metal-organic compounds

An oxo-centred trinuclear Fe^{III} complex: triaquahexakis(μ_2-betaine-O:O')-μ_3-oxo-triiron(III) bis(tetra-chloromanganate) trichloride hexahydrate

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The title compound, [Fe$_3$(C$_5$H$_{11}$NO$_2$)$_6$O(H$_2$O)$_3$](MnCl$_4$)$_2$Cl$_3$·6H$_2$O, contains a triiron core linked by a μ_3-bridging oxide ion. Each of the iron(III) ions has a distorted octahedral environment, being coordinated, in addition to the oxide ion, by four neutral betaine molecules and one water molecule. The N-alkylated α-amino acid betaine is present in the dipolar zwitterionic form and chelates pairs of Fe atoms at the vertices of the triangular [Fe$_3$O]$^{7+}$ ionic core. The Fe complex has a crystallographically imposed D3 symmetry. The water molecules fully exhaust their potential as hydrogen donors, forming a two-dimensional hydrogen-bond network in planes parallel to (001).

Comment

Within a project to study the structure and physical properties of low-dimensional magnetic compounds, we have synthesized the title compound, (I), which contains a trinuclear oxo-bridged complex of Fe^{III} with the N-alkylated α-amino acid betaine [Bet is trimethylglycine; IUPAC: 1-carboxy-N,N,N-trimethylmethanaminium inner salt] as chelating agent. It is well known that betaine chelates p-, d- and 4f-metals via the carboxy group and several crystal structures of coordination compounds of betaine have been reported (Chen & Mak, 1991; Chen et al., 1995). According to a recent search of the Cambridge Structural Database (CSD; release October 2000; Allen & Kennard, 1993), this paper reports the first crystal structure of a coordination compound of iron and betaine.

Trinuclear iron compounds are of interest because oxo-bridged polynuclear Fe^{III} centres have been found to perform important biological functions, such as oxygen storage and transport in a variety of proteins. These compounds initially attracted interest as a model for the unusual magnetic properties of ferritin, a family of iron-storage proteins that sequester iron inside a protein coat (Holt et al., 1974). The ferric core of ferritin exhibits superparamagnetism (Allen et al., 1998), a magnetic behaviour found in clusters with a large number of magnetic ions, where the thermal dependence of the magnetization in the paramagnetic region is similar to that of a classic ensemble of non-interacting moments. Due to a balance between the magnitude of the pairwise exchange interactions and the size of a given magnetic domain, the available orientations of the magnetic moments may be so close together as to appear continuous. Several studies have shown that not only the magnetic but also the spectroscopic, electronic and structural properties of compounds containing triangular oxo-bridged complexes of transition metal atoms are very interesting (Cannon & White, 1988). In particular, a lot of attention has been paid to mixed-valence trinuclear carboxylate complexes of iron with the general formula [Fe^{II}Fe^{III}O(RCO$_2$)$_6$(L)$_3$]·nS. These complexes are formed with a variety of carboxylate ligands (RCO$_2$), monodentate ligands (L), and solvate molecules (S) (Oh et al., 1984; Woehler, Wittebort et al., 1987; Sato et al., 1996). Focus has been on the interactions among the three Fe atoms via the bridging ligands, and the kinetics and mechanisms of electron transfer, which have been studied by several techniques, including IR spectroscopy, NMR, Mössbauer spectroscopy and neutron diffraction (Cannon et al., 1991).

(I)
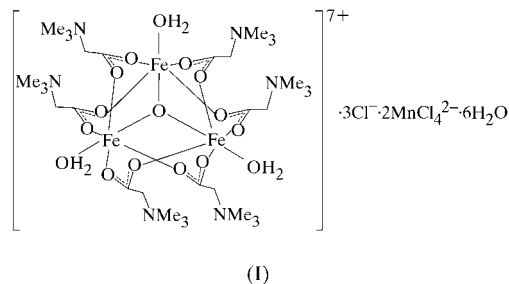
In mixed-valence iron acetate complexes and mono-oxidized biferrocene derivatives, phase transitions related to valence trapping have been observed at low temperature (Oh et al., 1984). The onset of such transitions appear to involve the co-operative effect of the dynamics of the ligand and/or solvate molecules (Woehler, Wittebort et al., 1987; Cannon et al., 1991). It has been found that the solvate molecules have a dramatic effect on the electron-transfer rate for a given mixed-valence complex, either by affecting the magnitude of the Fe$_3$O intermolecular interactions, or, in a more subtle way, by lowering the symmetry of the environment around the Fe$_3$O core (Woehler, Richard et al., 1987). It is well established that in both mixed-valence (Fe^{II}/Fe^{III}) and Fe^{III} compounds, the metal ions in the triiron oxo-centred units are antiferromagnetically coupled and spin frustration occurs due to the triangular geometry of the Fe$_3$O core. An equilateral triangular geometry is unstable and a lower energy is obtained by lifting the degeneracy of the ground state in what has been called a 'magnetic Jahn–Teller' effect (Cannon & White, 1988). In several crystallographic studies of carboxylate complexes of

oxo-centred trinuclear iron compounds with orthorhombic or monoclinic structures, a rather close non-crystallographic threefold symmetry of the complex was found, and in a few reported crystal structures, there is an exact crystallographically imposed C_3 or even higher D_{3h} symmetry. However, inelastic neutron-scattering experiments performed on two such compounds of trigonal symmetry indicate that the three magnetic coupling constants in the iron core are not equal (Cannon *et al.*, 1994). These inequalities may reflect the expected small structural differences in the metal environment due to the 'magnetic Jahn–Teller effect' and it has been argued that the crystal symmetry of these compounds might be higher than the molecular symmetry and correspond to an average disordered structure. Therefore, accurate structural data is demanded for this type of compound in order to understand their electronic and magnetic properties.

In the title compound, the $[Fe_3O(Bet)_6(H_2O)_3]^{7+}$ cation (Fig. 1) has a crystallographically imposed D_3 symmetry. The central $[Fe_3O]^{7+}$ ion and the O atoms of the coordinating water molecule, *trans* to the central oxide ion, are strictly planar. Each of the Fe^{III} ions is coordinated by four betaine molecules, one water molecule and the bridging oxide ion, in a slightly distorted octahedral environment. The complex ion has its charge balanced by three chlorine and two tetrachloromanganese(II) counter-ions. In addition, the structure contains six solvate water molecules per formula unit. Each pair of Fe^{III} ions is bridged by two betaine molecules related by a twofold axis *via* the carboxy groups, one above and another below the Fe_3O plane.

The coordination polyhedron of the Fe atoms is slightly distorted from ideal octahedral geometry, with the Fe atom lying 0.1651 (18) Å above the oxygen basal plane. The angles O4—Fe—O1 and O4—Fe—O2 deviate by 3.21 (7) and

6.22 (7)°, respectively, from the ideal value of 90°. The distances in the basal plane between the iron and the carboxy O atoms show a significant asymmetry [1.990 (2) and 2.051 (2) Å]. The shortest Fe⋯Fe distance is 3.3179 (9) Å, a value which is sufficiently large to preclude direct metal–metal bonding. The antiferromagnetic coupling between the moments of the metal ions in such triangular-bridged complexes is usually attributed to an indirect exchange mechanism *via* both the oxide ion and the carboxylate groups. The Fe—O distances are in the range 1.9156 (7)–2.051 (2) Å, the shortest distance being that to the central O^{2-} ion, which is believed to be the main magnetic superexchange pathway between the Fe atoms (Cannon *et al.*, 1994). The geometry of the inner core of the complex is similar to that in other carboxylate trinuclear complexes of Fe^{III}, such as $[Fe_3O(OOCCH_3)_6(H_2O)_3]Cl·6H_2O$ (Anso *et al.*, 1997) and $[Fe_3O(C_2H_5O_2N)_6(H_2O)_3](ClO_4)_7$ (Thundathil *et al.*, 1977).

The betaine molecules are present in the neutral zwitterionic form, featuring a strong dipole moment due to a tetravalent N atom carrying the positive charge and a negatively charged deprotonated carboxylic acid group. The carboxylate C—O distances are almost identical, with a value typical for a delocalized double bond and an O—C—O angle of 126.8 (3)°. The main skeleton of the betaine molecule defined by atoms C1, C2, N1 and C4 is planar, the deviations of these atoms from the least-squares plane being less than 0.006 (3) Å. The carboxylate group is only slightly rotated from this plane around the C1—C2 bond, by 2.9 (5)°. The C3 and C5 methyl groups lie above and below the plane of the skeleton at distances of 1.235 (7) and 1.210 (7) Å, respectively. The small asymmetry corresponds to a slight rotation of *ca* 1% of the trimethylammonium group around the C2—N1 bond. It is worthwhile mentioning that the value of the C2—N1—C4 angle [105.8 (3)°] is peculiar because it is not only shorter than the ideal tetrahedral value but also much shorter than that
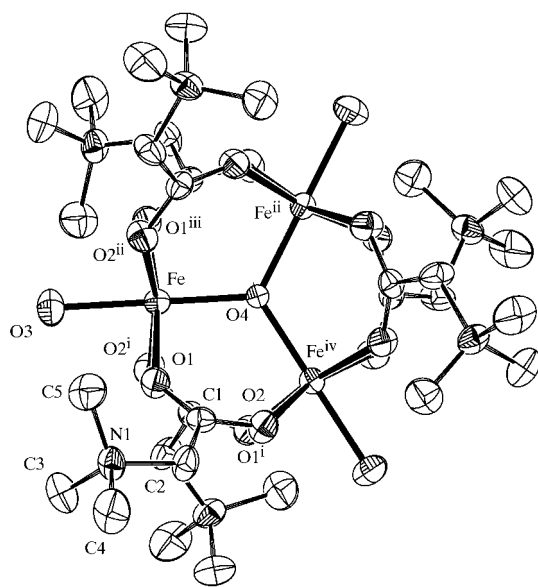

Figure 1
*ORTEP*II (Johnson, 1976) plot of the $[Fe_3O(Bet)_6(H_2O)_3]^{7+}$ cation. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are as in Table 1.
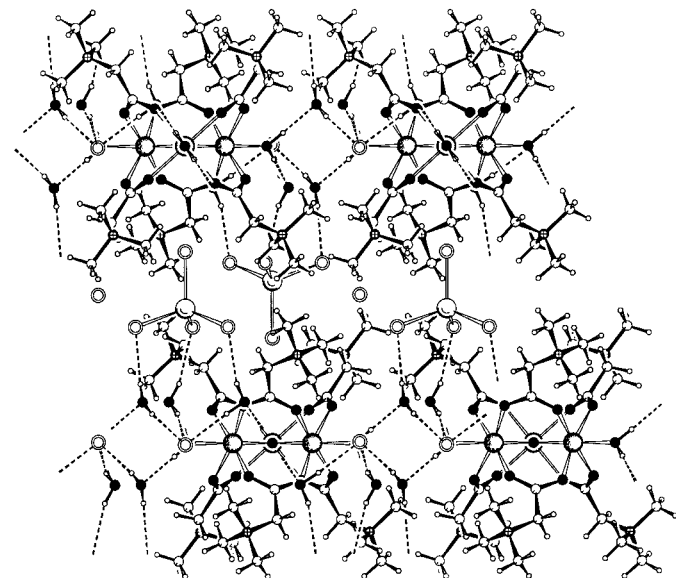

Figure 2
The hydrogen-bond pattern viewed along **a**.

observed in pure betaine (Viertorinne *et al.*, 1999), showing the flexibility of the amino acid molecule in adapting its shape to different crystal environments.

The tetrachloromanganese(II) ion has a crystallographically imposed C_3 symmetry, with the Mn and Cl2 atoms lying on the threefold axis. However, it features almost perfect *Td* symmetry. The maximum deviation of the Cl—Mn—Cl bond angle from the ideal tetrahedral value is 1.08 (4)° and the two symmetry-independent Mn—Cl bond lengths are equal within experimental error and compare well with typical values for this anion.

In addition to the chelating water molecules, the unit cell contains a total of 36 solvent water molecules, corresponding to six solvent molecules per formula unit. Such a high solvent content is not uncommon in this type of compound, which often have water contents as high as ten molecules per formula unit and for which zeolitic behaviour was reported (Cannon & White, 1988). The two symmetry-independent water molecules exhaust their full potential as hydrogen donors, forming a two-dimensional hydrogen-bond network. One of them (O3) lies on a binary axis and donates the H atoms to two symmetry-related water molecules occupying a general crystallographic position (O5). These water molecules, in turn, establish hydrogen bonds as donors to the isolated Cl⁻ ions and also to one of the Cl atoms of the tetrachloromanganate ion (Fig. 2). The resulting hydrogen-bond network extends in planes parallel to (001). It is remarkable that one of the isolated Cl⁻ ions accepts three H atoms from neighbouring water molecules, while the other ion does not establish any classical hydrogen bond.

Experimental

Hydrated iron chloride (5 mmol), hydrated manganese chloride (5 mmol) and betaine (20 mmol) were dissolved in a water/ethanol (50:50) solution. Metallic iron (2 mmol) and a few drops of HCl were added to the solution that was further dissolved in warm methanol. After a few months, good quality single crystals could be found in the inhomogeneous precipitate.

Crystal data

$[Fe_3O(C_5H_{11}NO_2)_6(H_2O)_3]$-	Mo $K\alpha$ radiation
$(MnCl_4)_2Cl_3\cdot6H_2O$	Cell parameters from 25
$M_r = 1548.41$	reflections
Hexagonal, $R\bar{3}c$	$\theta = 9.9–15.1°$
$a = 12.5921 (15)$ Å	$\mu = 1.49$ mm^{-1}
$c = 73.721 (7)$ Å	$T = 293 (2)$ K
$V = 10123 (2)$ Å^3	Prism, translucent light orange
$Z = 6$	$0.29 \times 0.25 \times 0.20$ mm
$D_x = 1.524$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffract-	$R_{int} = 0.044$
ometer	$\theta_{max} = 27.5°$
Profile data from ω scans	$h = -15 \rightarrow 0$
Absorption correction: ψ scan	$k = -12 \rightarrow 16$
(North *et al.*, 1968)	$l = -90 \rightarrow 94$
$T_{min} = 0.835$, $T_{max} = 0.912$	3 standard reflections
3330 measured reflections	frequency: 180 min
2570 independent reflections	intensity decay: 2.5%
1499 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 8.7323P]$
$wR(F^2) = 0.112$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
2570 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
126 parameters	$\Delta\rho_{min} = -0.57$ e Å^{-3}
H atoms: see below	

Table 1
Selected geometric parameters (Å, °).

Fe—O4	1.9156 (7)	Fe—O1	2.051 (2)
Fe—O2^i	1.990 (2)	Mn—Cl2	2.368 (2)
Fe—O3	2.025 (4)	Mn—Cl1	2.3699 (12)
O4—Fe—O2^i	96.22 (7)	O2^i—Fe—O1	92.22 (10)
O2^i—Fe—O2^{ii}	167.57 (14)	O2^{ii}—Fe—O1	87.09 (10)
O4—Fe—O2^{ii}	180.00 (18)	O3—Fe—O1	86.79 (7)
O2^i—Fe—O3	83.78 (7)	O1—Fe—O1^{iii}	173.59 (13)
O4—Fe—O1	93.21 (7)		
O2^i—Fe—O4—Fe^{ii}	129.24 (7)	O2^i—Fe—O4—Fe^{iv}	−50.75 (7)
O2^{ii}—Fe—O4—Fe^{ii}	−50.77 (7)	O2^{ii}—Fe—O4—Fe^{iv}	129.25 (7)
O1—Fe—O4—Fe^{ii}	−138.18 (7)	O1—Fe—O4—Fe^{iv}	41.84 (7)
O1^{iii}—Fe—O4—Fe^{ii}	41.82 (7)	O1^{iii}—Fe—O4—Fe^{iv}	−138.16 (7)

Symmetry codes: (i) $\frac{1}{3} + x - y, \frac{2}{3} - y, \frac{1}{6} - z$; (ii) $1 - y, x - y, z$; (iii) $\frac{1}{3} + y, x - \frac{1}{3}, \frac{1}{6} - z$; (iv) $1 - x + y, 1 - x, z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H31$\cdots$O5^i	0.86 (3)	1.83 (3)	2.690 (4)	178 (4)
O5—H51$\cdots$Cl3^{ii}	0.89 (3)	2.23 (4)	3.100 (4)	166 (6)
O5—H52$\cdots$Cl1^{iii}	0.87 (3)	2.43 (4)	3.269 (4)	163 (6)

Symmetry codes: (i) $-x + y, -x, z$; (ii) $\frac{1}{3} + y, \frac{2}{3} + x, \frac{1}{6} - z$; (iii) $x - y, x, -z$.

The H atoms of the water molecules were located in a difference Fourier map and refined with the O—H distances restrained to be equal with an effective s.u. of 0.03 Å and with an isotropic displacement parameter constrained to be 1.5 times larger than that of the parent O atom. The remaining H atoms were placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997) defaults. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that 2% of the unit-cell volume (194 Å^3) is available as additional potential solvent volume, but each of the voids (11 Å^3) is too small to accommodate an extra water molecule.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1445). Services for accessing these data are described at the back of the journal.

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