cdot 2\text{CH}_4\text{O}$
 $M_r = 949.04$
 Monoclinic, $P2_1/n$
 $a = 14.2375(15)$ Å
 $b = 7.9500(8)$ Å
 $c = 17.7456(18)$ Å
 $\beta = 95.293(1)^\circ$
 $V = 2000.0(4)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.19$ mm⁻¹
 $T = 100(2)$ K
 $0.33 \times 0.18 \times 0.16$ mm

Data collection

Bruker SMART APEX CCD-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.695$, $T_{\text{max}} = 0.831$
 10059 measured reflections
 4048 independent reflections
 3824 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.054$
 $S = 1.07$
 4048 reflections
 240 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{O1}-\text{H24}\cdots\text{N3}^{\text{i}}$ | 0.84 | 1.99 | 2.8014 (17) | 163 |
| $\text{N5}-\text{H20}\cdots\text{O1}$ | 0.93 | 1.86 | 2.7880 (17) | 172 |

Symmetry code: (i) $-x + 1, -y + 2, -z$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: KENX (Sakai, 2004); software used to prepare material for publication: SHELXL97, TEXSAN (Molecular Structure Corporation, 2001), KENX and ORTEPII (Johnson, 1976).

This work was supported in part by a Grant-in-Aid for Scientific Research (A) (No. 17205008), a Grant-in-Aid for Specially Promoted Research (No. 18002016), and a Grant-in-Aid for the Global COE Program ('Science for Future Molecular Systems') from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2741).

References

- Adams, M. W. W. (1990). *Biochim. Biophys. Acta*, **1020**, 115–145.
 Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Frey, M. (2002). *ChemBioChem*, **3**, 153–160.
 Georgakaki, I. P., Thomson, L. M., Lyon, E. J., Hall, M. B. & Darensbourg, M. Y. (2003). *Coord. Chem. Rev.* **238–239**, 255–266.
 Gloaguen, F., Lawrence, J. D. & Rauchfuss, T. B. (2001). *J. Am. Chem. Soc.* **123**, 9476–9477.
 Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Liu, X., Ibrahim, S. K., Tard, C. & Pickett, C. J. (2005). *Coord. Chem. Rev.* **249**, 1641–1652.

metal-organic compounds

- Molecular Structure Corporation (2001). *TEXSAN*. MSC, The Woodlands, Texas, USA.
- Nicolet, Y., Piras, C., Legrand, P., Hatchikian, C. E. & Fontecilla-Camps, J. C. (1999). *Structure*, **7**, 13–23.
- Peters, J. W., Lanzilotta, W. N., Lemon, B. J. & Seefeldt, L. C. (1998). *Science*, **282**, 1853–1858.
- Ribas, X., Dias, J. C., Morgado, J., Wurst, K., Molins, E., Ruiz, E., Almeida, M., Veciana, J. & Rovira, C. (2004). *Chem. Eur. J.* **10**, 1691–1704.
- Sakai, K. (2004). *KENX*. Kyushu University, Japan.
- Sakata, T. (2000). *Bull. Chem. Soc. Jpn.*, **73**, 297–305.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Simao, D., Ayllón, J. A., Rabaça, S., Figueira, M. J., Santos, I. C., Henriques, R. T. & Almeida, M. (2006). *CrystEngComm*, **8**, 658–661.
- Sun, L., Åkermark, B. & Ott, S. (2005). *Coord. Chem. Rev.* **249**, 1653–1663.
- Trasatti, S. (1972). *J. Electroanal. Chem.* **39**, 163–184.
- Yamaguchi, T., Masaoka, S. & Sakai, K. (2008). *Acta Cryst.* **E64**, m1557–m1558.

supplementary materials

Acta Cryst. (2009). E65, m77-m78 [doi:10.1107/S1600536808041949]

Bis(triethylammonium) bis(μ -pyrazine-2,3-dithiolato)bis(pyrazine-2,3-dithiolato)diferrate(III) methanol disolvate

T. Yamaguchi, S. Masaoka and K. Sakai

Comment

The Fe₂S₂ clusters (*i.e.*, H-clusters) in Fe-only hydrogenases (FeHases) are known to be highly active as catalysts towards H₂-evolving (HE) reaction (Adams, 1990; Peters *et al.*, 1998; Nicolet *et al.*, 1999; Frey, 2002). In contrast, metal iron itself exhibits much lower catalytic activity toward HE reaction than does platinum (Trasatti, 1972; Sakata, 2000). A large variety of structural and functional models of FeHases have been developed and their HE activities have been evaluated so far (Gloaguen *et al.*, 2001; Georgakaki *et al.*, 2003; Liu *et al.*, 2005; Sun *et al.*, 2005). On the other hand, an air-stable di-iron complex with a bio-relevant Fe₂(μ -S)₂ core, [Fe^{III}(mnt)₂]₂²⁻ (mnt = maleonitriledithiolate), was found to serve as an electrode catalyst towards HE reaction in aqueous media (Yamaguchi *et al.*, unpublished results). In the present study, [Fe^{III}(pdt)₂]₂²⁻ has been synthesized to develop the more highly effective HE catalysts with a bio-relevant Fe₂(μ -S)₂ core. The pdt ligand has been selected to examine the effect of introducing *N*(imine) donor in close proximity to the active center of the HE reaction. The HE activity of (I) will be separately reported elsewhere (Yamaguchi *et al.*, unpublished results).

The [Fe^{III}(pdt)₂]⁻ anions form a dimer in the crystal with an inversion center located at the center of the dimer (Figure 1). The monomer-monomer association is supported by two crystallographically equivalent Fe^{III}—S bonds [Fe1—S1ⁱ = 2.4787 (4) Å; symmetry code: (i) 1 - *x*, 2 - *y*, -*z*]. This structural feature well resembles those observed for other iron(III)-dithiolene complexes as follows. The above intermonomer Fe—S distance is quite comparable to those reported for (Ph₄As)₂[Fe^{III}(qdt)₂]₂ (qdt = quinoxaline-2,3-dithiolate) [Fe—S = 2.4884 (13) Å] (Simao *et al.*, 2006) and [Fe^{II}(15-crown-5)(OH₂)₂][Fe^{III}(mnt)₂]₂·2(15-crown-5) [Fe—S = 2.4715 (9) and 2.4452 (9) Å] (Yamaguchi *et al.*, 2008). The Fe^{III} ion is considered to have a distorted square pyramidal stereochemistry; the Fe^{III} ion is ligated by four sulfur atoms with shorter Fe—S distances [2.2264 (4)–2.2367 (4) Å] and axially ligated by a sulfur atom from the adjacent monomer with a longer Fe—S distance [2.4787 (4) Å]. Atom Fe1 is shifted out of the least-squares plane defined with four atoms S1—S4 by 0.3719 (3) Å, even though the four-atom r.m.s. deviation given in the calculation was 0.0650 Å.

The methanol molecule is stabilized with two different types of hydrogen bonding interactions (Figure 2). One type of hydrogen bond is formed between the hydroxyl unit of methanol and the nitrogen atom of pdt [O1—N3ⁱ = 2.8014 (17) Å; symmetry code: (i) 1 - *x*, 2 - *y*, -*z*]. The other is formed between the N—H group of the triethylammonium cation and the oxygen atom of methanol [O1—N5 = 2.7880 (17) Å].

Finally, the anion forms a one-dimensional stack along the *b* axis (Figure 3). The stack of anions is stabilized with a π - π interaction formed between two adjacent pdt moieties. As shown in Figure 4, a set of atoms S1—S2/C1—C4/N1—N2 and that of atoms S1ⁱⁱ, C1ⁱⁱ, and N1ⁱⁱ contribute to the π - π association at each interdimer association [symmetry code: (ii) 1 - *x*, 1 - *y*, -*z*]. The interplanar separation is calculated as 3.51 (2) Å based on the average shift of atoms S1ⁱⁱ, C1ⁱⁱ, and N1ⁱⁱ

supplementary materials

from the best plane defined by atoms S1—S2/C1—C4/N1—N2. An important short contact at this geometry is C1—C1ⁱⁱ = 3.493 (3) Å [symmetry code: (ii) 1 - x, 1 - y, -z].

Experimental

Compound (I) was prepared as follows. Pyrazine-2,3-dithiol was prepared as previously described (Ribas *et al.*, 2004). To a suspension of pyrazine-2,3-dithiol (0.146 g, 1.0 mmol) and triethylamine (0.42 ml, 3.0 mmol) in dry tetrahydrofuran (THF, 50 ml) was slowly added a solution of FeCl₃·6H₂O (0.137 g, 0.5 mmol) in dry THF (5 ml) under Ar atmosphere. Although a dark-brown solid immediately precipitated, the suspension was stirred at room temperature for 18 h. The dark-brown solid deposited was collected by filtration and washed with THF. The crude material was re-dissolved in a minimum amount of methanol followed by filtration for the removal of insoluble materials. Standing of the filtrate at room temperature for several days afforded the black needles of (I), which were collected by filtration, washed with cold methanol, and dried *in vacuo*. Yield: 0.098 g (41%). Single crystals of (I) suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a methanol solution of (I). Analysis calculated for C₃₀H₄₈Fe₂N₁₀O₂S₈: C, 37.97; H, 5.10; N, 14.76. Found: C, 38.04; H, 4.98; N, 15.04. IR (ν, cm⁻¹): 3028 (w), 2672 (w), 1531 (m), 1449 (m), 1416 (m), 1394 (m), 1320 (s), 1287 (m), 1196 (w), 1175 (m), 1144 (s), 1064 (m), 1045 (m), 1005 (m), 837 (m), 825 (s), 791 (m), 485 (m), 475 (m), 449 (s), 421 (m).

Refinement

All H atoms were placed in idealized position (ring C—H = 0.95 Å, methyl C—H = 0.98 Å, methylene C—H = 0.99 Å, hydroxyl O—H = 0.84 Å and tertiary N—H = 0.93 Å), and included in the refinement in a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ (ring C, methylene C and tertiary N) and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$ (methyl C and hydroxyl O). In the final Fourier map, the highest peak was located 0.99 Å from atom S4. The deepest hole was located 0.53 Å from atom Fe1.

Figures

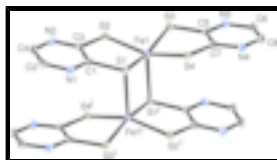


Fig. 1. The molecular structure of a $[\text{Fe}^{\text{III}}(\text{pdt})_2]^{2-}$ dimer, showing the atom-labeling scheme [symmetry code: (i) 1 - x, 2 - y, -z]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

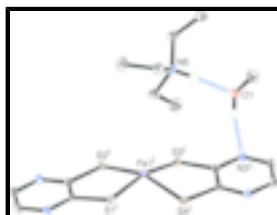


Fig. 2. The molecular structure of $(\text{Et}_3\text{NH})[\text{Fe}^{\text{III}}(\text{pdt})_2]\cdot\text{MeOH}$, showing how the hydrogen bonds are formed [symmetry code: (i) 1 - x, 2 - y, -z]. Hydrogen atoms except for those of N—H and O—H are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

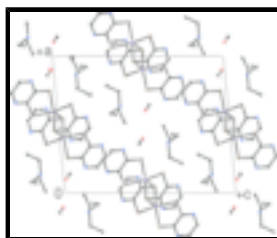


Fig. 3. A view down the *b* axis, showing the manner how the anions stack along the *b* axis to give one-dimensional chains. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

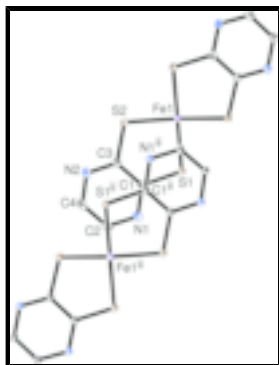


Fig. 4. A view perpendicular to the plane defined by atoms S1—S2/C1—C4/N1—N2 which has a weak π -stack to the plane defined by atoms S1ⁱⁱ, C1ⁱⁱ, and N1ⁱⁱ [Symmetry code: (ii) 1 - x, 1 - y, -z]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

Bis(triethylammonium) bis(μ -pyrazine-2,3-dithiolato)bis(pyrazine-2,3-dithiolato)diferrate(III) methanol disolvate

Crystal data

(C₆H₁₆N)₂[Fe₂(C₄H₂N₂S₂)₄] \cdot 2CH₄O

$M_r = 949.04$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 14.2375$ (15) Å

$b = 7.9500$ (8) Å

$c = 17.7456$ (18) Å

$\beta = 95.293$ (1)°

$V = 2000.0$ (4) Å³

$Z = 2$

$F_{000} = 988$

$D_x = 1.576$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 7956 reflections

$\theta = 2.3$ – 27.5 °

$\mu = 1.19$ mm⁻¹

$T = 100$ (2) K

Needles, black

$0.33 \times 0.18 \times 0.16$ mm

Data collection

Bruker SMART APEX CCD-detector diffractometer 4048 independent reflections

Radiation source: rotating anode with a mirror focusing unit 3824 reflections with $I > 2\sigma(I)$

Monochromator: graphite

$R_{\text{int}} = 0.013$

$T = 100$ (2) K

$\theta_{\text{max}} = 26.4$ °

φ and ω scans

$\theta_{\text{min}} = 2.3$ °

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

$h = -16 \rightarrow 17$

$T_{\text{min}} = 0.695$, $T_{\text{max}} = 0.831$

$k = -9 \rightarrow 9$

10059 measured reflections

$l = -22 \rightarrow 14$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.021$

H-atom parameters constrained

supplementary materials

| | |
|--|--|
| $wR(F^2) = 0.054$ | $w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 1.2723P]$ |
| $S = 1.07$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4048 reflections | $(\Delta/\sigma)_{\max} = 0.001$ |
| 240 parameters | $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$ |
| | Extinction coefficient: ? |

Special details

Experimental. The first 50 frames were rescanned at the end of data collection to evaluate any possible decay phenomenon. Since it was judged to be negligible, no decay correction was applied to the data.

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.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$$4.6834 (0.0016) x + 6.8874 (0.0009) y - 7.1795 (0.0020) z = 7.7711 (0.0010)$$

$$* 0.0655 (0.0002) S1 * -0.0639 (0.0002) S2 * 0.0645 (0.0002) S3 * -0.0661 (0.0002) S4 0.3719 (0.0003) Fe1$$

Rms deviation of fitted atoms = 0.0650

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$$5.7097 (0.0038) x + 6.0721 (0.0015) y - 9.5934 (0.0044) z = 7.6443 (0.0017)$$

$$* 0.0277 (0.0006) S1 * -0.0176 (0.0006) S2 * -0.0098 (0.0012) C1 * -0.0122 (0.0011) C2 * -0.0067 (0.0012) C3 * 0.0190 (0.0011) C4 * -0.0173 (0.0010) N1 * 0.0170 (0.0010) N2 - 3.5344 (0.0008) S1_S2 - 3.4970 (0.0017) C1_S2 - 3.4894 (0.0014) N1_S2$$

Rms deviation of fitted atoms = 0.0170

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 | 0.404540 (13) | 0.93135 (3) | 0.023150 (11) | 0.01057 (6) |
| S1 | 0.54285 (2) | 0.79904 (4) | 0.029127 (18) | 0.01130 (8) |
| S2 | 0.35609 (2) | 0.79099 (5) | -0.082403 (19) | 0.01420 (8) |
| S3 | 0.25466 (2) | 1.00013 (5) | 0.034182 (19) | 0.01363 (8) |
| S4 | 0.43700 (2) | 0.97513 (4) | 0.147331 (18) | 0.01193 (8) |
| O1 | 0.89754 (8) | 0.60915 (14) | -0.01530 (6) | 0.0209 (2) |
| H24 | 0.8767 | 0.6838 | -0.0459 | 0.031* |
| N1 | 0.61230 (9) | 0.57967 (15) | -0.06370 (7) | 0.0151 (3) |

| | | | | |
|-----|--------------|--------------|---------------|------------|
| N2 | 0.44848 (9) | 0.57864 (16) | -0.16542 (7) | 0.0163 (3) |
| N3 | 0.18638 (8) | 1.19999 (16) | 0.13603 (7) | 0.0147 (2) |
| N4 | 0.34506 (9) | 1.16211 (16) | 0.24079 (7) | 0.0141 (2) |
| N5 | 0.86540 (8) | 0.70235 (16) | 0.13156 (7) | 0.0151 (3) |
| H20 | 0.8819 | 0.6706 | 0.0841 | 0.018* |
| C1 | 0.53659 (10) | 0.67055 (18) | -0.05203 (8) | 0.0122 (3) |
| C2 | 0.60532 (11) | 0.48707 (19) | -0.12700 (9) | 0.0171 (3) |
| H1 | 0.6571 | 0.4184 | -0.1377 | 0.021* |
| C3 | 0.45350 (10) | 0.67025 (18) | -0.10198 (8) | 0.0132 (3) |
| C4 | 0.52528 (11) | 0.48836 (19) | -0.17707 (8) | 0.0178 (3) |
| H2 | 0.5246 | 0.4224 | -0.2218 | 0.021* |
| C5 | 0.26017 (10) | 1.10755 (18) | 0.12000 (8) | 0.0124 (3) |
| C6 | 0.19204 (10) | 1.27363 (19) | 0.20475 (8) | 0.0167 (3) |
| H3 | 0.1412 | 1.3416 | 0.2179 | 0.020* |
| C7 | 0.34105 (10) | 1.09206 (18) | 0.17242 (8) | 0.0119 (3) |
| C8 | 0.26953 (10) | 1.25302 (19) | 0.25642 (8) | 0.0161 (3) |
| H4 | 0.2696 | 1.3047 | 0.3047 | 0.019* |
| C9 | 0.92078 (11) | 0.5916 (2) | 0.18858 (8) | 0.0181 (3) |
| H5 | 0.8909 | 0.5936 | 0.2368 | 0.022* |
| H6 | 0.9856 | 0.6366 | 0.1985 | 0.022* |
| C10 | 0.92556 (12) | 0.4119 (2) | 0.16109 (9) | 0.0229 (3) |
| H7 | 0.8615 | 0.3687 | 0.1489 | 0.034* |
| H8 | 0.9583 | 0.3423 | 0.2008 | 0.034* |
| H9 | 0.9599 | 0.4082 | 0.1158 | 0.034* |
| C11 | 0.76030 (10) | 0.6761 (2) | 0.13087 (9) | 0.0197 (3) |
| H10 | 0.7471 | 0.5538 | 0.1296 | 0.024* |
| H11 | 0.7289 | 0.7259 | 0.0840 | 0.024* |
| C12 | 0.71813 (11) | 0.7525 (2) | 0.19835 (9) | 0.0253 (4) |
| H13 | 0.7530 | 0.7127 | 0.2451 | 0.038* |
| H12 | 0.6518 | 0.7189 | 0.1977 | 0.038* |
| H14 | 0.7223 | 0.8754 | 0.1958 | 0.038* |
| C13 | 0.89199 (11) | 0.8848 (2) | 0.14175 (9) | 0.0193 (3) |
| H16 | 0.8950 | 0.9141 | 0.1961 | 0.023* |
| H15 | 0.8428 | 0.9557 | 0.1144 | 0.023* |
| C14 | 0.98672 (13) | 0.9219 (2) | 0.11225 (10) | 0.0283 (4) |
| H19 | 1.0362 | 0.8578 | 0.1416 | 0.042* |
| H18 | 1.0004 | 1.0425 | 0.1173 | 0.042* |
| H17 | 0.9846 | 0.8894 | 0.0589 | 0.042* |
| C16 | 0.85896 (13) | 0.4489 (2) | -0.03924 (10) | 0.0263 (4) |
| H21 | 0.8600 | 0.4378 | -0.0942 | 0.040* |
| H22 | 0.7938 | 0.4406 | -0.0260 | 0.040* |
| H23 | 0.8968 | 0.3588 | -0.0139 | 0.040* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|---------------|---------------|
| Fe1 | 0.01022 (10) | 0.01220 (11) | 0.00912 (10) | 0.00046 (7) | 0.00004 (7) | -0.00049 (7) |
| S1 | 0.01119 (16) | 0.01259 (17) | 0.00985 (15) | 0.00098 (12) | -0.00040 (12) | -0.00008 (12) |

supplementary materials

| | | | | | | |
|-----|--------------|--------------|--------------|--------------|---------------|---------------|
| S2 | 0.01256 (17) | 0.01665 (18) | 0.01285 (16) | 0.00100 (13) | -0.00173 (13) | -0.00337 (13) |
| S3 | 0.01063 (16) | 0.01853 (19) | 0.01144 (16) | 0.00053 (13) | -0.00050 (12) | -0.00270 (13) |
| S4 | 0.01160 (16) | 0.01452 (17) | 0.00948 (16) | 0.00168 (13) | 0.00002 (12) | 0.00010 (12) |
| O1 | 0.0232 (6) | 0.0213 (6) | 0.0173 (5) | 0.0043 (5) | -0.0036 (4) | -0.0003 (4) |
| N1 | 0.0165 (6) | 0.0126 (6) | 0.0166 (6) | 0.0007 (5) | 0.0039 (5) | 0.0010 (5) |
| N2 | 0.0208 (6) | 0.0141 (6) | 0.0140 (6) | -0.0008 (5) | 0.0009 (5) | -0.0018 (5) |
| N3 | 0.0138 (6) | 0.0149 (6) | 0.0156 (6) | -0.0002 (5) | 0.0020 (5) | -0.0004 (5) |
| N4 | 0.0167 (6) | 0.0131 (6) | 0.0125 (6) | 0.0002 (5) | 0.0017 (5) | -0.0004 (5) |
| N5 | 0.0136 (6) | 0.0187 (7) | 0.0124 (6) | 0.0002 (5) | -0.0013 (5) | 0.0010 (5) |
| C1 | 0.0151 (7) | 0.0104 (7) | 0.0111 (6) | -0.0007 (5) | 0.0019 (5) | 0.0008 (5) |
| C2 | 0.0192 (7) | 0.0120 (7) | 0.0211 (7) | 0.0014 (6) | 0.0067 (6) | -0.0012 (6) |
| C3 | 0.0156 (7) | 0.0109 (7) | 0.0132 (6) | -0.0008 (5) | 0.0020 (5) | 0.0010 (5) |
| C4 | 0.0253 (8) | 0.0129 (7) | 0.0157 (7) | 0.0000 (6) | 0.0053 (6) | -0.0027 (6) |
| C5 | 0.0133 (7) | 0.0120 (7) | 0.0122 (6) | -0.0016 (5) | 0.0023 (5) | 0.0011 (5) |
| C6 | 0.0164 (7) | 0.0158 (7) | 0.0183 (7) | 0.0017 (6) | 0.0043 (6) | -0.0013 (6) |
| C7 | 0.0137 (7) | 0.0101 (7) | 0.0120 (6) | -0.0013 (5) | 0.0018 (5) | 0.0019 (5) |
| C8 | 0.0197 (7) | 0.0156 (7) | 0.0134 (7) | 0.0003 (6) | 0.0035 (6) | -0.0017 (5) |
| C9 | 0.0147 (7) | 0.0233 (8) | 0.0155 (7) | 0.0015 (6) | -0.0036 (6) | 0.0039 (6) |
| C10 | 0.0240 (8) | 0.0231 (9) | 0.0207 (8) | 0.0039 (6) | -0.0017 (6) | 0.0045 (6) |
| C11 | 0.0122 (7) | 0.0259 (8) | 0.0201 (7) | -0.0001 (6) | -0.0033 (6) | 0.0002 (6) |
| C12 | 0.0169 (8) | 0.0336 (9) | 0.0255 (8) | 0.0008 (7) | 0.0028 (6) | -0.0024 (7) |
| C13 | 0.0208 (8) | 0.0184 (8) | 0.0177 (7) | -0.0012 (6) | -0.0033 (6) | 0.0001 (6) |
| C14 | 0.0294 (9) | 0.0274 (9) | 0.0283 (9) | -0.0089 (7) | 0.0048 (7) | -0.0002 (7) |
| C16 | 0.0303 (9) | 0.0248 (9) | 0.0228 (8) | 0.0009 (7) | -0.0038 (7) | -0.0038 (7) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-------------|---------|-----------|
| Fe1—S1 | 2.2264 (4) | C9—C10 | 1.513 (2) |
| Fe1—S3 | 2.2289 (4) | C11—C12 | 1.515 (2) |
| Fe1—S2 | 2.2341 (4) | C13—C14 | 1.520 (2) |
| Fe1—S4 | 2.2367 (4) | N5—H20 | 0.9300 |
| Fe1—S1 ⁱ | 2.4787 (4) | C2—H1 | 0.9500 |
| S1—C1 | 1.7611 (14) | C4—H2 | 0.9500 |
| S1—Fe1 ⁱ | 2.4787 (4) | C6—H3 | 0.9500 |
| S2—C3 | 1.7477 (15) | C8—H4 | 0.9500 |
| S3—C5 | 1.7415 (14) | C9—H5 | 0.9900 |
| S4—C7 | 1.7438 (14) | C9—H6 | 0.9900 |
| O1—C16 | 1.436 (2) | C10—H7 | 0.9800 |
| O1—H24 | 0.8400 | C10—H8 | 0.9800 |
| N1—C1 | 1.3297 (19) | C10—H9 | 0.9800 |
| N1—C2 | 1.339 (2) | C11—H10 | 0.9900 |
| N2—C3 | 1.3372 (19) | C11—H11 | 0.9900 |
| N2—C4 | 1.340 (2) | C12—H13 | 0.9800 |
| N3—C5 | 1.3341 (19) | C12—H12 | 0.9800 |
| N3—C6 | 1.3483 (19) | C12—H14 | 0.9800 |
| N4—C7 | 1.3315 (18) | C13—H16 | 0.9900 |
| N4—C8 | 1.3456 (19) | C13—H15 | 0.9900 |
| N5—C13 | 1.506 (2) | C14—H19 | 0.9800 |
| N5—C9 | 1.5079 (18) | C14—H18 | 0.9800 |

| | | | |
|-------------------------|--------------|-------------|--------|
| N5—C11 | 1.5097 (19) | C14—H17 | 0.9800 |
| C1—C3 | 1.411 (2) | C16—H21 | 0.9800 |
| C2—C4 | 1.379 (2) | C16—H22 | 0.9800 |
| C5—C7 | 1.417 (2) | C16—H23 | 0.9800 |
| C6—C8 | 1.378 (2) | | |
| C1...C1 ⁱⁱ | 3.493 (3) | | |
| S1—Fe1—S3 | 164.042 (16) | C4—C2—H1 | 119.0 |
| S1—Fe1—S2 | 90.420 (15) | N2—C4—H2 | 118.6 |
| S3—Fe1—S2 | 88.401 (15) | C2—C4—H2 | 118.6 |
| S1—Fe1—S4 | 85.705 (14) | N3—C6—H3 | 119.1 |
| S3—Fe1—S4 | 89.299 (14) | C8—C6—H3 | 119.1 |
| S2—Fe1—S4 | 157.445 (17) | N4—C8—H4 | 118.9 |
| S1—Fe1—S1 ⁱ | 97.462 (14) | C6—C8—H4 | 118.9 |
| S3—Fe1—S1 ⁱ | 98.369 (15) | N5—C9—H5 | 109.3 |
| S2—Fe1—S1 ⁱ | 101.461 (15) | C10—C9—H5 | 109.3 |
| S4—Fe1—S1 ⁱ | 101.073 (15) | N5—C9—H6 | 109.3 |
| C1—S1—Fe1 | 104.91 (5) | C10—C9—H6 | 109.3 |
| C1—S1—Fe1 ⁱ | 100.94 (5) | H5—C9—H6 | 107.9 |
| Fe1—S1—Fe1 ⁱ | 82.538 (14) | C9—C10—H7 | 109.5 |
| C3—S2—Fe1 | 104.58 (5) | C9—C10—H8 | 109.5 |
| C5—S3—Fe1 | 103.35 (5) | H7—C10—H8 | 109.5 |
| C7—S4—Fe1 | 103.82 (5) | C9—C10—H9 | 109.5 |
| C1—N1—C2 | 115.52 (13) | H7—C10—H9 | 109.5 |
| C3—N2—C4 | 116.15 (13) | H8—C10—H9 | 109.5 |
| C5—N3—C6 | 116.71 (12) | N5—C11—H10 | 108.8 |
| C7—N4—C8 | 116.39 (12) | C12—C11—H10 | 108.8 |
| C13—N5—C9 | 111.84 (11) | N5—C11—H11 | 108.8 |
| C13—N5—C11 | 111.85 (12) | C12—C11—H11 | 108.8 |
| C9—N5—C11 | 112.41 (12) | H10—C11—H11 | 107.7 |
| N1—C1—C3 | 123.08 (13) | C11—C12—H13 | 109.5 |
| N1—C1—S1 | 117.51 (11) | C11—C12—H12 | 109.5 |
| C3—C1—S1 | 119.40 (11) | H13—C12—H12 | 109.5 |
| N1—C2—C4 | 121.97 (14) | C11—C12—H14 | 109.5 |
| N2—C3—C1 | 120.42 (13) | H13—C12—H14 | 109.5 |
| N2—C3—S2 | 119.00 (11) | H12—C12—H14 | 109.5 |
| C1—C3—S2 | 120.58 (11) | N5—C13—H16 | 109.3 |
| N2—C4—C2 | 122.84 (14) | C14—C13—H16 | 109.3 |
| N3—C5—C7 | 121.06 (13) | N5—C13—H15 | 109.3 |
| N3—C5—S3 | 118.93 (11) | C14—C13—H15 | 109.3 |
| C7—C5—S3 | 119.98 (11) | H16—C13—H15 | 108.0 |
| N3—C6—C8 | 121.84 (14) | C13—C14—H19 | 109.5 |
| N4—C7—C5 | 121.71 (13) | C13—C14—H18 | 109.5 |
| N4—C7—S4 | 119.13 (11) | H19—C14—H18 | 109.5 |
| C5—C7—S4 | 119.14 (11) | C13—C14—H17 | 109.5 |
| N4—C8—C6 | 122.20 (13) | H19—C14—H17 | 109.5 |
| N5—C9—C10 | 111.80 (12) | H18—C14—H17 | 109.5 |
| N5—C11—C12 | 113.75 (12) | O1—C16—H21 | 109.5 |

supplementary materials

| | | | |
|----------------------------|--------------|----------------|--------------|
| N5—C13—C14 | 111.52 (13) | O1—C16—H22 | 109.5 |
| C16—O1—H24 | 109.5 | H21—C16—H22 | 109.5 |
| C13—N5—H20 | 106.8 | O1—C16—H23 | 109.5 |
| C9—N5—H20 | 106.8 | H21—C16—H23 | 109.5 |
| C11—N5—H20 | 106.8 | H22—C16—H23 | 109.5 |
| N1—C2—H1 | 119.0 | | |
| C2—N1—C1—C3 | 0.5 (2) | Fe1—S3—C5—N3 | 164.68 (10) |
| C2—N1—C1—S1 | -178.40 (11) | Fe1—S3—C5—C7 | -17.12 (12) |
| Fe1—S1—C1—N1 | 178.17 (10) | C5—N3—C6—C8 | -0.8 (2) |
| Fe1 ⁱ —S1—C1—N1 | 93.07 (11) | C8—N4—C7—C5 | -2.2 (2) |
| Fe1—S1—C1—C3 | -0.74 (12) | C8—N4—C7—S4 | 178.97 (11) |
| Fe1 ⁱ —S1—C1—C3 | -85.84 (11) | N3—C5—C7—N4 | 3.2 (2) |
| C1—N1—C2—C4 | 0.9 (2) | S3—C5—C7—N4 | -174.98 (11) |
| C4—N2—C3—C1 | 0.9 (2) | N3—C5—C7—S4 | -177.96 (11) |
| C4—N2—C3—S2 | -179.75 (11) | S3—C5—C7—S4 | 3.87 (16) |
| N1—C1—C3—N2 | -1.4 (2) | Fe1—S4—C7—N4 | -169.57 (10) |
| S1—C1—C3—N2 | 177.43 (11) | Fe1—S4—C7—C5 | 11.55 (12) |
| N1—C1—C3—S2 | 179.20 (11) | C7—N4—C8—C6 | -0.2 (2) |
| S1—C1—C3—S2 | -1.95 (17) | N3—C6—C8—N4 | 1.8 (2) |
| Fe1—S2—C3—N2 | -175.86 (10) | C13—N5—C9—C10 | -156.73 (13) |
| Fe1—S2—C3—C1 | 3.53 (12) | C11—N5—C9—C10 | 76.48 (16) |
| C3—N2—C4—C2 | 0.5 (2) | C13—N5—C11—C12 | -52.48 (17) |
| N1—C2—C4—N2 | -1.5 (2) | C9—N5—C11—C12 | 74.31 (17) |
| C6—N3—C5—C7 | -1.5 (2) | C9—N5—C13—C14 | 75.40 (15) |
| C6—N3—C5—S3 | 176.64 (11) | C11—N5—C13—C14 | -157.50 (13) |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|-------|-------------|-------------|---------------|
| O1—H24 \cdots N3 ⁱ | 0.84 | 1.99 | 2.8014 (17) | 163 |
| N5—H20 \cdots O1 | 0.93 | 1.86 | 2.7880 (17) | 172 |

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

Fig. 1

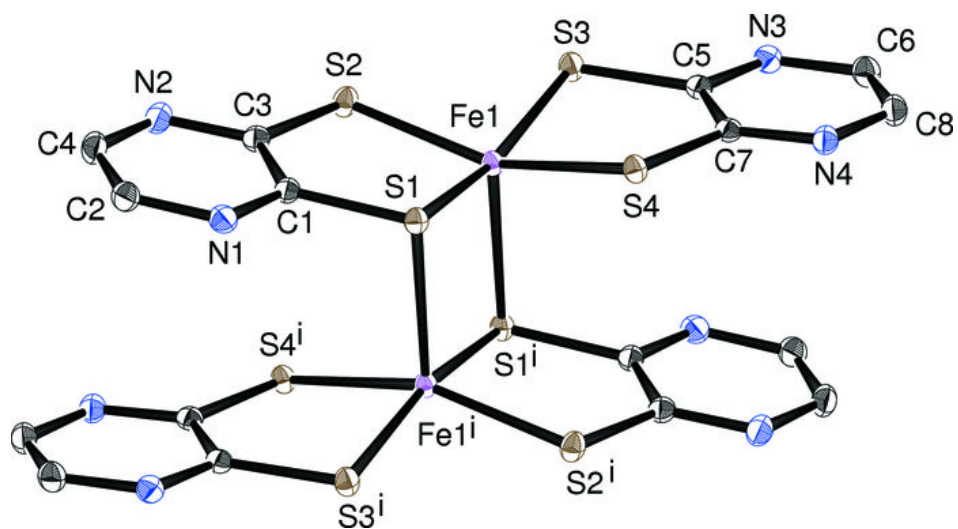


Fig. 2

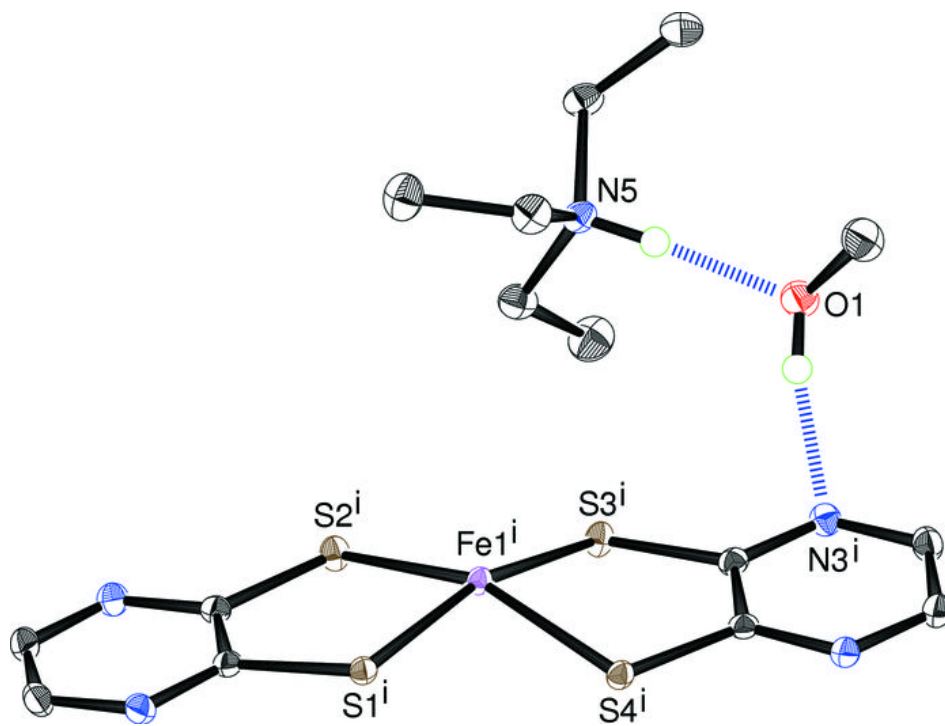


Fig. 3

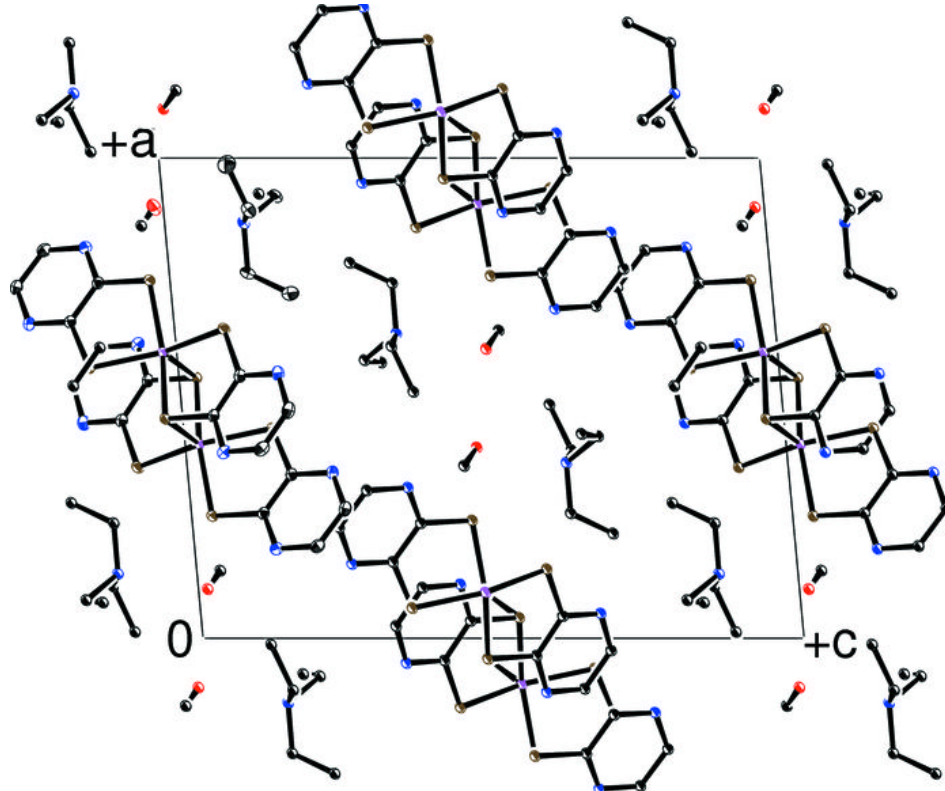


Fig. 4

