Supporting Information

A Three Dimensional Magnetically Frustrated Metal-Organic Framework *via* Vertices Augmentation of Underlying Net

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S1. Materials and Measurements

All chemicals were reagent grade and used as purchased without further purification. The XRPD spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectrum was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the internet at http://www.iucr.org. IR spectra were measured in the range of 400-4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German). UV-vis spectra were recorded on a Varian Cary5000 spectrophotometer. Thermogravimetric (TG) analyses were carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min^{-1} from ambient temperature to 800 °C under nitrogen gas. Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID). Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders. Gas adsorption measurements were performed using an ASAP 2020 M gas adsorption analyzer. UHP-grade gases were used in measurements. The CO_2 sorption isotherms were collected at 273 K.

S2. X-ray Data Collection and Structure Determinations.

The single-crystal X-ray diffraction data of **1** were collected on a Rigaku MSC diffractometer at 113 (2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The diffraction profiles were integrated by the program *CrystalClear*.[S1] The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL-2014.[S2] The non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. All hydrogen atoms of were generated theoretically at the specific atoms and refined isotropically with fixed thermal factors. The selected bond lengths and angles are given in Tables S1.

Reference:

1. CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005.

2. Sheldrick, G. M. *SHELXTL* Version 2014/7. *http://shelx.uni-ac.gwdg.de/SHELX/index.php*.

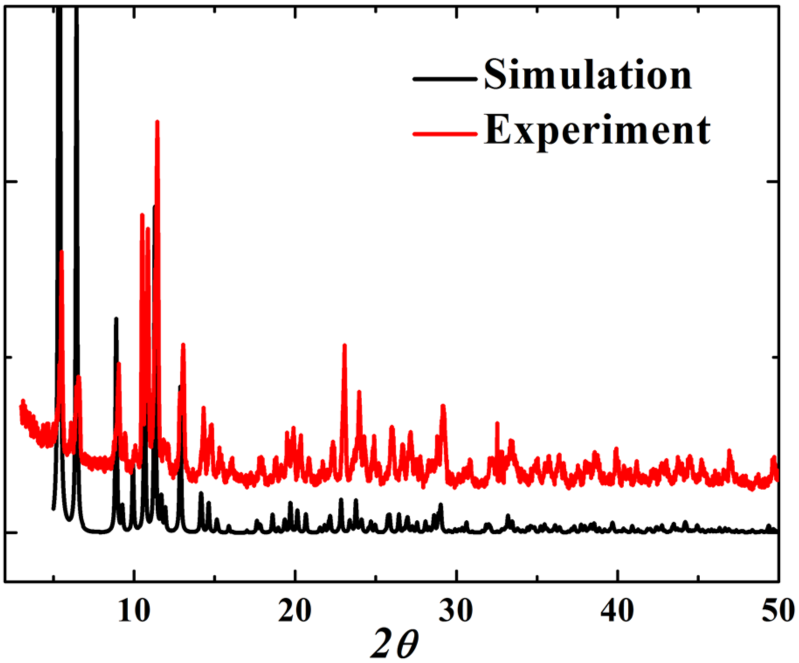


Fig. S1 The Powder X-ray diffraction pattern of **1**.

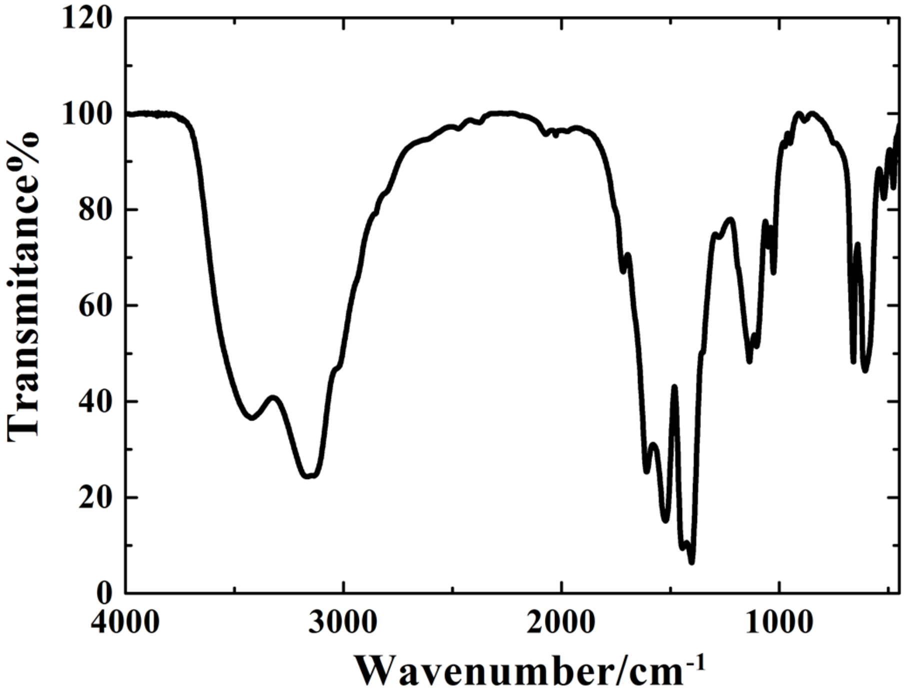


Fig. S2 The IR spectrum for **1** with a KBr pellet.

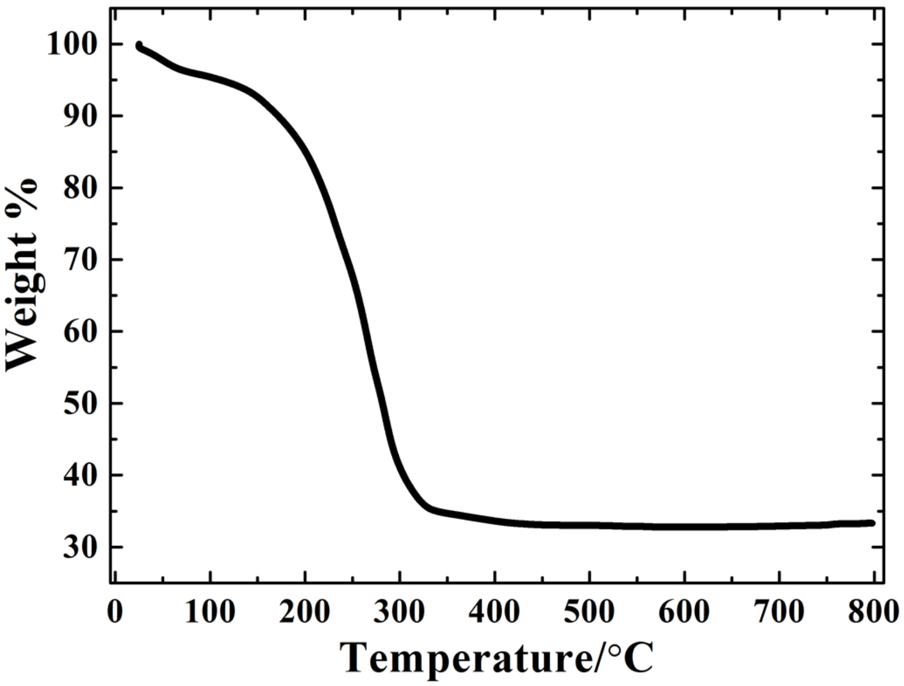


Fig. S3 The TGA of **1** heated at 10 deg/min in N_2 atmosphere.

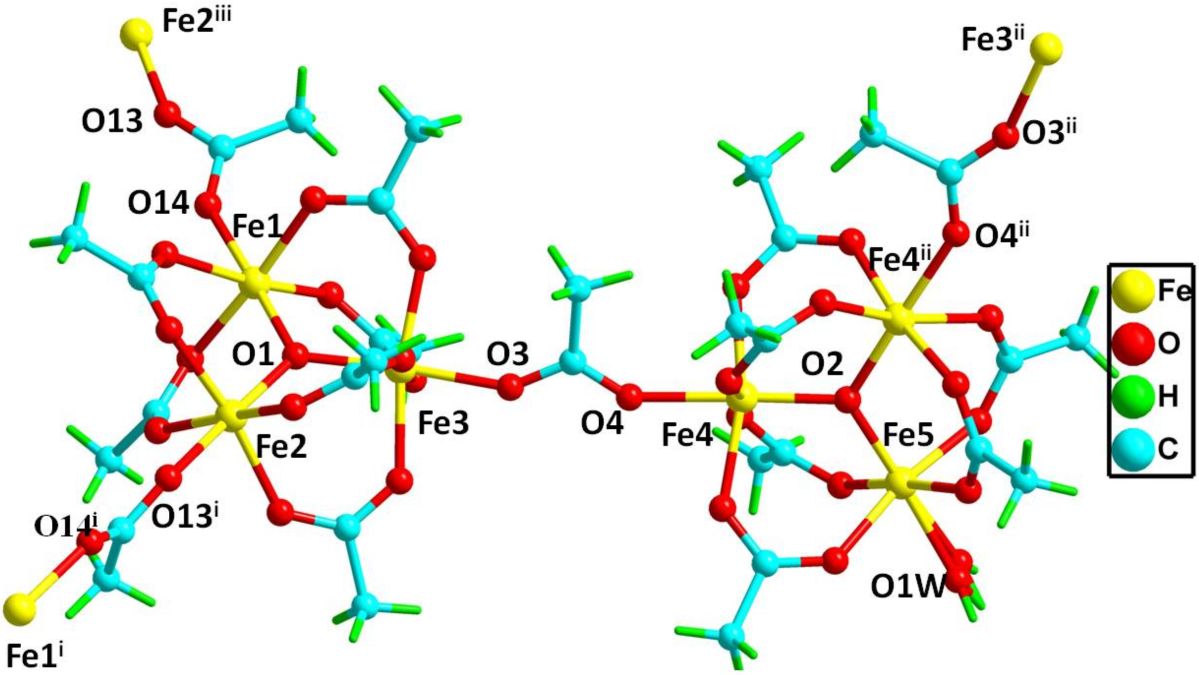


Fig. S4 The coordination and linkage mode of the Fe^{III} ions and acetates in **1**. Symmetry codes: ^{i} -y, -1-x+y, -1/3+z; ^{ii} 2-x,1-x+y; 2/3-z; ^{iii} -1-x+y, x; 1/3+z.

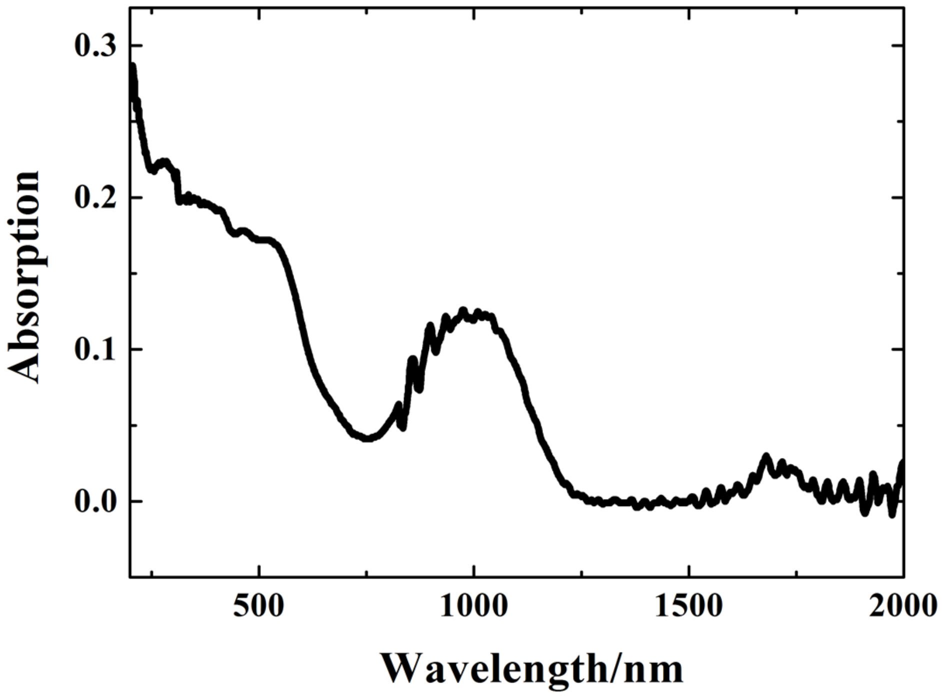


Fig. S5 The UV-Vis spectrum of **1** in solid state.

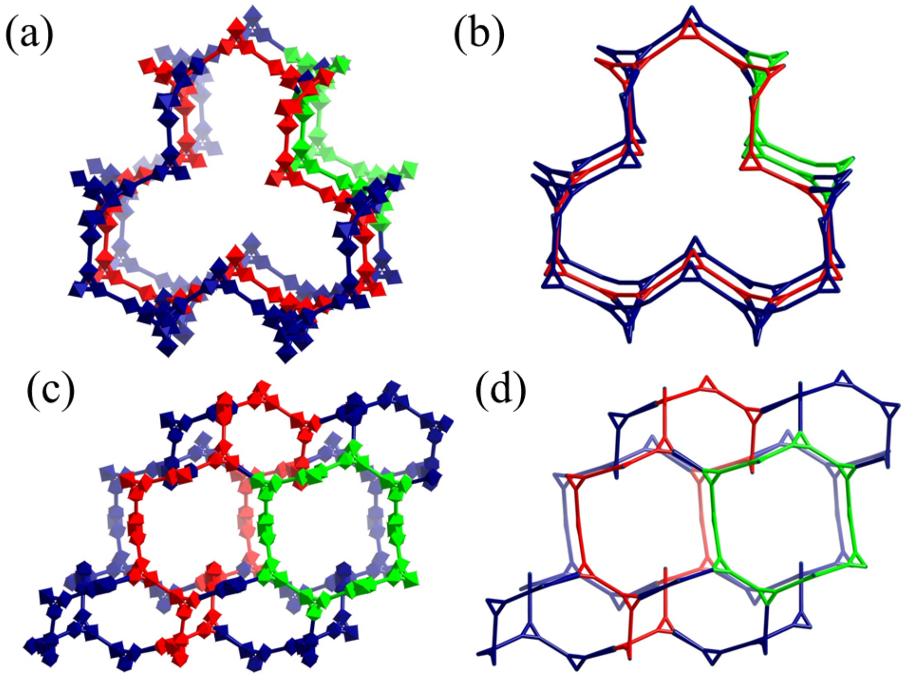


Fig. S6 Polyhedra (a) and predigested (b) view of the 43-membered ring (red) channel of **1**. Polyhedra (c) and predigested (d) of the 20-membered ring channels (green) along the [001] and the [110] or [100].

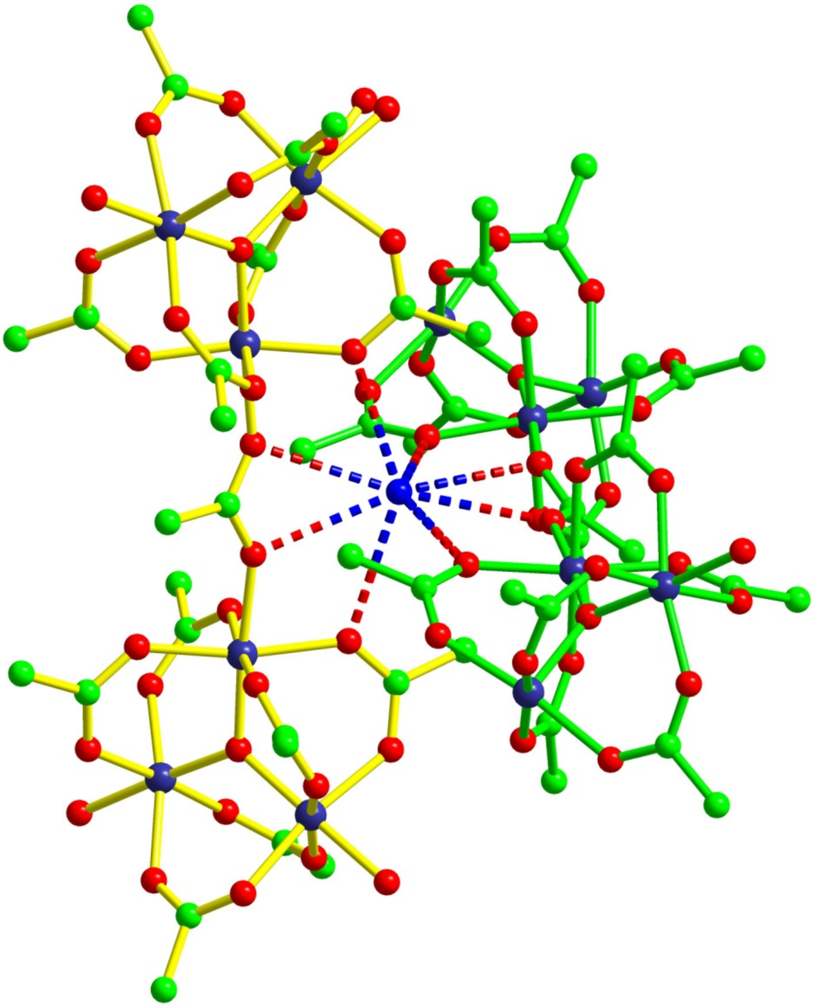
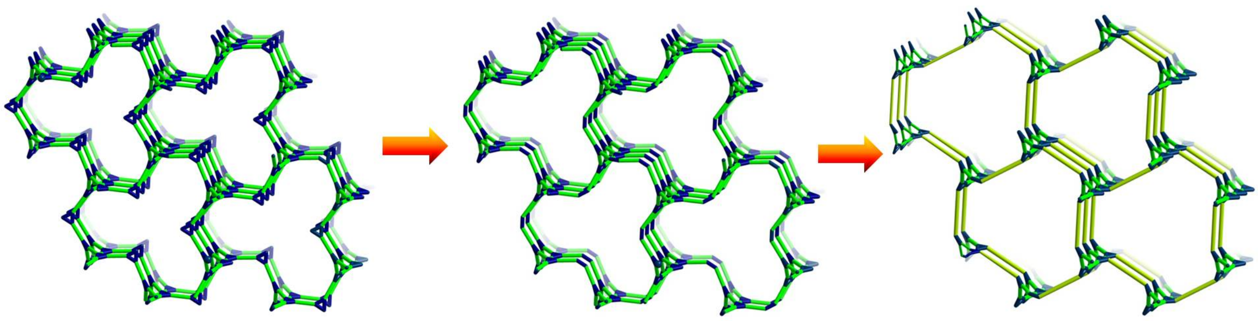


Fig. S7 The ammonium cation stabilized by the H-bonds from two individual *eta* nets.



$\{3;20;21\}_2\{3;20^2\}_6\{3\}$ $\{20\}\{3;20^2\}_3$ $\{3;16^2\}$

Fig. S8 The predigestion of a three dimensional iron triangular net to a $\{3;16^2\}$ net of **1**.

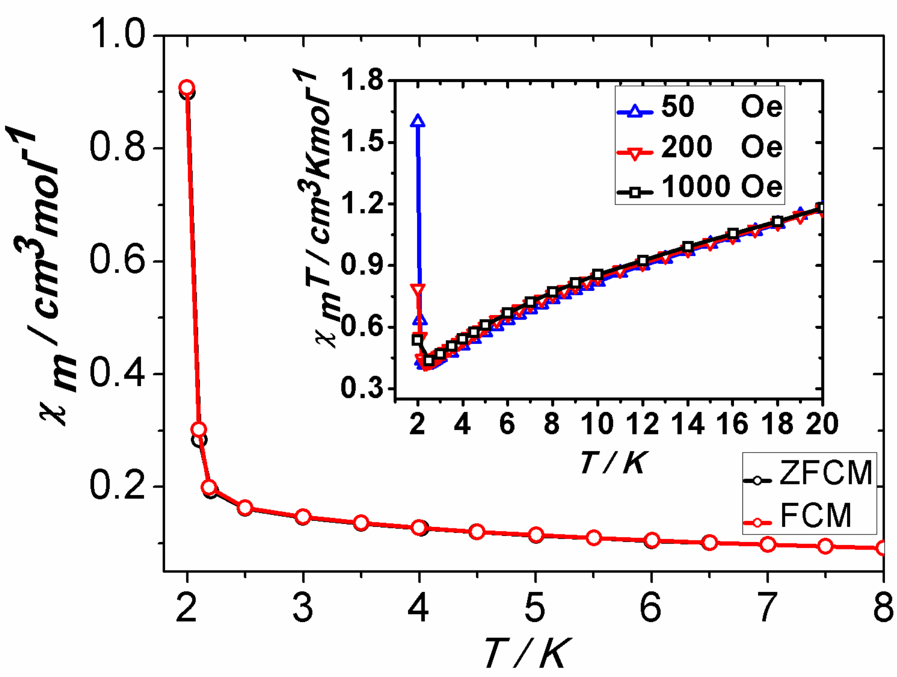


Fig. S9 The zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities of **1** obtained in a dc applied field of 0.05 T. Inset: The field dependence of the molar magnetic susceptibility of **1** obtained below 20 K.

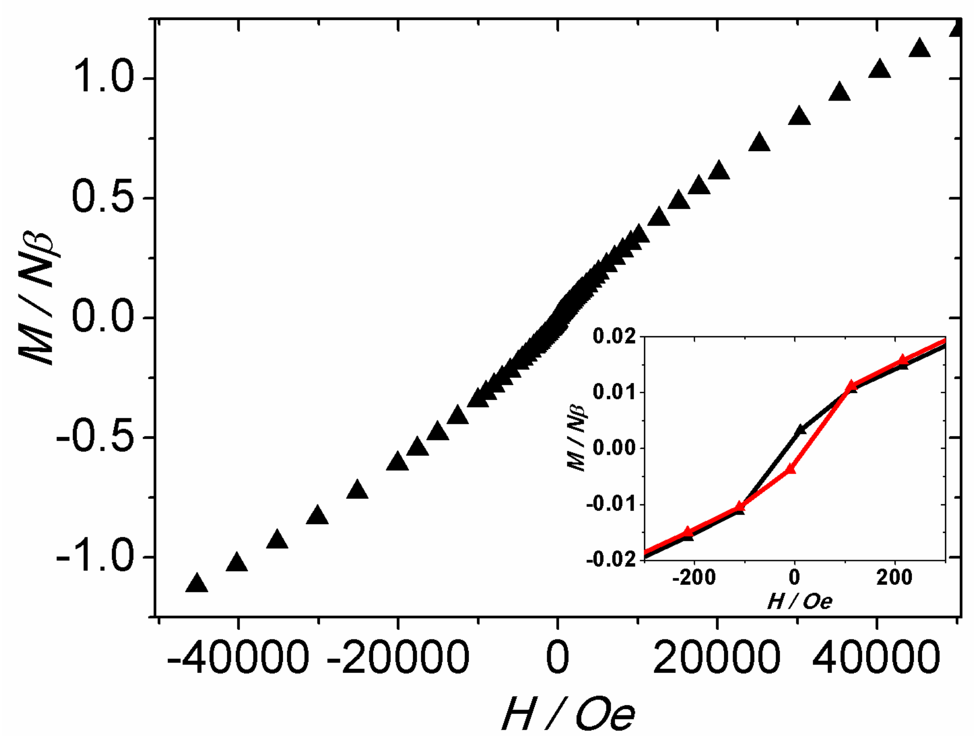


Fig. S10 Hysteresis loop of **1** at 2 K. Insert: the loop between low field -300 and 300 Oe range.

Table S1. Selected bond lengths [Å] and angles **[°]** for **1**.

Fe1—O1	1.915 (5)	Fe3—O17	2.028 (5)
Fe1—O14	2.006 (5)	Fe3—O15	2.032 (5)
Fe1—O5	2.016 (5)	Fe3—O10	2.037 (5)
Fe1—O8	2.034 (6)	Fe4—O2	1.902 (4)
Fe1—O12	2.034 (6)	Fe4—O23	2.017 (6)
Fe1—O9	2.047 (5)	Fe4—O19	2.023 (6)
Fe2—O1	1.901 (5)	Fe4—O4	2.026 (5)
Fe2—O3	2.008 (5)	Fe4—O20$^{\mathrm{ii}}$	2.026 (6)
Fe2—O7	2.010 (5)	Fe4—O21	2.060 (5)
Fe2—O6	2.032 (5)	Fe5—O2	1.910 (7)
Fe2—O16	2.034 (5)	Fe5—O22$^{\mathrm{ii}}$	2.024 (6)
Fe2—O18	2.044 (5)	Fe5—O22	2.024 (6)
Fe3—O1	1.896 (5)	Fe5—O24$^{\mathrm{ii}}$	2.032 (7)
Fe3—O13$^{\mathrm{i}}$	2.006 (5)	Fe5—O24	2.032 (7)
Fe3—O11	2.008 (5)	Fe5—O1W	2.073 (11)
Fe3—O1—Fe2	121.1 (2)	Fe4—O2—Fe4$^{\mathrm{ii}}$	118.9 (4)
Fe3—O1—Fe1	119.7 (3)	Fe4—O2—Fe5	120.55 (18)
Fe2—O1—Fe1	119.2 (2)	Fe4$^{\mathrm{ii}}$—O2—Fe5	120.55 (18)

Symmetry codes: $^{\mathrm{i}}$ $-y+1, x-y+1, z-1/3$; $^{\mathrm{ii}}$ $x-y, -y, -z+4/3$.