

Crystal structure of a water oxidation catalyst solvate with composition $(\text{NH}_4)_2[\text{Fe}^{\text{IV}}(\text{L}-6\text{H})]\cdot 3\text{CH}_3\text{COOH}$ (L = clathrochelate ligand)

Maksym O. Plutenko,^{a*} Sergii I. Shylin,^b Sergiu Shova,^c Aleksander V. Blinder^d and Igor O. Fritsky^{a,d}

Received 31 October 2023
Accepted 7 December 2023

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: clathrochelate; cage complex; high-valent iron; template synthesis; crystal structure.

CCDC reference: 2312686

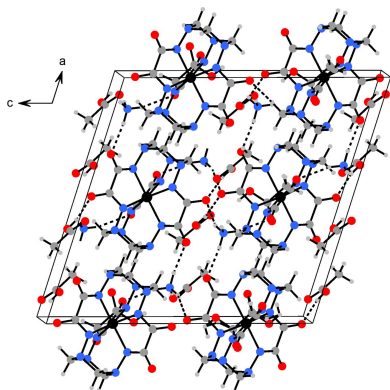
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Chemistry, Taras Shevchenko National University of Kyiv, 01601 Kyiv, Ukraine, ^bDepartment of Chemistry - Ångström Laboratory, Uppsala University, 75335, Uppsala, Sweden, ^c"Petru Poni" Institute of Macromolecular Chemistry, Department of Inorganic, Polymers, 700487 Iasi, Romania, and ^dInnovation Development Center ABN, Pirogov Str. 2/37, 01030 Kyiv, Ukraine. *Correspondence e-mail: plutenkom@gmail.com

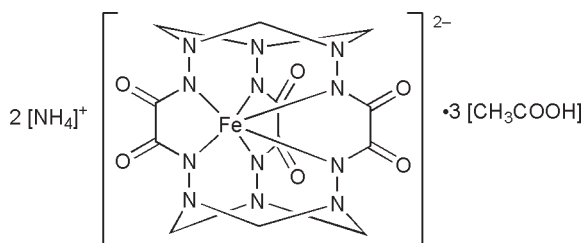
The synthetic availability of molecular water oxidation catalysts containing high-valent ions of $3d$ metals in the active site is a prerequisite to enabling photo- and electrochemical water splitting on a large scale. Herein, the synthesis and crystal structure of diammonium $\{\mu\text{-}1,3,4,7,8,10,12,13,16,17,19,22\text{-dodecaazatetracyclo}[8.8.4.1^{3,17}.1^{8,12}]\text{tetracosane-}5,6,14,15,20,21\text{-hexaonato}\}\text{ferrate(IV) acetic acid trisolvate}$, $(\text{NH}_4)_2[\text{Fe}^{\text{IV}}(\text{C}_{12}\text{H}_{12}\text{N}_{12}\text{O}_6)]\cdot 3\text{CH}_3\text{COOH}$ or $(\text{NH}_4)_2[\text{Fe}^{\text{IV}}(\text{L}-6\text{H})]\cdot 3\text{CH}_3\text{COOH}$ is reported. The Fe^{IV} ion is encapsulated by the macropolycyclic ligand, which can be described as a dodeca-aza-quadricyclic cage with two capping triazacyclohexane fragments making three five- and six six-membered alternating chelate rings with the central Fe^{IV} ion. The local coordination environment of Fe^{IV} is formed by six deprotonated hydrazide nitrogen atoms, which stabilize the unusual oxidation state. The Fe^{IV} ion lies on a twofold rotation axis (multiplicity 4, Wyckoff letter e) of the space group $C2/c$. Its coordination geometry is intermediate between a trigonal prism (distortion angle $\varphi = 0^\circ$) and an antiprism ($\varphi = 60^\circ$) with $\varphi = 31.1^\circ$. The $\text{Fe}-\text{N}$ bond lengths lie in the range 1.9376 (13)–1.9617 (13) Å, as expected for tetravalent iron. Structure analysis revealed that three acetic acid molecules additionally co-crystallize per one iron(IV) complex, and one of them is positionally disordered over four positions. In the crystal structure, the ammonium cations, complex dianions and acetic acid molecules are interconnected by an intricate system of hydrogen bonds, mainly *via* the oxamide oxygen atoms acting as acceptors.

1. Chemical context

The design of robust and efficient water oxidation catalysts based on $3d$ metals requires a rational approach that considers both their redox properties and crystal structure (Blakemore *et al.*, 2015). The intrinsic lability of the $M-L$ bonds (M = central $3d$ metal cation, L = ligand) in aqueous solution is one of the main design challenges (Gil-Sepulcre & Llobet, 2022). In addition, the ligand in the catalyst has to be simple and oxidatively robust, otherwise it will be oxidized in the course of the catalysis (Boniolo *et al.*, 2022). Efficient chemical (Shylin *et al.*, 2019a) and photochemical (Shylin *et al.*, 2019b) water splitting using a clathrochelate complex $\text{Na}_2[\text{Fe}^{\text{IV}}(\text{L}-6\text{H})]$ as a catalyst has recently been reported. The relatively high reaction rate and turnover number have been attributed to the exceptional stability of this cage compound bearing the Fe ion in the unusual oxidation state +IV. Clathrochelate complexes $[\text{Fe}^{\text{IV}}(\text{L}-6\text{H})]^{2-}$ with various cations (hexamethylenetetraminium, Bu_4N^+ , Ph_4As^+ , $[\text{Ca}(\text{H}_2\text{O})_2]^{2+}$, Li^+) have been obtained and characterized structurally and spectroscopically (Tomyn *et al.*, 2017; Plutenko *et al.*, 2023). The



Fe^{IV} ion can be reduced to Fe^{III} or oxidized to Fe^V, either chemically or electrochemically, but at ambient conditions it spontaneously returns to the Fe^{IV} state in air, showcasing the stability of the oxidation state +IV in this specific ligand environment. Related compounds with [Mn^{IV}(L-6H)]²⁻ clathrochelate anions have also been described recently (Shylin *et al.*, 2021).



In this communication, we report on the template synthesis and crystal structure of the co-crystal compound (NH₄)₂[Fe^{IV}(C₁₂H₁₂N₁₂O₆)]·3CH₃COOH or (NH₄)₂[Fe^{IV}(L-6H)]·3CH₃COOH, which was obtained in an attempt to explore alternative crystallization strategies of cage compounds. We thus demonstrate that Fe^{IV} clathrochelates can be obtained in the form of single crystals under mild conditions.

2. Structural commentary

The title compound consists of two ammonium cations, a clathrochelate dianion [Fe^{IV}(L-6H)]²⁻, and three co-crystallized acetic acid molecules per one formula unit (Fig. 1). The core of the macrocyclic ligand *L* is the hexahydrazide N-donor cage capped by two 1,3,5-triazacyclohexane fragments, thus featuring three five- and six six-membered chelate rings. All six hydrazide groups are deprotonated, and the formal charge of the ligand (L-6H) is 6-. The cage encapsulates the Fe ion in the oxidation state +IV, stabilized by the strong σ -donor capacity of the ligand (L-6H), as well as its ability to shield the ion from external factors. The shape of the coordination polyhedron [Fe^{IV}N₆] cannot be described as octahedral, which is typical for most ferrous and ferric complexes. It is rather intermediate between an ideal trigonal prism ($\varphi = 0^\circ$) and an antiprism ($\varphi = 60^\circ$) with an average $\varphi = 31.1^\circ$, calculated as a mean rotation of the N1-N3-N5 triangular base relative to N1ⁱ-N3ⁱ-N5ⁱ. It is within the range of 28.0–32.3° reported for other Fe^{IV} and Mn^{IV} clathrochelates (Tomyn *et al.*, 2017; Shylin *et al.*, 2021).

The Fe^{IV} ion lies on a special position of space group *C2/c* (twofold rotation axis, multiplicity 4, Wyckoff letter *e*), making half of the trigonal prism crystallographically independent. As such, the title compound is the first hexahydrazide complex with point group symmetry *C*₂ for the complex anion, while all previous clathrochelates have symmetry *C*₁ (Tomyn *et al.*, 2017; Shylin *et al.*, 2021; Plutenko *et al.*, 2023). The Fe–N bond lengths in (NH₄)₂[Fe^{IV}(L-6H)]·3CH₃COOH are between 1.9376 (13) and 1.9617 (13) Å, which are close to those reported for related compounds bearing the [Fe^{IV}(L-6H)]²⁻ complex anion [1.915 (5)–1.969 (3) Å; Tomyn *et al.*,

Table 1

Selected geometric parameters (Å, °) for the coordination polyhedron [Fe^{IV}N₆].

Fe1–N1	1.9610 (13)	Fe1–N5	1.9376 (13)
Fe1–N3	1.9617 (13)		
N1–Fe1–N3	86.36 (5)	N1–Fe1–N3 ⁱ	80.01 (5)
N1–Fe1–N5	87.15 (5)	N5–Fe1–N5 ⁱ	80.18 (7)
N5–Fe1–N3	87.56 (5)		

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

2017]. The apical bite angles N–Fe–N fall in the range 86.36 (5)–87.56 (5)°, and equatorial bite angles are 80.01 (5)–80.18 (7)° (Table 1). The height of the trigonal prism (*i.e.* the distance between the triangular bases) is 2.374 (3) Å, which is in the range 2.36–2.38 Å reported for other clathrochelates (Tomyn *et al.*, 2017; Shylin *et al.*, 2021).

The macropolycyclic ligand in (NH₄)₂[Fe^{IV}(L-6H)]·3CH₃COOH exhibits noticeable distortions, especially with respect to the oxamide moieties. While the hydrazide

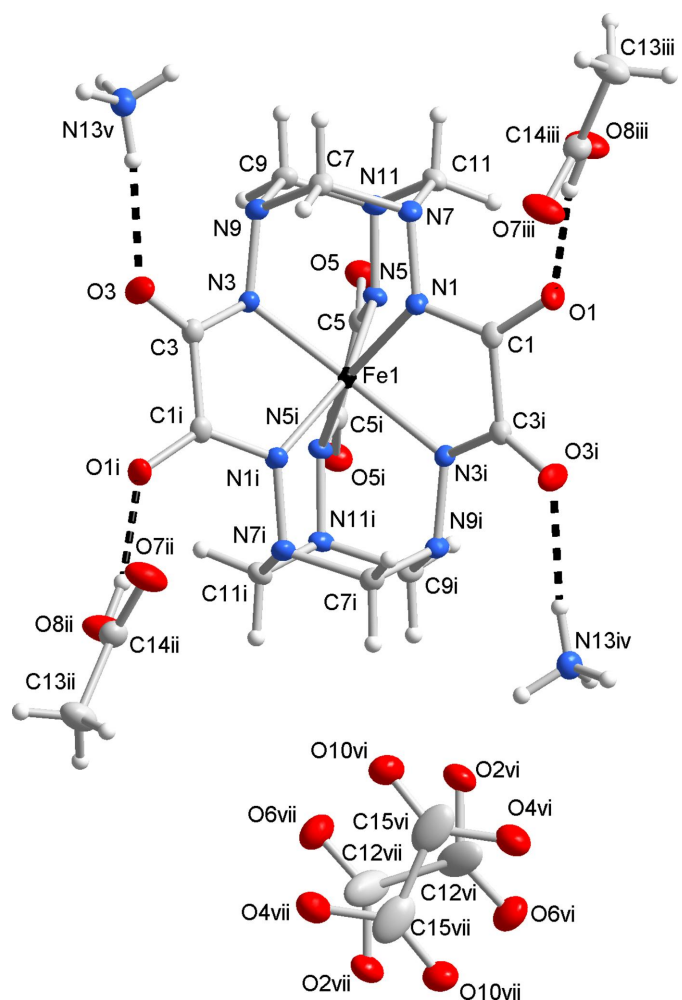


Figure 1

The molecular moieties in the crystal structure of (NH₄)₂[Fe^{IV}(L-6H)]·3CH₃COOH with ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines; H atoms of the disordered CH₃COOH molecule are omitted for clarity. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $1 - x, 1 - y, 2 - z$; (iii) $x, 1 - y, -\frac{1}{2} + z$; (iv) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

groups O1–C1–N1–N7 and O3–C3–N3–N9 remain virtually planar, the oxamide moieties are significantly bent with noticeably large torsion angles around the C–C bonds. The O1–C1–C3ⁱ–O3ⁱ and O5–C5–C5ⁱ–O5ⁱ torsion angles are 20.15 (15) and 12.33 (16)°, respectively, with the larger torsion angle associated with O1 and O3 atoms involved in intermolecular hydrogen bonding (see below). The five-membered chelate rings in the complex exhibit a non-symmetric twist conformation with N1–C1–C3ⁱ–N3ⁱ and N5–C5–C5ⁱ–N5ⁱ torsion angles of 20.11 (13) and 13.52 (15)°, respectively. The six-membered chelate rings have chair conformations with the Fe and C atoms deviating from the N₄ mean plane, with corresponding dihedral angles in the range 35.45 (6)–36.38 (5)° and 59.50 (11)–60.62 (15)°, respectively.

One of three acetic acid molecules is disordered, leading to four equivalent positions (Fig. 1). Specifically, the two C atoms of CH₃COOH are disordered along the C–C bond – each can serve as either a methyl or a carboxyl C atom. They are additionally disordered between two positions each by means of the twofold symmetry axis. As such, occupancy factors of C and O atoms are 0.5 and 0.25, respectively.

3. Supramolecular features

In the crystal structure of the title compound, the ammonium cations; complex anions and acetic acid molecules are associated *via* an intricate set of O–H···O, N–H···O, N–H···N, and non-classical C–H···O hydrogen bonds (Table 2). Most of these contacts show angles far from linearity, indicating that

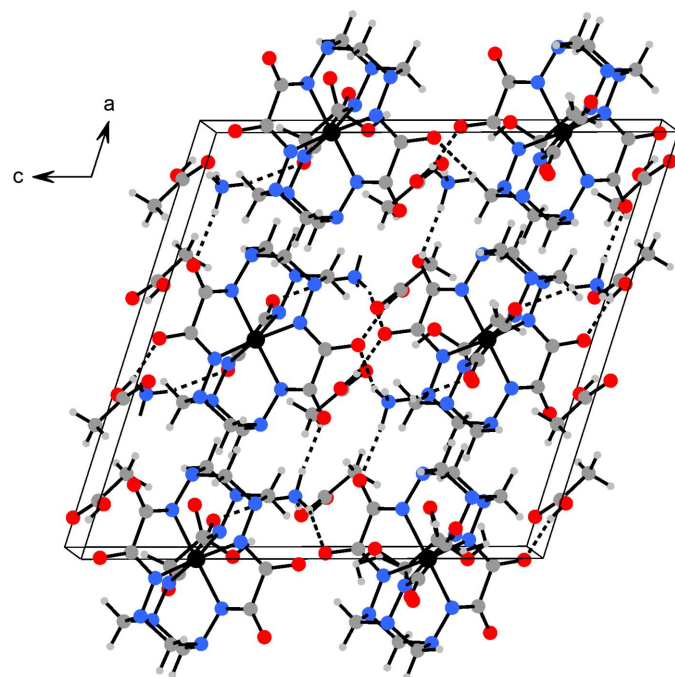


Figure 2
The crystal packing in (NH₄)₂[Fe^{IV}(L-6H)]·3CH₃COOH. Relevant hydrogen bonds are shown as dashed lines. The disordered CH₃COOH molecule is shown with only one possible orientation. Color code: Fe, black; N, blue; O, red; C, dark gray; H, light gray; the unit-cell is outlined.

Table 2
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>
O2–H2···O7 ⁱⁱ	0.84	1.94	2.763 (6)	165
O2–H12B···N1	1.00	2.66	3.338 (6)	125
O2–H12A···O5 ⁱⁱⁱ	1.17	2.58	3.356 (6)	122
O4–H4···O7 ⁱⁱ	0.84	1.96	2.792 (7)	169
O8–H8···O1 ^{iv}	0.81 (3)	1.80 (3)	2.6007 (17)	168 (3)
O10–H15C···O5 ⁱⁱⁱ	1.15	2.39	3.425 (6)	148
N13–H13D···O7 ^v	0.94 (2)	1.99 (2)	2.913 (2)	166.4 (18)
N13–H13E···O3 ^{vi}	0.91 (2)	2.00 (2)	2.9073 (19)	173.2 (19)
N13–H13E···N9 ^{vi}	0.91 (2)	2.64 (2)	3.146 (2)	116.5 (16)
N13–H13F···O5	0.88 (2)	2.12 (2)	2.9606 (19)	160.7 (19)
N13–H13F···N11	0.88 (2)	2.63 (2)	3.252 (2)	128.3 (17)
N13–H13G···O1 ^{vii}	0.87 (2)	2.09 (2)	2.9241 (19)	158.8 (19)
N13–H13G···O3 ⁱⁱⁱ	0.87 (2)	2.48 (2)	3.0698 (19)	125.0 (17)
C7–H3A···O5 ^{viii}	0.99	2.47	3.4109 (19)	159
C7–H3B···O10	0.99	2.43	3.366 (6)	158
C9–H4A···O2 ^{vi}	0.99	2.35	3.312 (7)	165
C9–H4A···O10 ^{vi}	0.99	2.17	3.132 (5)	165
C11–H6B···O1 ^{vii}	0.99	2.31	3.2606 (19)	160
C12–H12B···N1	0.98	2.66	3.575 (7)	155
C12–H12A···O5 ⁱⁱⁱ	0.98	2.58	3.448 (7)	147
C13–H13B···O5	0.90 (3)	2.67 (3)	3.480 (2)	151 (2)
C13–H13C···O8 ^{ix}	0.91 (3)	2.63 (3)	3.416 (3)	146 (2)
C15–H15C···O5 ⁱⁱⁱ	0.98	2.39	3.245 (6)	146

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

they correspond to rather weak interactions. However, a few of them can be considered as significant intermolecular contacts and are discussed in more detail. Each clathrochelate anion appears to be associated with two CH₃COOH co-crystallized molecules and four NH₄⁺ cations, thus employing all six oxamide O atoms as acceptors for hydrogen bonding. The oxamide ribs of the clathrochelate exhibit different binding modes. Specifically, the (O1,O3) ribs are bound to CH₃COOH and NH₄⁺ through the O8–H8···O1ⁱ and N13–H13E···O3ⁱⁱⁱ contacts, while the (O5,O5′) ribs are bound to two NH₄⁺ ions through the crystallographically equivalent N13–H13F···O5 contacts (Fig. 2). The latter contacts are somewhat weaker than the former (note their *D*···*A* distances and angles, Table 2), which creates higher distortion of the oxamide moieties O1–C1–C3ⁱ–O3ⁱ in favor of virtually linear hydrogen bonds. The non-protonated O atom of CH₃COOH serves as an acceptor for another NH₄⁺ proton, making N13–H13D···O7ⁱⁱ contacts. The fourth remaining proton of NH₄⁺ is involved in binding the neighboring clathrochelate anion through the N13–H13G···O1^{iv} contact.

All in all, the NH₄⁺ cations, isolated complex anions and co-crystallized CH₃COOH are connected into a tri-periodic supramolecular framework by means of hydrogen bonds, mainly *via* oxamide O atoms as proton acceptors, and NH₄⁺ and CH₃COOH as donor groups.

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.43, update of November 2022; Groom *et al.*, 2016) for complexes with the central metal cation coordinated by six hydrazide ligands revealed nine structures, six of them containing the clathrochelate complex [Fe^{IV}(L-6H)]²⁻. Two

of these structures represent mononuclear complexes with Bu_4N^+ and Ph_4As^+ cations (Tomyn *et al.*, 2017), and four are coordination polymers in which Ca^{2+} (Tomyn *et al.*, 2017), Mn^{2+} (Xu *et al.*, 2020a), or Cu^{2+} (2 structures; Xu *et al.*, 2020b) cations are exo-coordinated to the vacant (O, O') and/or (O, N) chelating units of the hexahydrazide ligand. To the best of our knowledge, there has been only one structure of the Fe^{IV} hexahydrazide complex reported after November 2022 (Plutenko *et al.*, 2023).

5. Synthesis and crystallization

A powder of $(\text{Bu}_4\text{N})_2[\text{Fe}^{\text{IV}}(\text{L}-6\text{H})]$ was obtained by a metal template synthesis as described previously (Tomyn *et al.*, 2017). Then, 0.5 mmol of $(\text{Bu}_4\text{N})_2[\text{Fe}^{\text{IV}}(\text{L}-6\text{H})]$ and 1 mmol of $\text{CH}_3\text{COONH}_4$ were dissolved in 10 ml of water, and 10 ml of glacial acetic acid was added to this mixture. The resulting mixture was evaporated under vacuum on a rotary evaporator to a volume of *ca* 10 ml and left in a closed flask. After two weeks, dark-green crystals of $(\text{NH}_4)_2[\text{Fe}^{\text{IV}}(\text{L}-6\text{H})]\cdot 3\text{CH}_3\text{COOH}$ suitable for the X-ray diffraction analysis were obtained. FTIR (in KBr pellet, cm^{-1}): 3424 (O–H), 3184 (N–H), 2953 (C–H), 1636 (C=O, amide I).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms attached to C were placed in fixed idealized positions using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene and 1.5 for methyl groups. The non-disordered H atoms attached to N and O were located in difference-Fourier maps and their positional parameters were verified according to the hydrogen-bonding geometry. Occupancy factors of C and O atoms of the disordered CH_3COOH molecule were fixed to 0.5 and 0.25, respectively. The H atoms attached to disordered O atoms were placed in fixed positions with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, and their coordinates were refined according to the riding model described above.

Funding information

This work was supported by the Ministry of Education and Science of Ukraine through grant No. 22BF03–03, the European Union’s Horizon 2020 Research and Innovation Programme under the Marie Skłodowska-Curie grant agreement No. 778245, and the Swedish Foundation for Strategic Research.

References

Blakemore, J. D., Crabtree, R. H. & Brudvig, G. W. (2015). *Chem. Rev.* **115**, 12974–13005.
 Boniolo, M., Hossain, M. K., Chernev, P., Suremann, N. F., Heizmann, P. A., Lyvik, A. S. L., Beyler, P., Haumann, M., Huang, P., Salhi, N., Cheah, M. H., Shylin, S. I., Lundberg, M., Thapper, A. & Messinger, J. (2022). *Inorg. Chem.* **61**, 9104–9118.
 Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* **A51**, 887–897.

Table 3
Experimental details.

Crystal data	
Chemical formula	$(\text{NH}_4)_2[\text{Fe}(\text{C}_{12}\text{H}_{12}\text{N}_{12}\text{O}_6)]\cdot 3\text{C}_2\text{H}_4\text{O}_2$
M_r	692.42
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	120
a, b, c (Å)	15.5352 (2), 11.5178 (1), 16.0472 (2)
β (°)	107.616 (2)
V (Å ³)	2736.70 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.64
Crystal size (mm)	0.45 × 0.20 × 0.13
Data collection	
Diffraction	Rigaku SuperNova, Single source at offset, Eos
Absorption correction	Analytical [<i>CrysAlis PRO</i> (Rigaku OD, 2015) based on analytical numerical absorption correction using a multifaceted crystal model (Clark & Reid, 1995)]
$T_{\text{min}}, T_{\text{max}}$	0.888, 0.954
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19869, 2431, 2345
R_{int}	0.025
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.064, 1.07
No. of reflections	2431
No. of parameters	265
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.31, -0.30

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *CrystaMaker* (*CrystalMaker*, 2017), and *pubCIF* (Westrip, 2010).

CrystalMaker (2017). *CrystalMaker*. CrystalMaker Software, Bicester, England.
 Gil-Sepulcre, M. & Llobet, A. (2022). *Nat. Catal.* **5**, 79–82.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Plutenko, M. O., Shova, S., Pavlenko, V. A., Golenya, I. A. & Fritsky, I. O. (2023). *Acta Cryst.* **E79**, 1059–1062.
 Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
 Shylin, S. I., Pavliuk, M. V., D’Amario, L., Fritsky, I. O. & Berggren, G. (2019a). *Faraday Discuss.* **215**, 162–174.
 Shylin, S. I., Pavliuk, M. V., D’Amario, L., Mamedov, F., Sá, J., Berggren, G. & Fritsky, I. O. (2019b). *Chem. Commun.* **55**, 3335–3338.
 Shylin, S. I., Pogrebetsky, J. L., Husak, A. O., Bykov, D., Mokhir, A., Hampel, F., Shova, S., Ozarowski, A., Gumienna-Kontecka, E. & Fritsky, I. O. (2021). *Chem. Commun.* **57**, 11060–11063.
 Tomyn, S., Shylin, S. I., Bykov, D., Ksenofontov, V., Gumienna-Kontecka, E., Bon, V. & Fritsky, I. O. (2017). *Nat. Commun.* **8**, 14099.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
 Xu, Y., Hu, Z.-B., Wu, L.-N., Li, M.-X., Wang, Z.-X. & Song, Y. (2020a). *Polyhedron*, **175**, 114243.
 Xu, Y., Wu, L.-N., Li, M.-X., Shi, F.-N. & Wang, Z.-X. (2020b). *Inorg. Chem. Commun.* **117**, 107950.

supporting information

Acta Cryst. (2024). E80, 25-28 [https://doi.org/10.1107/S2056989023010514]

Crystal structure of a water oxidation catalyst solvate with composition $(\text{NH}_4)_2[\text{Fe}^{\text{IV}}(\text{L-6H})]\cdot 3\text{CH}_3\text{COOH}$ (L = clathrochelate ligand)

Maksym O. Plutenko, Sergii I. Shylin, Sergiu Shova, Aleksander V. Blinder and Igor O. Fritsky

Computing details

Diammonium $\{\mu\text{-}1,3,4,7,8,10,12,13,16,17,19,22\text{-dodecaazatetracyclo}[8.8.4.1^{3,17}.1^{8,12}]$ tetracosane-5,6,14,15,20,21-hexaonato}ferrate(IV) acetic acid trisolvate

Crystal data

$(\text{NH}_4)_2[\text{Fe}(\text{C}_{12}\text{H}_{12}\text{N}_{12}\text{O}_6)]\cdot 3\text{C}_2\text{H}_4\text{O}_2$
 $M_r = 692.42$
 Monoclinic, $C2/c$
 $a = 15.5352$ (2) Å
 $b = 11.5178$ (1) Å
 $c = 16.0472$ (2) Å
 $\beta = 107.616$ (2)°
 $V = 2736.70$ (6) Å³
 $Z = 4$

$F(000) = 1440$
 $D_x = 1.681$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 18947 reflections
 $\theta = 3.8\text{--}34.6^\circ$
 $\mu = 0.64$ mm⁻¹
 $T = 120$ K
 Block, black
 $0.45 \times 0.20 \times 0.13$ mm

Data collection

Rigaku SuperNova, Single source at offset, Eos diffractometer
 Radiation source: micro-source
 Detector resolution: 16.0107 pixels mm⁻¹
 φ scans and ω scans with κ offset
 Absorption correction: analytical [CrysAlisPro (Rigaku OD, 2015) based on analytical numerical absorption correction using a multifaceted crystal model (Clark & Reid, 1995)]

$T_{\text{min}} = 0.888$, $T_{\text{max}} = 0.954$
 19869 measured reflections
 2431 independent reflections
 2345 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.2^\circ$
 $h = -18 \rightarrow 18$
 $k = -13 \rightarrow 13$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.064$
 $S = 1.07$
 2431 reflections
 265 parameters
 0 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 4.4687P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Fe1	0.500000	0.51456 (3)	0.750000	0.01084 (10)	
O1	0.49183 (7)	0.33179 (10)	0.53250 (7)	0.0185 (3)	
O3	0.67899 (8)	0.34064 (11)	0.94355 (8)	0.0230 (3)	
O5	0.58025 (8)	0.84207 (10)	0.72496 (8)	0.0219 (3)	
O7	0.58585 (9)	0.91495 (11)	1.02775 (9)	0.0309 (3)	
O8	0.62188 (9)	0.74720 (11)	0.97758 (10)	0.0306 (3)	
H8	0.5866 (19)	0.722 (2)	1.0013 (18)	0.054 (8)*	
N1	0.54198 (8)	0.41708 (11)	0.66990 (8)	0.0140 (3)	
N3	0.61583 (9)	0.47931 (11)	0.83762 (8)	0.0130 (3)	
N5	0.55986 (8)	0.64326 (11)	0.71280 (8)	0.0137 (3)	
N7	0.63190 (9)	0.42275 (12)	0.66460 (8)	0.0156 (3)	
N9	0.69873 (9)	0.48505 (11)	0.81754 (8)	0.0148 (3)	
N11	0.64693 (9)	0.63143 (12)	0.70168 (9)	0.0155 (3)	
N13	0.63652 (10)	0.84256 (13)	0.56441 (10)	0.0185 (3)	
H13D	0.6113 (14)	0.916 (2)	0.5469 (13)	0.028*	
H13E	0.6955 (16)	0.8442 (18)	0.5665 (13)	0.028*	
H13F	0.6296 (14)	0.8293 (18)	0.6159 (15)	0.028*	
H13G	0.6080 (14)	0.789 (2)	0.5275 (14)	0.028*	
C1	0.48051 (10)	0.37867 (13)	0.59867 (10)	0.0143 (3)	
C3	0.61482 (10)	0.39725 (13)	0.89673 (10)	0.0149 (3)	
C5	0.54073 (10)	0.75177 (14)	0.73270 (10)	0.0146 (3)	
C7	0.69757 (10)	0.39761 (14)	0.74949 (10)	0.0162 (3)	
H3A	0.758539	0.393247	0.742223	0.019*	
H3B	0.683704	0.320624	0.769698	0.019*	
C9	0.71270 (10)	0.60121 (14)	0.78697 (10)	0.0166 (3)	
H4A	0.774496	0.605943	0.781768	0.020*	
H4B	0.708119	0.658987	0.831114	0.020*	
C11	0.64715 (11)	0.54171 (14)	0.63704 (10)	0.0173 (3)	
H6A	0.705955	0.543798	0.624954	0.021*	
H6B	0.599543	0.560094	0.581832	0.021*	
C13	0.68764 (14)	0.91648 (18)	0.94181 (14)	0.0283 (4)	
H13A	0.7117 (17)	0.984 (2)	0.9689 (16)	0.042*	
H13B	0.6571 (16)	0.926 (2)	0.8850 (17)	0.042*	
H13C	0.7317 (17)	0.867 (2)	0.9373 (15)	0.042*	
C14	0.62703 (11)	0.86083 (15)	0.98682 (11)	0.0211 (4)	
O2	0.5695 (5)	0.1300 (5)	0.6914 (4)	0.0264 (14)	0.25
H2	0.564306	0.114115	0.639008	0.040*	0.25
O4	0.4878 (4)	0.1137 (5)	0.6462 (5)	0.0307 (15)	0.25
H4	0.523622	0.105568	0.616529	0.046*	0.25

O6	0.4189 (3)	0.1429 (5)	0.6588 (4)	0.0316 (12)	0.25
O10	0.6091 (4)	0.1341 (5)	0.7634 (4)	0.0303 (12)	0.25
C12	0.4935 (6)	0.1199 (6)	0.7018 (6)	0.039 (2)	0.5
H12A	0.520573	0.050427	0.684862	0.058*	0.25
H12B	0.520573	0.189367	0.684862	0.058*	0.25
H12C	0.428294	0.119897	0.672332	0.058*	0.25
C15	0.5341 (6)	0.1169 (5)	0.7245 (7)	0.041 (2)	0.5
H15C	0.571635	0.047433	0.741920	0.061*	0.25
H15B	0.571635	0.186372	0.741920	0.061*	0.25
H15A	0.506375	0.116903	0.660900	0.061*	0.25

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.01181 (17)	0.01133 (17)	0.00910 (16)	0.000	0.00276 (12)	0.000
O1	0.0187 (6)	0.0216 (6)	0.0146 (6)	0.0041 (5)	0.0039 (4)	-0.0050 (5)
O3	0.0175 (6)	0.0266 (6)	0.0234 (6)	0.0029 (5)	0.0039 (5)	0.0125 (5)
O5	0.0253 (6)	0.0152 (6)	0.0282 (6)	-0.0036 (5)	0.0126 (5)	0.0001 (5)
O7	0.0368 (8)	0.0237 (7)	0.0423 (8)	-0.0063 (6)	0.0269 (7)	-0.0046 (6)
O8	0.0316 (7)	0.0218 (7)	0.0475 (8)	-0.0062 (6)	0.0254 (7)	-0.0035 (6)
N1	0.0126 (6)	0.0156 (7)	0.0138 (6)	0.0024 (5)	0.0038 (5)	-0.0008 (5)
N3	0.0114 (6)	0.0151 (6)	0.0120 (6)	-0.0015 (5)	0.0027 (5)	0.0009 (5)
N5	0.0130 (6)	0.0151 (7)	0.0149 (6)	0.0011 (5)	0.0067 (5)	0.0023 (5)
N7	0.0122 (6)	0.0197 (7)	0.0156 (7)	0.0035 (5)	0.0050 (5)	0.0006 (5)
N9	0.0117 (6)	0.0172 (7)	0.0153 (7)	-0.0006 (5)	0.0039 (5)	0.0019 (5)
N11	0.0132 (6)	0.0181 (7)	0.0170 (7)	0.0015 (5)	0.0074 (5)	0.0035 (5)
N13	0.0203 (8)	0.0174 (8)	0.0173 (7)	-0.0037 (6)	0.0048 (6)	-0.0026 (6)
C1	0.0174 (8)	0.0120 (7)	0.0128 (7)	0.0034 (6)	0.0033 (6)	0.0011 (6)
C3	0.0163 (8)	0.0149 (8)	0.0126 (7)	-0.0018 (6)	0.0033 (6)	-0.0007 (6)
C5	0.0160 (8)	0.0151 (8)	0.0115 (7)	-0.0003 (6)	0.0024 (6)	0.0012 (6)
C7	0.0143 (8)	0.0182 (8)	0.0159 (8)	0.0039 (6)	0.0041 (6)	0.0019 (6)
C9	0.0138 (7)	0.0178 (8)	0.0182 (8)	-0.0020 (6)	0.0049 (6)	0.0029 (6)
C11	0.0166 (8)	0.0221 (8)	0.0150 (8)	0.0036 (6)	0.0075 (6)	0.0031 (6)
C13	0.0318 (10)	0.0263 (10)	0.0330 (11)	-0.0074 (8)	0.0193 (9)	-0.0042 (8)
C14	0.0186 (8)	0.0230 (9)	0.0217 (9)	-0.0042 (7)	0.0058 (7)	-0.0019 (7)
O2	0.027 (4)	0.030 (3)	0.026 (4)	0.001 (2)	0.015 (3)	0.004 (2)
O4	0.031 (4)	0.035 (3)	0.030 (4)	0.005 (2)	0.015 (3)	0.004 (3)
O6	0.024 (3)	0.034 (3)	0.033 (3)	0.002 (2)	0.001 (3)	0.006 (2)
O10	0.024 (3)	0.035 (3)	0.033 (3)	-0.005 (2)	0.010 (3)	-0.003 (2)
C12	0.029 (4)	0.029 (3)	0.056 (7)	0.001 (3)	0.009 (4)	0.026 (3)
C15	0.041 (5)	0.015 (2)	0.053 (6)	-0.001 (3)	-0.005 (5)	0.007 (2)

Geometric parameters (Å, °)

Fe1—N1	1.9610 (13)	C7—H3B	0.9900
Fe1—N1 ⁱ	1.9610 (13)	C9—H4A	0.9900
Fe1—N3 ⁱ	1.9617 (13)	C9—H4B	0.9900
Fe1—N3	1.9617 (13)	C11—H6A	0.9900

Fe1—N5	1.9376 (13)	C11—H6B	0.9900
Fe1—N5 ⁱ	1.9376 (13)	C13—C14	1.493 (2)
O1—C1	1.2502 (19)	C13—H13A	0.92 (3)
O3—C3	1.2370 (19)	C13—H13B	0.90 (3)
O5—C5	1.2330 (19)	C13—H13C	0.91 (3)
O7—C14	1.218 (2)	O2—C12	1.246 (11)
O8—C14	1.317 (2)	O2—H2	0.8400
O8—H8	0.81 (3)	O2—H12A	1.1750
N1—C1	1.324 (2)	O2—H12B	1.0032
N1—N7	1.4266 (18)	O4—C15	1.244 (12)
N3—C3	1.342 (2)	O4—H4	0.8399
N3—N9	1.4205 (18)	O4—H15A	0.3140
N5—C5	1.345 (2)	O6—C12	1.186 (10)
N5—N11	1.4236 (17)	O6—H12C	0.3459
N7—C7	1.463 (2)	O10—C15	1.161 (10)
N7—C11	1.481 (2)	O10—H15C	1.1550
N9—C9	1.464 (2)	O10—H15B	0.8358
N9—C7	1.482 (2)	C12—C12 ⁱ	1.50 (2)
N11—C11	1.465 (2)	C12—H12A	0.9800
N11—C9	1.481 (2)	C12—H12B	0.9800
N13—H13D	0.94 (2)	C12—H12C	0.9802
N13—H13E	0.91 (2)	C15—H15A	0.9798
N13—H13F	0.88 (2)	C15—C15 ⁱ	1.52 (2)
N13—H13G	0.87 (2)	C15—H15C	0.9800
C1—C3 ⁱ	1.520 (2)	C15—H15B	0.9800
C5—C5 ⁱ	1.528 (3)	C15—H15A	0.9798
C7—H3A	0.9900		
N5 ⁱ —Fe1—N1	157.78 (5)	N7—C11—H6A	108.8
N5—Fe1—N1 ⁱ	157.78 (5)	N11—C11—H6B	108.8
N5 ⁱ —Fe1—N1 ⁱ	87.15 (5)	N7—C11—H6B	108.8
N1—Fe1—N1 ⁱ	110.14 (8)	H6A—C11—H6B	107.7
N5—Fe1—N3 ⁱ	111.05 (5)	C14—C13—H13A	111.3 (15)
N5 ⁱ —Fe1—N3 ⁱ	87.56 (5)	C14—C13—H13B	109.2 (15)
N1 ⁱ —Fe1—N3 ⁱ	86.36 (5)	H13A—C13—H13B	113 (2)
N1—Fe1—N3	86.36 (5)	C14—C13—H13C	111.9 (15)
N1 ⁱ —Fe1—N3	80.01 (5)	H13A—C13—H13C	111 (2)
N1—Fe1—N5	87.15 (5)	H13B—C13—H13C	100 (2)
N5—Fe1—N3	87.56 (5)	O7—C14—O8	123.05 (16)
N1—Fe1—N3 ⁱ	80.01 (5)	O7—C14—C13	123.51 (17)
N5 ⁱ —Fe1—N3	111.05 (5)	O8—C14—C13	113.44 (15)
N5—Fe1—N5 ⁱ	80.18 (7)	C12—O2—H2	107.9
N3 ⁱ —Fe1—N3	156.12 (8)	C12—O2—H12A	47.6
C14—O8—H8	109 (2)	H2—O2—H12A	82.9
C1—N1—N7	115.28 (12)	C12—O2—H12B	50.2
C1—N1—Fe1	117.46 (10)	H2—O2—H12B	101.8
N7—N1—Fe1	122.60 (10)	H12A—O2—H12B	94.2
C3—N3—N9	113.47 (12)	C15—O4—H4	107.3

C3—N3—Fe1	116.60 (10)	C15—O4—H15A	28.6
N9—N3—Fe1	121.71 (9)	H4—O4—H15A	79.9
C5—N5—N11	113.90 (12)	C12—O6—H12C	46.5
C5—N5—Fe1	118.46 (10)	C15—O10—H15C	50.1
N11—N5—Fe1	121.89 (9)	C15—O10—H15B	56.0
N1—N7—C7	110.79 (12)	H15C—O10—H15B	105.9
N1—N7—C11	107.95 (11)	O6—C12—O2	134.3 (9)
C7—N7—C11	109.38 (12)	O6—C12—C12 ⁱ	113.8 (10)
N3—N9—C9	110.80 (12)	O2—C12—C12 ⁱ	107.6 (9)
N3—N9—C7	109.02 (12)	O6—C12—H12A	116.5
C9—N9—C7	110.14 (12)	O2—C12—H12A	62.4
N5—N11—C11	111.24 (12)	C12 ⁱ —C12—H12A	110.6
N5—N11—C9	108.82 (11)	O6—C12—H12B	94.6
C11—N11—C9	109.88 (12)	O2—C12—H12B	51.9
H13D—N13—H13E	108.6 (18)	C12 ⁱ —C12—H12B	110.6
H13D—N13—H13F	106.2 (18)	H12A—C12—H12B	109.5
H13E—N13—H13F	112.3 (18)	O6—C12—H12C	14.8
H13D—N13—H13G	110.3 (18)	O2—C12—H12C	144.8
H13E—N13—H13G	109.8 (19)	C12 ⁱ —C12—H12C	107.2
H13F—N13—H13G	109.6 (19)	H12A—C12—H12C	109.5
O1—C1—N1	128.86 (14)	H12B—C12—H12C	109.5
O1—C1—C3 ⁱ	119.45 (13)	H15A—C15—O10	127.8
N1—C1—C3 ⁱ	111.69 (13)	H15A—C15—O4	8.8
O3—C3—N3	128.37 (14)	O10—C15—O4	136.6 (10)
O3—C3—C1 ⁱ	120.94 (14)	H15A—C15—C15 ⁱ	113.7
N3—C3—C1 ⁱ	110.69 (13)	O10—C15—C15 ⁱ	117.4 (11)
O5—C5—N5	127.40 (14)	O4—C15—C15 ⁱ	105.1 (10)
O5—C5—C5 ⁱ	121.93 (9)	H15A—C15—H15C	109.5
N5—C5—C5 ⁱ	110.67 (8)	O10—C15—H15C	64.6
N7—C7—N9	113.67 (12)	O4—C15—H15C	112.1
N7—C7—H3A	108.8	C15 ⁱ —C15—H15C	107.3
N9—C7—H3A	108.8	H15A—C15—H15B	109.5
N7—C7—H3B	108.8	O10—C15—H15B	45.0
N9—C7—H3B	108.8	O4—C15—H15B	115.1
H3A—C7—H3B	107.7	C15 ⁱ —C15—H15B	107.3
N9—C9—N11	113.19 (13)	H15C—C15—H15B	109.5
N9—C9—H4A	108.9	H15A—C15—H15A	0.0
N11—C9—H4A	108.9	O10—C15—H15A	127.8
N9—C9—H4B	108.9	O4—C15—H15A	8.8
N11—C9—H4B	108.9	C15 ⁱ —C15—H15A	113.7
H4A—C9—H4B	107.8	H15C—C15—H15A	109.5
N11—C11—N7	113.98 (12)	H15B—C15—H15A	109.5
N11—C11—H6A	108.8		
C1—N1—N7—C7	-146.37 (14)	N9—N3—C3—C1 ⁱ	-168.31 (12)
Fe1—N1—N7—C7	58.47 (15)	Fe1—N3—C3—C1 ⁱ	-19.18 (16)
C1—N1—N7—C11	93.89 (15)	N11—N5—C5—O5	15.8 (2)
Fe1—N1—N7—C11	-61.27 (14)	Fe1—N5—C5—O5	169.60 (13)

C3—N3—N9—C9	-154.44 (13)	N11—N5—C5—C5 ⁱ	-164.79 (14)
Fe1—N3—N9—C9	58.19 (15)	Fe1—N5—C5—C5 ⁱ	-11.0 (2)
C3—N3—N9—C7	84.19 (15)	N1—N7—C7—N9	-65.02 (16)
Fe1—N3—N9—C7	-63.18 (14)	C11—N7—C7—N9	53.87 (16)
C5—N5—N11—C11	-148.26 (13)	N3—N9—C7—N7	67.24 (16)
Fe1—N5—N11—C11	58.90 (15)	C9—N9—C7—N7	-54.54 (16)
C5—N5—N11—C9	90.56 (15)	N3—N9—C9—N11	-66.79 (16)
Fe1—N5—N11—C9	-62.28 (14)	C7—N9—C9—N11	53.92 (16)
N7—N1—C1—O1	11.1 (2)	N5—N11—C9—N9	68.10 (16)
Fe1—N1—C1—O1	167.61 (13)	C11—N11—C9—N9	-53.92 (16)
N7—N1—C1—C3 ⁱ	-168.97 (12)	N5—N11—C11—N7	-66.46 (16)
Fe1—N1—C1—C3 ⁱ	-12.47 (17)	C9—N11—C11—N7	54.10 (16)
N9—N3—C3—O3	11.7 (2)	N1—N7—C11—N11	66.44 (16)
Fe1—N3—C3—O3	160.86 (14)	C7—N7—C11—N11	-54.19 (16)

Symmetry code: (i) $-x+1, y, -z+3/2$.

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots O7 ⁱⁱ	0.84	1.94	2.763 (6)	165
O2—H12B \cdots N1	1.00	2.66	3.338 (6)	125
O2—H12A \cdots O5 ⁱⁱⁱ	1.17	2.58	3.356 (6)	122
O4—H4 \cdots O7 ⁱⁱ	0.84	1.96	2.792 (7)	169
O8—H8 \cdots O1 ^{iv}	0.81 (3)	1.80 (3)	2.6007 (17)	168 (3)
O10—H15C \cdots O5 ⁱⁱⁱ	1.15	2.39	3.425 (6)	148
N13—H13D \cdots O7 ^v	0.94 (2)	1.99 (2)	2.913 (2)	166.4 (18)
N13—H13E \cdots O3 ^{vi}	0.91 (2)	2.00 (2)	2.9073 (19)	173.2 (19)
N13—H13E \cdots N9 ^{vi}	0.91 (2)	2.64 (2)	3.146 (2)	116.5 (16)
N13—H13F \cdots O5	0.88 (2)	2.12 (2)	2.9606 (19)	160.7 (19)
N13—H13F \cdots N11	0.88 (2)	2.63 (2)	3.252 (2)	128.3 (17)
N13—H13G \cdots O1 ^{vii}	0.87 (2)	2.09 (2)	2.9241 (19)	158.8 (19)
N13—H13G \cdots O3 ⁱⁱ	0.87 (2)	2.48 (2)	3.0698 (19)	125.0 (17)
C7—H3A \cdots O5 ^{viii}	0.99	2.47	3.4109 (19)	159
C7—H3B \cdots O10	0.99	2.43	3.366 (6)	158
C9—H4A \cdots O2 ^{vi}	0.99	2.35	3.312 (7)	165
C9—H4A \cdots O10 ^{vi}	0.99	2.17	3.132 (5)	165
C11—H6B \cdots O1 ^{vii}	0.99	2.31	3.2606 (19)	160
C12—H12B \cdots N1	0.98	2.66	3.575 (7)	155
C12—H12A \cdots O5 ⁱⁱⁱ	0.98	2.58	3.448 (7)	147
C13—H13B \cdots O5	0.90 (3)	2.67 (3)	3.480 (2)	151 (2)
C13—H13C \cdots O8 ^{ix}	0.91 (3)	2.63 (3)	3.416 (3)	146 (2)
C15—H15C \cdots O5 ⁱⁱⁱ	0.98	2.39	3.245 (6)	146

Symmetry codes: (ii) $x, -y+1, z-1/2$; (iii) $x, y-1, z$; (iv) $x, -y+1, z+1/2$; (v) $x, -y+2, z-1/2$; (vi) $-x+3/2, y+1/2, -z+3/2$; (vii) $-x+1, -y+1, -z+1$; (viii) $-x+3/2, y-1/2, -z+3/2$; (ix) $-x+3/2, -y+3/2, -z+2$.