metal-organic papers

Dodeca-μ_2-hydroxo-di-μ_3-oxo-hexakis(1,4,7-triaza-cyclononane-$\kappa^3 N,N',N''$)octairon(III) octabromide octahydrate

Ignasi Mata, Elisenda Rodríguez and Elies Molins*

Institut de Ciència de Materials de Barcelona, Bellaterra, Spain

Correspondence e-mail: elies.molins@icmab.es

The title compound, $[Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}(C_6H_{12}N_3)_6]Br_8\cdot 8H_2O$, which crystallizes as an octahydrate, has a different arrangement of cations, anions and water molecules from the known nonahydrate [Wieghardt, Pohl, Jibril & Huttner (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 77–78.]. In the present phase, the cluster is generated by inversion symmetry and the bromide ions display substantial positional disorder.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
H-atom completeness 87%
Disorder in solvent or counterion
R factor = 0.059
wR factor = 0.209
Data-to-parameter ratio = 28.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

As in the previously reported nonahydrate structure (Wieghardt *et al.*, 1984), there is one $[(C_6N_3H_{12})_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]^{8+}$ cluster per unit cell of the title compound, (I) (Fig. 1). The two structures present a similar conformation of the cluster but a completely different distribution of bromide ions and water molecules. In (I), the cluster is generated by inversion symmetry (Table 1), whereas in the nonahydrate, the cluster possesses no symmetry.

(I)
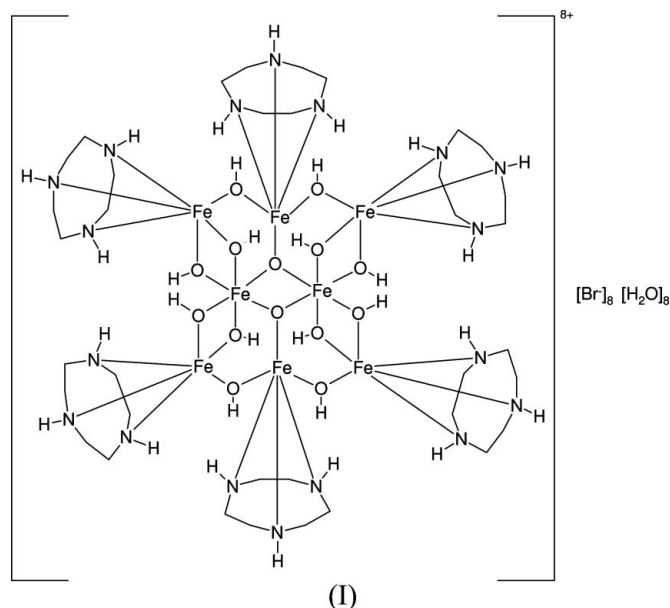
According to charge balance, four Br^- ions per asymmetric unit should be present to compensate the positive charge of the cluster. There is substantial disorder in the positions of the anions, and the four Br^- ions appear distributed over nine sites with occupancy factors ranging from 0.181 (2) to 0.838 (2). The bromide ions in six of these sites act as acceptors for one or two hydrogen bonds with the OH groups, forming μ_2-hydroxo bridges, and with the N atoms in the cyclic amine ligands. The sum of the occupancy factors of the six bromide sites hydrogen bonded to the cluster is 2.97, that is, each cluster is linked by hydrogen bonds to 5.94 Br atoms on

average. The bromide ions in the remaining three sites, together with the solvent water molecules, fill the space between the clusters, forming a complex network of hydrogen bonds which crosslinks the clusters and gives cohesion to the crystal structure.

This distribution of hydrogen bonds is very different from that observed in the previously reported nonahydrate structure. In that case, there were seven bromide ions and one water molecule acting as acceptors for hydrogen bonds between solvent water molecules and the cluster. Owing to the disorder in the bromide positions in (I), the unit-cell volume is larger in this case [2163.0 (8) Å^3 versus 1959 Å^3], in spite of containing one fewer water molecule.

Experimental

Crystals of (I) were obtained while following the literature procedure to grow crystals of the known nonahydrate (Wieghardt *et al.*, 1984).

Crystal data

[Fe$_8$O$_2$(OH)$_{12}$(C$_6$H$_{12}$N$_3$)$_6$]Br$_8$·8H$_2$O
$M_r = 2241.56$
Triclinic, $P\bar{1}$
$a = 13.257$ (2) Å
$b = 13.564$ (1) Å
$c = 14.831$ (4) Å
$\alpha = 108.15$ (1)°
$\beta = 113.34$ (1)°
$\gamma = 101.43$ (1)°
$V = 2163.0$ (8) Å^3

$Z = 1$
$D_x = 1.721$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15
  reflections
$\theta = 10.8$–$12.6°$
$\mu = 5.06$ mm^{-1}
$T = 293$ (2) K
Prism, brown
$0.5 \times 0.37 \times 0.28$ mm

Data collection

Enraf–Nonius CAD-4
  diffractometer
Non–profiled $\omega/2\theta$ scans
Absorption correction: ψ scan
  (North *et al.*, 1968)
  $T_{min} = 0.142$, $T_{max} = 0.241$
13602 measured reflections
13085 independent reflections
8217 reflections with $I > 2\sigma(I)$

$R_{int} = 0.029$
$\theta_{max} = 30.4°$
$h = 0 \rightarrow 18$
$k = -19 \rightarrow 18$
$l = -21 \rightarrow 19$
3 standard reflections
  every 90 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.209$
$S = 1.12$
13085 reflections
467 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.116P)^2$
  $+ 2.3967P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.048$
$\Delta\rho_{max} = 2.53$ e Å^{-3}
$\Delta\rho_{min} = -1.03$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Fe1—O1^i	1.959 (3)	Fe4—O1	1.872 (3)
Fe1—O1	1.967 (3)	Fe4—O6	1.989 (3)
Fe1—O2	2.030 (3)	Fe4—O7	2.011 (3)
Fe1—O4	2.031 (3)	Fe4—N41	2.156 (4)
Fe1—O5	2.040 (3)	Fe4—N44	2.167 (4)
Fe1—O3	2.084 (3)	Fe4—N47	2.241 (4)
Fe3—O5	1.922 (3)	Fe2—O3	1.939 (3)
Fe3—O4	1.950 (3)	Fe2—O2	1.957 (3)
Fe3—O6	1.964 (3)	Fe2—N24	2.160 (5)
Fe3—N37	2.159 (4)	Fe2—N21	2.170 (4)
Fe3—N34	2.161 (4)	Fe2—N27	2.179 (5)
Fe3—N31	2.181 (4)		

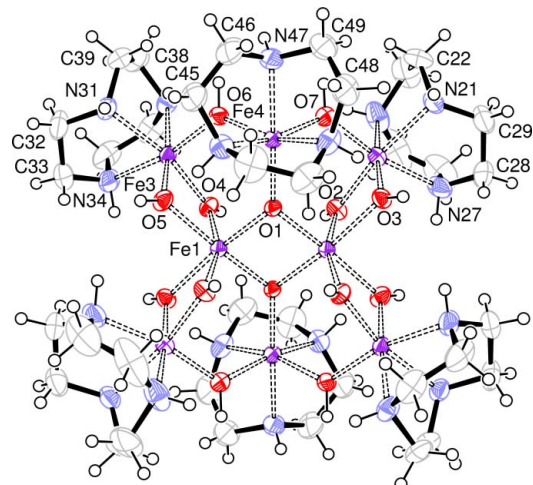Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Figure 1
View of the cluster in (I), showing 50% probability displacement ellipsoids for the non-H atoms. Unlabelled atoms are generated from the labelled atoms by the symmetry operation $(1 - x, 1 - y, 1 - z)$.
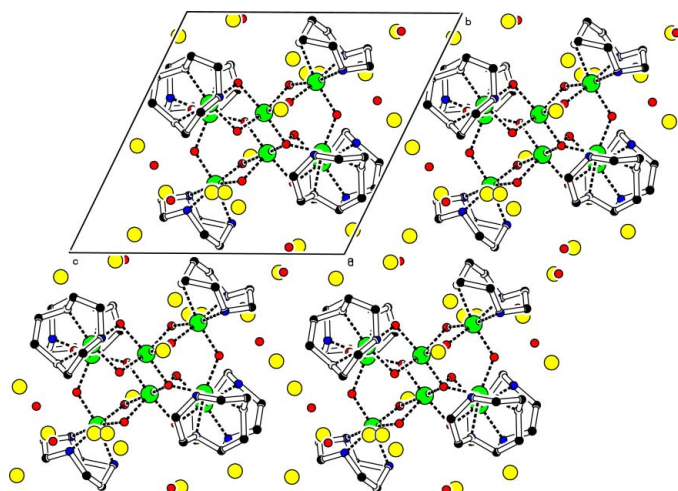

Figure 2
Molecular packing in (I) viewed along the *a* axis. H atoms have been omitted for clarity. Colour key: Fe green, C black, N blue, O red, Br yellow. Fe—N and Fe—O bonds are shown as dashed lines.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···Br1	0.93	2.24	3.142 (3)	165
O6—H6···Br2	0.93	2.52	3.271 (3)	139
O7—H7···Br2	0.93	2.52	3.306 (3)	143
O3—H3···Br3^i	0.93	2.32	3.242 (3)	171
O2—H2···Br6	0.93	2.31	3.116 (10)	145
O4—H4···Br6^i	0.93	2.29	3.123 (10)	149
O2—H2···Br8	0.93	2.55	3.274 (5)	135
O4—H4···Br8^i	0.93	2.55	3.298 (5)	138
N24—H24···Br7	0.91	2.64	3.519 (6)	164
N24—H24···Br8	0.91	2.96	3.591 (8)	128
N27—H27···Br1	0.91	2.72	3.562 (5)	155
N31—H31···Br1	0.91	2.94	3.643 (4)	136
N34—H34···Br3^i	0.91	2.54	3.403 (5)	159
N37—H37···Br7^i	0.91	2.79	3.578 (5)	146
N37—H37···Br2	0.91	3.00	3.731 (5)	139
N41—H41···Br3	0.91	3.08	3.853 (5)	144
N47—H47···Br2	0.91	2.89	3.689 (5)	148

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

H atoms in the cluster were placed in calculated positions (C—H = 0.97 Å, N—H = 0.91 Å and O—H = 0.93 Å) and refined as riding with the constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) applied. The H atoms of the solvent water molecules could not be located in difference Fourier maps. The highest peak and deepest hole at the end of the refinement were located close to atoms Br3 and O2w, respectively.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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