Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Triaqua-1κO,2κO,3κO-hexakis-μ-chloroacetato-1:2$\kappa^4 O$:O';2:3$\kappa^4 O$:O';1:3$\kappa^4 O$:O'-μ_3-oxo-triiron(III) nitrate trihydrate

X. M. Ren,* H. Okudera and R. K. Kremer

Max-Planck-Institut für Festkörperforschung,
Heisenbergstrasse 1, Postfach 800665,
D-70569 Stuttgart, Germany

Correspondence e-mail: x.ren@fkf.mpg.de

Received 10 October 2003
Accepted 17 November 2003
Online 6 December 2003

Key indicators

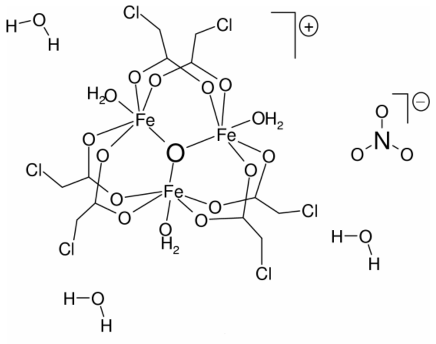
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.035
wR factor = 0.099
Data-to-parameter ratio = 13.4

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

The title compound, $[Fe_3O(C_2H_2ClO_2)_6(H_2O)_3]NO_3\cdot 3H_2O$, contains an Fe^{III} trimeric cation in which the three Fe^{III} ions are at the corners of a slightly distorted triangle with an O atom in the centre. Two monochloroacetate ligands bridge each pair of Fe^{III} ions and a water molecule coordinates each Fe^{III} ion at the apex, opposite to the central O atom. Hence, the Fe^{III} ions are surrounded by distorted oxygen octahedra. The distances between the Fe^{III} ions and the central O atoms are considerably shorter than those between the Fe^{III} ions and the other coordinated O atoms. The trimeric cations form a three-dimensional connected network *via* hydrogen-bonding interactions to extra-cluster water molecules and nitrate anions.

Comment

Trinuclear oxo-centred carboxylate-bridged Fe or Cr complexes have attracted particular interest, due to their unusual magnetic properties (Figgis & Robertson, 1965; Earnshaw *et al.*, 1966; Duncan *et al.*, 1969; Long *et al.*, 1973; Rakitin *et al.*, 1977). In this type of trinuclear magnetic system, the magnetic exchange interactions among the three Fe or Cr ions have been characterized by two coupling constants, J and J' (Long *et al.*, 1973). However, J and J' do not reveal any clear correspondence with the chemical nature of the carboxylate ligands. This lack of correlation may result from the use of an oversimplified Hamiltonian in the theoretical analysis of the magnetic properties, and suggests that second-order coupling terms should also be considered. An alternative reason may arise from the influence of solvent molecules of crystallization, which are generally incorporated in this type of trinuclear compound. The discrepancies mentioned above motivated us to re-investigate this type of trinuclear complex, with emphasis on their magnetic behaviour. Here, we report the crystal structure of the title compound, (I).



(I)

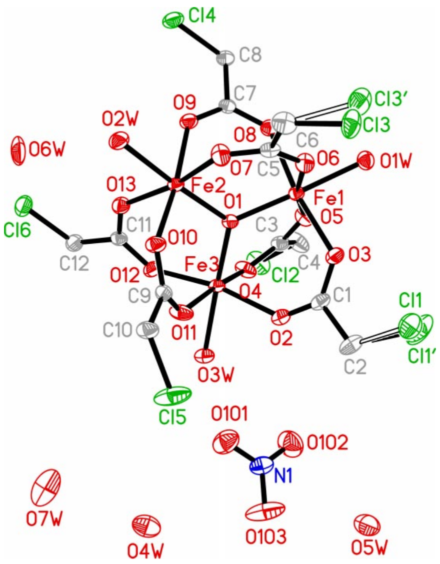


Figure 1
The crystal structure of (I), with 30% probability displacement ellipsoids; H atoms have been omitted for clarity. The disorder of the chloro ligands and one water molecule is shown.

In the structure of (I), there are three extra-cluster water molecules (one of which is disordered over two sites), one nitrate counteranion and one Fe^{III} trinuclear cation in the asymmetric unit. In the trinuclear cation, the Fe^{III} ions lie at the apices of a triangle, resulting in Fe1···Fe2, Fe2···Fe3 and Fe3···Fe1 separations of 3.3272 (8), 3.3015 (8) and 3.2968 (12) Å, respectively, and the triangle formed by these three Fe^{III} ions is almost equilateral.

Each Fe^{III} ion is octahedrally coordinated by O atoms. The three octahedra share a common vertex, which is almost coplanar with, and at the centre of, the triangle of Fe^{III} ions. A single O atom occupies this shared vertex. The vertex of each octahedron *trans* to the shared vertex is occupied by a water molecule, and the other vertices of each octahedron about the Fe^{III} ions are occupied by four O atoms, one from each of four different carboxylate groups. The carboxylate ions thus connect adjacent octahedra as bridging ligands. The octahedral coordination for each Fe^{III} ion is slightly distorted; the bond lengths between the central O atom and the three Fe^{III} ions are 1.910 (2) for Fe1, 1.914 (2) for Fe2 and 1.907 (2) Å for Fe3. These are shorter than the other Fe—O bond lengths in (I) [1.987 (3)–2.073 (3) Å]. These results are in agreement with values reported in the literature for related materials (Overgaard *et al.*, 2003).

The hydrogen-bonding interactions in (I) (Fig. 2 and Table 2) involve numerous O—H···O and O—H···Cl links. These result in a three-dimensional network linking the Fe^{III} cations, nitrate anions and water molecules.

Experimental

Compound (I) was prepared using a procedure similar to that described by Taft *et al.* (1992), allowing Fe(NO$_3$)$_3$·9H$_2$O to react with a large excess of monochloroacetic acid in a boiling solution of mixed water and ethanol (*v*:*v* *ca* 1:1) for several hours. Slow evaporation of the mixed solvent gave large red crystals of (I) (yield > 75%).

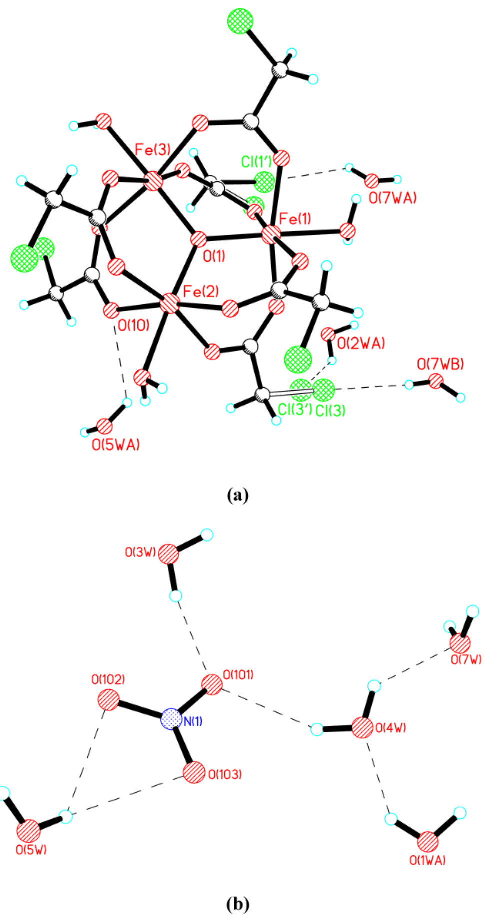


Figure 2
Detail of the hydrogen-bonding interactions in (I) around (*a*) the trinuclear cation and (*b*) a nitrate anion.

Crystal data

$[Fe_3O(C_2H_2ClO_2)_6(H_2O)_3]$-
NO$_3$·3H$_2$O
$M_r = 914.57$
Monoclinic, $P2_1/c$
$a = 12.523$ (3) Å
$b = 14.768$ (3) Å
$c = 17.601$ (4) Å
$\beta = 96.35$ (3)°
$V = 3235.1$ (11) Å^3
$Z = 4$

$D_x = 1.878$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 332 reflections
$\theta = 1.8$–32.2°
$\mu = 1.91$ mm^{-1}
$T = 293$ (2) K
Block, red
0.4 × 0.4 × 0.3 mm

Data collection

Stoe IPDS II diffractometer
φ scans
Absorption correction: numerical (*IPDS*; Stoe & Cie, 1998)
$T_{min} = 0.598$, $T_{max} = 0.677$
20 401 measured reflections
5682 independent reflections

4634 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 25.0°$
$h = -14 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.099$
$S = 1.06$
5682 reflections
425 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0037 (4)

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	1.909 (2)	Fe2—O9	2.020 (2)
Fe1—O8	2.007 (2)	Fe2—O2*W*	2.037 (2)
Fe1—O5	2.015 (2)	Fe2—O10	2.041 (2)
Fe1—O6	2.034 (2)	Fe3—O1	1.907 (2)
Fe1—O1*W*	2.040 (2)	Fe3—O2	1.987 (3)
Fe1—O3	2.043 (2)	Fe3—O12	1.995 (2)
Fe2—O1	1.914 (2)	Fe3—O11	2.014 (2)
Fe2—O7	2.001 (3)	Fe3—O4	2.032 (2)
Fe2—O13	2.015 (2)	Fe3—O3*W*	2.076 (2)
Fe3—O1—Fe1	119.49 (11)	Fe1—O1—Fe2	120.99 (11)
Fe3—O1—Fe2	119.52 (11)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O4*W*$^{\mathrm{i}}$	0.85	2.02	2.721 (4)	139
O1*W*—H1*WB*···O6*W*$^{\mathrm{ii}}$	0.85	2.23	3.071 (5)	168
O2*W*—H2*WA*···O4*W*$^{\mathrm{iii}}$	0.85	2.34	2.828 (3)	117
O2*W*—H2*WA*···Cl3$'^{\mathrm{iv}}$	0.85	2.55	3.172 (10)	130
O3*W*—H3*WA*···O101	0.85	1.94	2.774 (4)	166
O6*W*—H6*WB*···O7*W*$^{\mathrm{v}}$	0.85	2.08	2.904 (15)	162
O4*W*—H4*WA*···O101	0.85	2.29	3.071 (5)	153
O4*W*—H4*WA*···O103	0.85	2.49	3.258 (6)	152
O4*W*—H4*WB*···O7*W*	0.85	2.13	2.796 (12)	135
O5*W*—H5*WA*···O10$^{\mathrm{i}}$	0.86	2.60	3.085 (3)	117
O5*W*—H5*WB*···O102	0.85	2.44	3.084 (5)	133
O5*W*—H5*WB*···O103	0.85	2.46	3.214 (6)	148
O7*W*—H7*WA*···Cl1$'^{\mathrm{vi}}$	0.85	2.46	3.08 (2)	131
O7*W*—H7*WB*···Cl3$^{\mathrm{vii}}$	0.85	2.30	3.03 (3)	143
O6*W*—H6*WA*···Cl1$^{\mathrm{iv}}$	0.85	2.71	3.365 (10)	135
O6*W*—H6*WB*···O7*W*$^{\mathrm{v}}$	0.85	2.08	2.904 (15)	162

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

All H atoms were placed in geometrically calculated positions (C—H = 0.93 and 0.97 Å, and O—H = 0.8500–0.8551 Å), with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\,U_{\mathrm{eq}}$(parent atom). The fractional site occupancies of the disordered atom pairs Cl1/Cl1′, Cl3/Cl3′ and O6*W*/O7*W* were constrained to sum to unity, resulting in refined occupancies of 0.58 (2)/0.42 (2), 0.54 (4)/0.46 (4) and 0.670 (8)/0.330 (8), respectively.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *X-RED* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

XMR acknowledges financial support from the Max Planck Society and the National Natural Science Foundation of China (Project No.20171001).

References

Duncan, J. F., Kanekar, C. R. & Mok, K. F. (1969). *J. Chem. Soc. A*, pp. 480–482.

Earnshaw, A., Figgis, B. N. & Lewis, J. (1966). *J. Chem. Soc. A*, pp. 1656–1663.

Figgis, B. N. & Robertson, G. B. (1965). *Nature*, **205**, 694–695.

Long, G. J., Robinson, W. T., Tappmeyer, W. P. & Bridges, D. L. (1973). *J. Chem. Soc. Dalton Trans.* pp. 573–579.

Overgaard, J., Larsen, F. K., Schiott, B. & Iversen, B. B. (2003). *J. Am. Chem. Soc.* **125**, 11088–11099.

Rakitin, Yu. V., Zhemchuzhnikova, T. A. & Zelentsov, V. V. (1977). *Inorg. Chim. Acta*, **23**, 145–148.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997*a*). *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Stoe & Cie (1998). *IPDS* (Version 2.87) and *X-RED*. Stoe & Cie, Darmstadt, Germany.

Taft, K. L., Masschelein, A., Liu, S. & Lippard, S. J. (1992). *Inorg. Chim. Acta*, **198–200**, 627–631.