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Key indicators

Single-crystal X-ray study
 $T = 250$ K
Mean $\sigma(\text{I-O}) = 0.005$ Å
 R factor = 0.046
 wR factor = 0.114
Data-to-parameter ratio = 16.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Hexaaquairon(III) perchlorate trihydrate

A single crystal of commercially available 'iron(III) perchlorate hexahydrate' has been structurally characterized and shown to be hexaaquairon(III) tris(perchlorate) trihydrate, $[\text{Fe}(\text{H}_2\text{O})_6](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$. The structure contains $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ complex ions, charge-balancing perchlorate ions and three water molecules of crystallization per Fe atom. A network of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds helps to stabilize the crystal packing. Fe, Cl and one water O atom occupy special positions with site symmetries $\bar{3}$, 2, and 2, respectively.

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Comment

Surprisingly, the structures of some simple metal perchlorate hydrates have not yet been determined. One of these compounds is iron(III) perchlorate. Commercial 'iron(III) perchlorate hexahydrate' (AlfaAesar) consisted of single crystals of a quality sufficient for a structure determination, which showed its composition really to be hexaaquairon(III) perchlorate trihydrate, (I).

Compound (I) crystallizes in the trigonal system, space group $R\bar{3}c$, with the Fe atom on Wyckoff position $6b$ (Fig. 1). Fe1 (site symmetry $\bar{3}$) is coordinated by water molecules with the O atom on position $18f$, thus yielding an essentially regular octahedral coordination by six crystallographically equivalent water molecules [$\text{Fe1}-\text{O1} = 1.988$ (2) Å]. The Cl atom lies on Wyckoff position $18e$ (site symmetry 2) with a tetrahedral coordination by two pairs of equivalent O atoms. The water

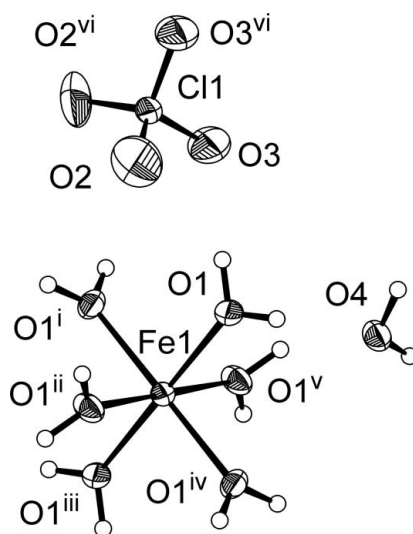


Figure 1

The structural units in the title compound. Displacement ellipsoids are drawn at the 30% probability level (arbitrary spheres for the H atoms). [Symmetry codes: (i) $x - y, x, -z$; (ii) $-y, x - y, z$; (iii) $-x, -y, -z$; (iv) $-x + y, -x, z$; (v) $y, -x + y, -z$; (vi) $\frac{1}{3} + x - y, \frac{2}{3} - y, \frac{1}{6} - z$.]

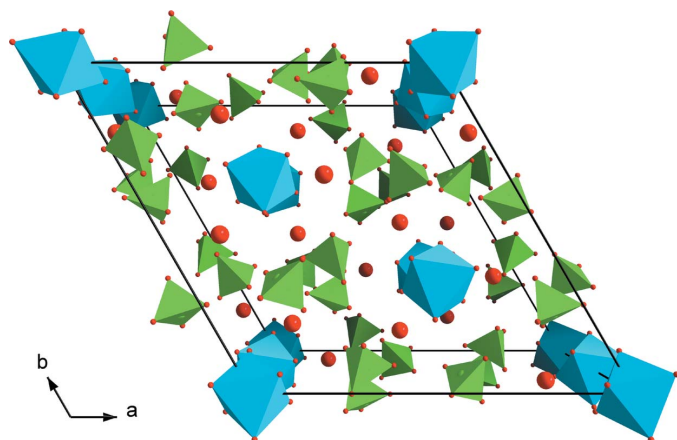


Figure 2
A packing diagram of (I), in a view along c . Key: blue polyhedra $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, green polyhedra ClO_4^- , and large red spheres H_2O .

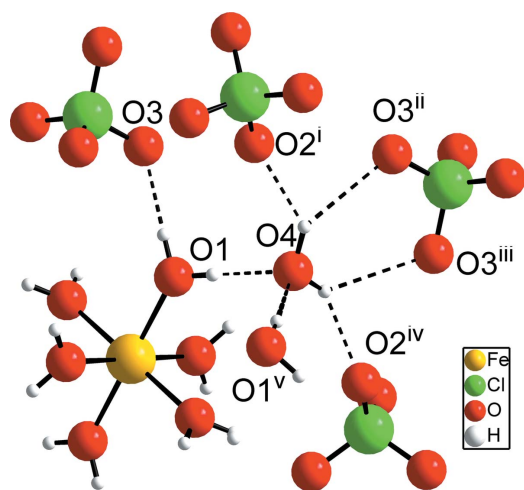


Figure 3
The hydrogen-bonding (dashed lines) pattern in (I). [Symmetry codes: (i) $y, x, \frac{1}{2} - z$; (ii) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iii) $\frac{1}{3} - x + y, -\frac{1}{3} + y, \frac{1}{6} + z$; (iv) $-x + y, -x, z$; (v) $x - y, -y, \frac{1}{2} - z$.]

molecule of crystallization lies on position $18e$ (site symmetry 2) yielding a total number of nine water molecules per Fe^{3+} . A network of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 1) stabilizes the crystal packing (Figs. 2 and 3).

Only a few perchlorate hydrates of M^{3+} metal ions have been structurally characterized, the lanthanides being by far the biggest group. Six-coordinate $[\text{Ln}(\text{H}_2\text{O})_6]^{3+}$ complex ions are uncommon, but one series of exceptions is the perchlorate hexahydrates of La, Tb, Er and Tl (Glaser & Johansson, 1981). In these structures, however, no additional water molecules of crystallization are present.

Experimental

A single crystal of commercial iron(III) perchlorate 'hexahydrate' (AlfaAesar, Reagent grade) was used without further treatment. Owing to its sensitivity towards water, the selected crystal was cooled to 250 K during the data collection.

Crystal data

$[\text{Fe}(\text{H}_2\text{O})_6](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$
 $M_r = 516.33$
 Trigonal, $R\bar{3}c$
 $a = 16.047(2) \text{ \AA}$
 $c = 11.3561(13) \text{ \AA}$
 $V = 2532.5(5) \text{ \AA}^3$
 $Z = 6$
 $D_x = 2.031 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 44 reflections
 $\theta = 9.2\text{--}20.2^\circ$
 $\mu = 1.47 \text{ mm}^{-1}$
 $T = 250 \text{ K}$
 Needle, colourless
 $0.45 \times 0.10 \times 0.09 \text{ mm}$

Data collection

Bruker-Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: none
 8799 measured reflections
 652 independent reflections

555 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -16 \rightarrow 20$
 $k = -20 \rightarrow 20$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.114$
 $S = 1.06$
 652 reflections
 39 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 20.7174P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$

Table 1

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O4}-\text{H4}\cdots\text{O2}^{\text{i}}$	0.97	1.97	2.745 (4)	136
$\text{O4}-\text{H4}\cdots\text{O3}^{\text{ii}}$	0.97	2.36	3.052 (3)	128
$\text{O1}-\text{H1A}\cdots\text{O3}$	0.87	1.91	2.775 (4)	172
$\text{O1}-\text{H1B}\cdots\text{O4}$	0.82	1.82	2.632 (2)	173

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

H atoms were located in a difference map and refined in their as-found positions using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD* (Duisenberg, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

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