Hexakis(μ_4-2-amino-2-methylpropane-1,3-diolato)hexachloroheptairon(II,III) acetonitrile disolvate monohydrate

Gaël Labat,[a]* Colette Boskovic[b] and Hans U. Güdel[b]

[a]Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2007 Neuchâtel, Switzerland, and [b]Departement für Chemie und Biochemie, Universität Bern, Freiestraße 3, CH-3012 Bern, Switzerland

Correspondence e-mail: gael.labat@unine.ch

Single crystals of a new mixed-valence compound, [Fe$_7$(C$_4$H$_9$NO$_2$)$_6$Cl$_6$]·2CH$_3$CN·H$_2$O, were synthesized by solvothermal methods. The crystal structure consists of discrete heptanuclear complexes which are linked by weak intermolecular C—H···Cl hydrogen bonds to form a two-dimensional network. In each complex, a central Fe atom is connected to six surrounding Fe centres by alkoxo-type O atoms from the organic ligand. Bond-valence sum calculations indicate that the central Fe ion is Fe^{II}, as are two of the outer Fe centers, while the remaining four Fe centers are Fe^{III}. Although the outer Fe atoms are crystallographically equivalent, it is uncertain whether this arises from positional disorder or charge delocalization. The molecular structure has S_6 point symmetry.

## Comment

The structural motif of a ring of six metal centres linked to a central metal atom by bridging ligands has been observed for several homometallic heptanuclear transition metal complexes (Bolcar *et al.*, 1997; Tesmer *et al.*, 1997; Abbati *et al.*, 1998; Oshio *et al.*, 2003). These contain hydroxo-, alkoxo- and/or phenoxo-type O atoms bridging the essentially coplanar metal centres. To date, only one such Fe$_7$ example is known and it has a mixed-valence [Fe$_6^{II}$Fe^{III}] configuration (Oshio *et al.*, 2003).

2CH$_3$CN · H$_2$O

(I)
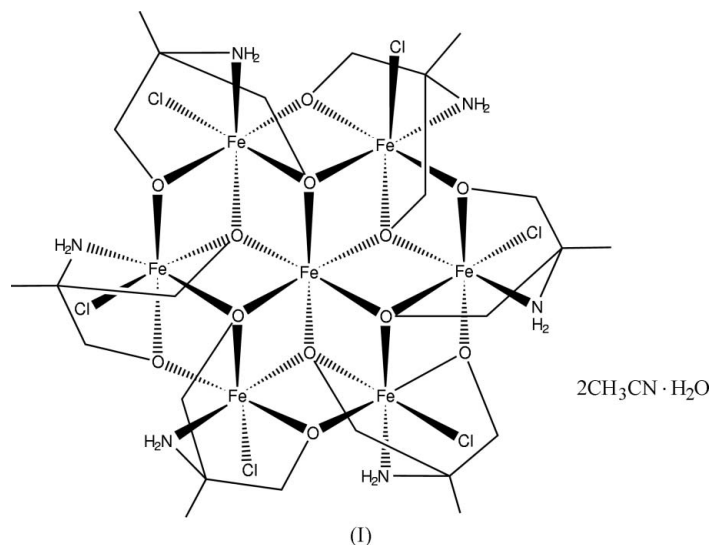
In the present work, the solvothermal reaction between Fe(OAc)$_2$ and one equivalent of 2-amino-2-methyl-1,3-propanediol in the presence of HCl has afforded single crystals of the title compound, (I), which possesses an analogous
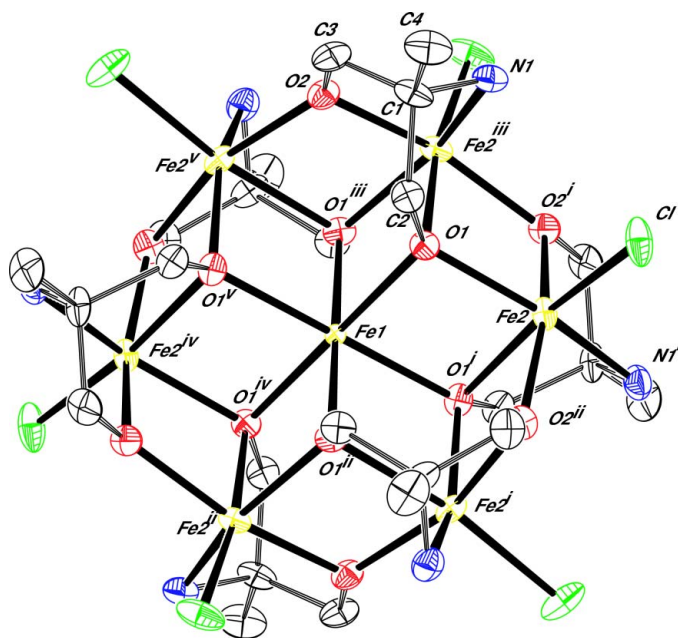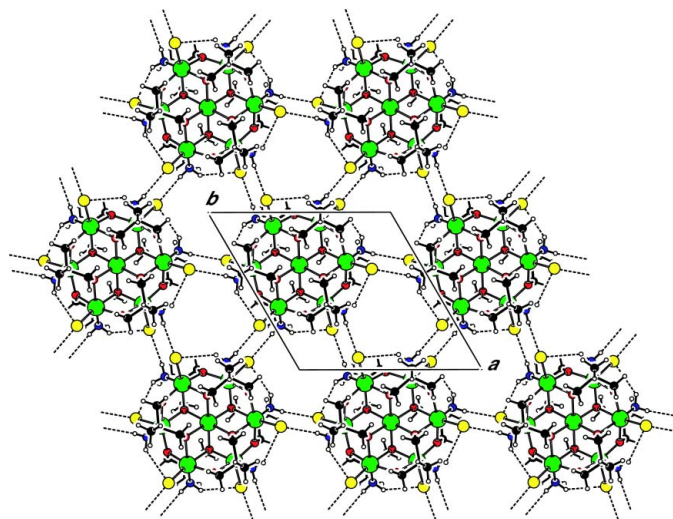
Figure 1
The molecular structure of (I), showing the numbering scheme and with displacement ellipsoids at the 30% probability level (see Table 1 for symmetry codes). Solvent molecules and H atoms have been omitted for clarity.

Figure 2
A view of the crystal packing in (I), showing the formation in the *ab* plane of the hydrogen-bonded (dashed lines) two-dimensional network.

wheel-like structure. The proligand, 2-amino-2-methyl-1,3-propanediol, has been little used in coordination chemistry and the structural characterization of only one complex of this ligand has been reported to date (McKee *et al.*, 1987).

The molecular structure of (I) has crystallographically imposed S_6 point symmetry, with the asymmetric unit consisting of one sixth of the heptanuclear complex together with disordered solvent. Compound (I) comprises a central iron atom, Fe1, linked to six additional iron centers, atoms Fe2, by alkoxo-type O atoms provided by the dianionic organic ligand (Fig. 1). Atom O1 bridges in a μ_3-mode, while atom O2 bridges the Fe2 centers in a μ_2-mode. Selected bond distances and angles in (I) are given in Table 1.

The coordination about Fe1 is distorted octahedral, with Fe1—O1 bond lengths of 2.138 (5) Å, *cis*-O—Fe1—O bond angles of 82.91 (16) and 97.09 (16)°, and *trans*-O—Fe1—O bond angles of 180°. The coordination about atom Fe2 is distorted octahedral with a ClNO$_4$ configuration, through coordination by the O and N atoms of the organic ligand and by a terminal Cl atom. Fe2—O bond lengths are in the range 1.994 (5)–2.203 (5) Å.

Bond-valence sum calculations (Thorp, 1992) are consistent with a +2 oxidation state for atom Fe1 and oxidation states intermediate between +2 and +3 for atom Fe2. Charge-balance considerations require an Fe$_3^{II}$Fe$_4^{III}$ configuration. Thus, two of the Fe2 ions must be Fe^{II}, with the remaining three being Fe^{III}. There is insufficient evidence to determine if this results from a trapped-valence Class I compound, with crystallographic disorder, or if there is charge delocalization, *i.e.* Class II or III (Robin & Day, 1967). Although variable-

temperature Mössbauer spectroscopy would allow the elucidation of this problem, we were not able to obtain sufficient material for these measurements. However, Mössbauer measurements on the structurally related Fe^{II}Fe$_6^{III}$ compound were consistent with a trapped-valence description (Oshio *et al.*, 2003) and it is likely that such a description is the most appropriate for (I).

In the crystal structure of (I), the molecules are linked to six symmetry-related molecules by weak N—H···Cl hydrogen bonds (Table 2). This results in the formation of a two-dimensional network (Fig. 2) arranged as layers in the *ab* plane.

Experimental

Crystal data

[Fe$_7$(C$_4$H$_9$NO$_2$)$_6$Cl$_6$]·2CH$_3$CN·H$_2$O	Mo $K\alpha$ radiation
$M_r = 1322.51$	Cell parameters from 3857
Hexagonal, $R\bar{3}$	reflections
$a = 12.4150$ (7) Å	$\theta = 2.2–25.8°$
$c = 28.030$ (3) Å	$\mu = 2.36$ mm^{-1}
$V = 3741.5$ (5) Å^3	$T = 153$ (2) K
$Z = 3$	Brown, block
$D_x = 1.761$ Mg m^{-3}	$0.30 \times 0.30 \times 0.20$ mm

Data collection

Stoe IPDS-I diffractometer	1622 independent reflections
φ oscillation scans	916 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.180$
(*MULABS* in *PLATON*; Spek, 2003)	$\theta_{max} = 25.9°$
	$h = -15 \rightarrow 15$
$T_{min} = 0.402, T_{max} = 0.624$	$k = -15 \rightarrow 15$
9917 measured reflections	$l = -34 \rightarrow 34$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0981P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.169$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.88$	$\Delta\rho_{max} = 1.52$ e Å^{-3}
1622 reflections	$\Delta\rho_{min} = -1.12$ e Å^{-3}
105 parameters	Extinction correction: none
H-atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Fe1—O1	2.138 (5)	Fe2—O2^i	2.005 (5)
Fe2—O1	2.203 (5)	Fe2—N1	2.168 (7)
Fe2—O1	2.076 (5)	Fe2—Cl1	2.313 (2)
Fe2—O2	1.994 (5)		
O1^{ii}—Fe1—O1	180	N1—Fe2—O1	75.2 (2)
O1^{ii}—Fe1—O1^i	82.91 (16)	O1—Fe2—Cl1	101.15 (15)
O1—Fe1—O1^i	97.09 (16)	N1—Fe2—Cl1	103.4 (2)
O2—Fe2—O2^i	161.6 (2)	O1—Fe2—Cl1	171.65 (16)
O2—Fe2—O1	79.1 (2)	O2—Fe2—Cl1	102.20 (17)
O2^i—Fe2—O1	99.2 (2)	O2^i—Fe2—Cl1	96.16 (16)
O2—Fe2—O1	85.7 (2)	Fe2—O1—Fe1	98.8 (2)
O2^i—Fe2—O1	75.8 (2)	Fe2—O1—Fe2^{iii}	97.57 (19)
O1—Fe2—O1	82.8 (3)	Fe1—O1—Fe2^{iii}	94.96 (19)
O2^i—Fe2—N1	94.2 (3)	Fe2^{iii}—O2—Fe2^{iv}	107.3 (3)
O1—Fe2—N1	150.5 (2)		

Symmetry codes: (i) $-y+1, x-y+1, z$; (ii) $-x+\frac{2}{3}, -y+\frac{4}{3}, -z+\frac{1}{3}$; (iii) $y-\frac{1}{3}, -x+y+\frac{1}{3}, -z+\frac{1}{3}$; (iv) $-x+y, -x+1, z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Cl1	0.89 (2)	2.75 (6)	3.470 (8)	139 (8)
N1—H2$\cdots$Cl1^v	0.89 (2)	2.52 (4)	3.370 (8)	158 (8)

Symmetry code: (v) $-y+1, x-y+2, z$.

The crystal diffracted weakly above 40° in 2θ and, despite long exposure times, the R_{int} value was found to be 0.18. This also resulted in a poor (< 10) ratio of observed reflections to parameters. The amine N—H bond distances were restrained to 0.89 (2) Å and refined with $U_{iso}(H) = 1.5U_{eq}(N)$. The remaining H atoms were included in calculated positions and treated as riding atoms, with C—H distances in the range 0.98–0.99 Å and with $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(C)$. The highest peak is located at 1.00 Å from atom Cl1 and the deepest hole is located 0.98 Å from atom Fe1.

Data collection: *EXPOSE* in *IPDS-I* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS-I*; data reduction: *INTEGRATE* in *IPDS-I*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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