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A new core topology in hexanuclear iron(III) carboxylate chemistry: $[Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2](ClO_4)$ †

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The structural, spectroscopic, and magnetochemical characteristics of a new hexanuclear iron-oxo complex are reported. $[Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2]ClO_4\cdot\frac{1}{4}EtOH\cdot\frac{1}{4}H_2O$ (**3**$\cdot\frac{1}{4}EtOH\cdot\frac{1}{4}H_2O$) crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.524(1)$ Å, $b = 15.865(2)$ Å, $c = 17.029(2)$ Å, $\alpha = 65.92(1)°$, $\beta = 81.49(1)°$, $\gamma = 76.40(1)°$, $V = 2758$ Å^3, and $Z = 2$. The $[Fe_6O_3]^{12+}$ core of the cation contains an arrangement of six iron atoms not previously seen in iron-oxo compounds. In this arrangement, two $[Fe_3O]^{7+}$ triangular units are bridged by a distorted tetrahedral oxide ion. ^{1}H- and ^{2}H-NMR spectra are reported for two $[Fe_6O_3]^{12+}$ complexes, **3** and the 4,4′-Me$_2$bpy analog **4**, as well as $CD_3CO_2^-$ and/or $CD_3CD_2O^-$ derivatives of **3**. Assignment of the resonances was made based on the ^{1}H-NMR chemical shift data and changes seen in the ^{1}H- and ^{2}H-NMR spectra of the related deuterated complexes. The magnetic susceptibility of complex **3** was measured in the range of 5–300 K. The effective magnetic moment per molecule decreases gradually from 6.44 μ_B at 300 K to 3.31 μ_B at 70 K then more dramatically to 0.84 μ_B at 5 K, indicating a diamagnetic $S = 0$ ground state consistent with the expected presence of antiferromagnetic exchange interactions between the Fe^{III} ions.

Introduction

Polynuclear oxo-, hydroxo- and alkoxo-bridged iron clusters have received a great deal of attention in recent years, as a result of the role of these species in a number of biological systems.[1–5] The active sites of a variety of proteins such as hemerythrin, methane monooxygenase and ribonucleotide reducatase have been shown to contain diiron cores bridged by oxo or hydroxo ligands. The protein ferritin has also received attention, owing to the biological importance of the role of this protein in the storage and recycling of iron.[2,3,5–7] A variety of compounds of high metal nuclearity that model the storage of iron in the protein have been synthesized.[8–25]

Another interesting aspect of large polynuclear iron clusters is the potential for these clusters to possess large spin (S) values in their ground states, leading to the possibility of obtaining new examples of a cluster that will behave as a single-molecule-magnet (SMM) (*i.e.*, show a slow (ms) relaxation rate of the magnetization). Most complexes that function as SMMs identified to date contain manganese ions, although a few vanadium and iron complexes have also been shown to behave as SMMs.[26–31] Iron is a particularly interesting metal to investigate in this area, owing to the large number (five) of unpaired electrons on each Fe^{3+} ion ($S = 5/2$), a property which, for certain topologies, offers the potential to form clusters with large numbers of unpaired electrons, such as Fe$_{17}$ and Fe$_{19}$, one of which has a ground state spin value of $S = 33/2$.[25–27]

One approach to the synthesis of large iron-oxo complexes is the controlled hydrolysis of a ferric salt in the presence of carboxylate ligands.[8–11] A variety of polynuclear Fe complexes have been synthesized in this manner. A similar approach utilizes controlled alcoholysis reactions of simple salts or more complicated starting materials to achieve clusters of Fe$_6$, Fe$_7$, Fe$_{10}$ and Fe$_{12}$.[12–20]

In this paper, the products of the controlled alcoholysis of Fe$_4$ or Fe$_3$ complexes are presented. The structural, magnetochemical, and NMR properties of a new type of Fe$_6$ product are described and compared with the properties of the Fe$_4$ starting material.

Experimental

Syntheses

All manipulations were carried out under aerobic conditions using materials as received. $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ **1**, $[Fe_3O(O_2CCD_3)_6(H_2O)_3](NO_3)$ **1a**, $[Fe_3O(O_2CPh)_6(H_2O)_3](NO_3)$ **1b**, and $[Fe_4O_2(O_2CMe)_7(bpy)_2](ClO_4)$ **2** were prepared as described elsewhere.[32,33] Products were stored in a desiccator.

$[Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2](ClO_4)$ 3. *Method 1.* A brown solution of complex **1** (0.40 g, 0.61 mmol), bpy (0.10 g, 0.64 mmol), NaOEt (0.083 g, 1.2 mmol) and NaClO$_4$ (0.11 g, 0.90 mmol) in EtOH (100 mL, 100%) was stirred for 10 min, then allowed to stand uncovered at room temperature for one week. The dark brown crystalline solid (0.24 g, 56% yield) was separated by filtration from a dark brown solution, washed with 100% EtOH and dried under vacuum. Anal. Calc. (Found) for $C_{42}H_{55}ClFe_6N_4O_{28}$ **3**$\cdot H_2O$: C, 35.17 (35.24); H, 3.86 (4.09); N, 3.91 (3.81)%. IR examination confirmed this product to be identical with crystallographically-characterized complex **3** from Method 2.

Method 2. A concentrated solution of complex **2** in EtOH was allowed to stand at room temperature. The solution was periodically filtered to remove $[Fe(bpy)_3](ClO_4)_2$. After 5 months, brown crystals of **3**$\cdot\frac{1}{4}EtOH\cdot\frac{1}{4}H_2O$ of crystallographic quality were collected in very low yield. Selected IR data (cm^{-1}): 1576 (s), 1545 (s), 1496 (m), 1471 (m), 1444 (s), 1420 (s), 1106 (m), 1057 (m), 1026 (m), 898 (w), 768 (m), 735.9 (w), 706 (m, br), 658 (m), 621 (m), 554 (m, br), 489 (w,br).

$[Fe_6O_3(O_2CCD_3)_9(OEt)_2(bpy)_2](ClO_4)$ 3a. The corresponding d_3-OAc complex was prepared on a smaller scale in a manner

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† Electronic supplementary information (ESI) available: selected interatomic distances and angles for complex **3**. See http://www.rsc.org/suppdata/dt/b0/b006150f/

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analogous to complex **3** (Method 1), but using complex **1a** in place of **1**. The yield was 0.12 g (28%). IR examination confirmed this product to be complex **3a**, and ^{1}H-NMR examination confirmed it to be pure.

[$Fe_6O_3(O_2CCD_3)_9(OCD_2CD_3)_2(bpy)_2](ClO_4)$ 3b. A brown solution of complex **1a** (30 mg, 0.045 mmol) and bpy (7.0 mg, 0.045 mmol) in EtOD (3 mL, 100%) was treated with a solution of Na (2.0 mg, 0.087 mmol) in EtOD (2 mL, 100%) followed by addition of $NaClO_4$ (9.0 mg, 0.074 mmol). After being stirred for 10 min, the resulting solution was allowed to stand uncovered at room temperature for three days. A mixture of brown crystals and powder was recovered in low yield; crystals were handpicked for IR and ^{1}H-NMR examination, which established that they were complex **3b**.

[$Fe_6O_3(O_2CMe)_9(OEt)_2(4,4'\text{-}Me_2bpy)_2](ClO_4)$ 4. A brown solution of complex **1** (0.40 g, 0.61 mmol), 4,4′-Me_2bpy (0.11 g, 0.60 mmol), NaOEt (0.083 g, 1.2 mmol) and $NaClO_4$ (0.11 g, 0.90 mmol) in EtOH (100 mL, 100%) was stirred for 10 min, then allowed to stand uncovered at room temperature for two days. The brown microcrystalline solid (0.11 g, 24% yield) was washed with 100% EtOH and dried under vacuum. Anal. Calc. (Found) for $C_{46}H_{67}ClFe_6N_4O_{32}$ **4**·5H_2O: C, 35.45 (35.31); H, 4.33 (4.15); N, 3.59 (3.74)%. Selected IR data (cm^{-1}): 1579 (s, br), 1491 (m), 1446 (s, br), 1093 (m), 1050 (m), 1024 (m), 922 (m), 899 (w), 855 (w), 829 (m), 743 (w), 707 (m, br), 657 (m, br), 619 (m), 556 (m, br), 522 (w, br), 490 (w, br).

[$Fe_6O_3(O_2CPh)_9(OEt)_2(bpy)_2](ClO_4)$ 5. A brown solution of complex **1c** (0.31 g, 0.30 mmol), bpy (0.043 g, 0.28 mmol), NaOEt (0.042 g, 0.62 mmol) and $NaClO_4$ (0.076 g, 0.62 mmol) in EtOH (50 mL, 100%) was stirred for 10 min, then allowed to stand uncovered at room temperature for ten days. A mixture of powder and brown crystalline needles was separated by filtration from a dark brown solution. The solid was washed with 100% EtOH, the crystalline portion separated by decantation, and the crystals (0.055 g, 19% yield) collected by filtration and dried under vacuum. Anal. Calc. (Found) for $C_{87}H_{72}ClFe_6N_4O_{27.5}$ (**5**·0.5H_2O): C, 52.67 (52.71); H, 3.66 (3.58); N, 2.89 (2.89)%. Selected IR data (cm^{-1}): 1598.0 (s), 1556.5 (s), 1530 (s), 1493.0 (m), 1474.8 (m), 1414 (s, br), 1176 (m), 1157.7 (w), 1094.9 (m), 1068.8 (m), 1054.44 (m), 1025.6 (m), 898.7 (w, br), 840.3 (w), 817.7 (w), 767.9 (m), 718.8 (m, br), 686.9 (m), 674.2 (m), 655.2 (w), 634.5 (w), 622.9 (w), 597.2 (m, br), 472.8 (m, br).

X-Ray crystallography and solution of structures

Data were collected on a Bruker SMART 6000 sealed-tube system comprising a three-circle platform goniostat, an HOG crystal monochromator, a four kilopixel by four kilopixel single-chip CCD-based detector, a K761 high voltage generator, and a PC interface running Bruker's SMART software.[34] The detector to sample distance was 6.4 cm, with a take-off angle of 6.0°.

A suitable crystal was selected from the reaction solution; a 0.30 × 0.30 × 0.30 mm fragment was affixed to a glass fiber using silicone grease and then transferred to a goniostat where it was cooled to −165 °C for characterization and data collection. The Bruker SMART autoindexing program was used to determine that the crystal possessed no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement confirmed the choice of $P\bar{1}$.

Data were collected using the standard hemisphere setting for the SMART 6000. Data were integrated and merged using SAINT,[35] and the structure was solved using direct methods (SHELXTL)[36] and Fourier techniques. A slight disorder is present in one of the ethoxy groups (C(35)–C(36)) with two equal conformations (each with 50% occupancy) located and refined. In addition to the Fe_6 cation, a ClO_4^- anion was readily located as were a single atom assigned as the O of a H_2O with 25% occupancy, and a disordered EtOH molecule lying on an inversion center with approximately 25% total occupancy. A final difference Fourier map was essentially featureless, the largest peak being 0.57 e Å^{-3}. Table 1 lists the crystallographic data for **3**.

Table 1 Crystallographic data for [$Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2$]-($ClO_4$) **3**

Formula	$C_{42}H_{53}ClFe_6N_4O_{27}$ [a]
a/Å	11.524(1)
b/Å	15.865(2)
c/Å	17.029(2)
α/°	65.92(1)
β/°	81.49(1)
γ/°	76.40(1)
V/Å^3	2758
Z	2
Space group	$P\bar{1}$
T/°C	−165
λ/Å	0.71069 [b]
ρ_{calc}/g cm^{-3}	1.766
μ(Mo-Kα)/cm^{-1}	16.786
F_w/g mol^{-1}	1466.49
R (F_o) [c]	0.0375
R_w (F_o) [c]	0.0353

[a] Excluding ¼EtOH and ¼H_2O solvate molecules. [b] Graphite monochromator. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 1/\sigma^2(|F_o|)$.

CCDC reference number 186/2225.

See http://www.rsc.org/suppdata/dt/b0/b006150f/ for crystallographic files in .cif format.

Physical measurements

IR spectra were recorded on KBr pellets with a Nicolet Model 510P spectrophotometer. ^{1}H- and ^{2}H-NMR spectroscopy was performed on a 300 MHz Varian Gemini 2000 and 400 MHz Varian Inova spectrometers, respectively; chemical shifts are quoted on the δ scale (shifts downfield of TMS are positive). Variable-temperature magnetic susceptibility measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 Tesla (70 kOe) magnet. A diamagnetic correction to the observed susceptibility was applied using Pascal's constants.

Results and discussion

Syntheses

Much work has been done in the past which has been directed towards the synthesis of tetranuclear iron complexes with $[Fe_4O_2]^{8+}$ cores, and several of these "butterfly" complexes have been well characterized.[37] It has been previously noted that certain of these complexes undergo color changes in the presence of alcohols, but no study had been done of the product(s) of these reactions. In the light of recently published controlled alcoholysis reactions of tetranuclear manganese complexes,[38] it was of interest to investigate the nature of the alcoholysis reactions of $[Fe_4O_2]^{8+}$ butterfly complexes as a potential route to interesting new species.

When a concentrated ethanolic solution of [$Fe_4O_2(O_2CMe)_7$-$(bpy)_2$](ClO_4) at room temperature was monitored with time, a slow color change from green to red was observed. Red crystalline [$Fe(bpy)_3$](ClO_4)$_2$ slowly formed and it was periodically removed by decantation until no further red crystals were observed to form. Subsequent to this, brown crystals began to appear very slowly, and after a total reaction time of five months, these well-formed brown crystals were isolated. They were suitable for X-ray crystallographic analysis, and were structurally characterized as [$Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2$]-

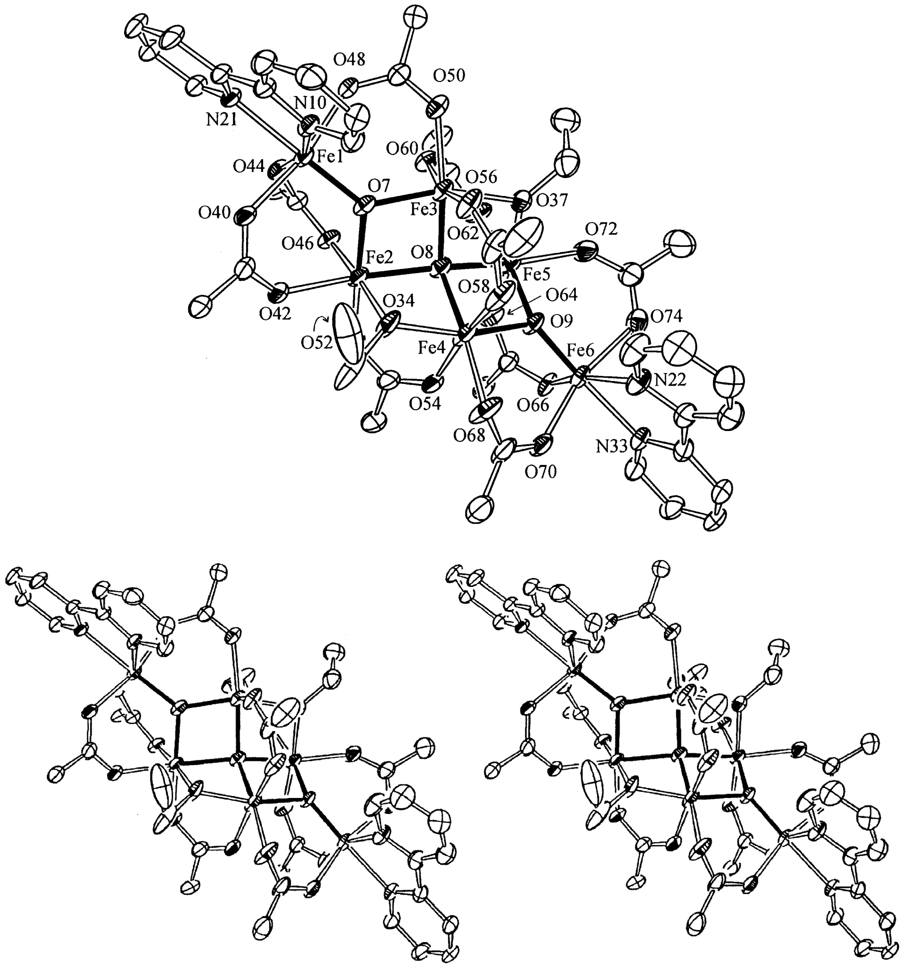


Fig. 1 ORTEP plot and stereoview of the $[Fe_6O_3(O_2CCH_3)_9(OCH_2CH_3)_2(bpy)_2]^+$ cation of complex **3**. Atoms are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity.

$(ClO_4)\cdot\frac{1}{4}EtOH\cdot\frac{1}{4}H_2O$ (**3**·¼EtOH·¼H_2O). A balanced alcoholysis equation cannot be obtained by assuming the formation of only the above two identified products, however, and there are probably a number of species in equilibrium in solution. It is likely that the formation of **3** is driven by the crystallization of sparingly soluble $[Fe(bpy)_3](ClO_4)_2$, which decreases the bpy:Fe ratio in solution and fosters formation of higher nuclearity species. The final filtrate is not colorless, indicating additional Fe-containing species in solution, as suggested by balanced eqn. (1).

$$3\,[Fe_4O_2(O_2CMe)_7(bpy)_2](ClO_4) + 2EtOH \xrightarrow{+e^-} [Fe(bpy)_3](ClO_4)_2 + [Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2](ClO_4) + 5Fe^{3+} + O^{2-} + 12MeCO_2^- + bpy + 2OH^- \qquad (1)$$

Once the existence of this new type of hexanuclear iron complex had been established, it was possible to design a rational synthesis that gave this complex in good yield (56%) in a much shorter reaction time (24 hours). In this improved procedure, an ethanolic solution of $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ was treated with bpy, two equivalents of NaOEt and $NaClO_4$. Exact stoichiometric ratios were initially used (as in eqn. (2)), but no

$$2[Fe_3O(O_2CMe)_6(H_2O)_3]^+ + 2bpy + 2EtO^- \longrightarrow [Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2]^+ + 3MeCO_2^- + 5H_2O + 2H^+ \qquad (2)$$

complex **3** was isolated under those conditions. It was found necessary to increase the amount of NaOEt used, and to keep the solution relatively dilute. Concentrated solutions gave the known $[Fe_4O_2(O_2CMe)_7(bpy)_2](ClO_4)$, in addition to the desired product. This new procedure also proved to be a very useful method for the synthesis of derivatives of complex **3**, and was employed for the 4,4′-Me_2bpy **4** and benzoate **5** versions, as well as the deuterated analogues **3a** (O_2CCD_3) and **3b** (O_2CCD_3/OCD_2CD_3).

Description of structure

A labeled ORTEP[49] plot and stereopair of complex **3** are depicted in Fig. 1. The dimensions of the core are summarized conveniently in Fig. 2. Complex **3**·¼EtOH·¼H_2O crystallizes in the triclinic spacegroup $P\bar{1}$. The cation contains an unusual $[Fe_6(\mu_4\text{-}O)(\mu_3\text{-}O)_2]^{12+}$ core comprising two linked Fe_3O units; a distorted tetrahedral oxide, three acetate and two ethoxide ligands bridge the two Fe_3 halves of the complex, and a distorted trigonal planar oxide and three acetate ligands bridge within the Fe_3 units at each end. Each iron atom is six-coordinate in a distorted octahedral environment; iron atoms Fe(1) and Fe(6) are bound to the chelating bpy ligands.

The structure of this complex is related to that of $[Fe_4O_2(O_2CMe)_7(bpy)_2](ClO_4)$ **2**[33] from which **3** can be synthesized in Method 2. Both complexes have identical connectivity around the μ_3-oxide ligands, as shown below; the difference lies in the central core. The latter of the butterfly complex **2** consists of an acetate group bridging the two "body" iron atoms (Fe_b). The central $[Fe_6O_3]$ core of complex **3** can be structurally achieved by inserting an [FeOFe] group into the core of complex **2**, and adding an additional two bridging acetate and two bridging ethoxide ligands. Overall, both **2** and **3** can be described as being composed of two $[Fe_3O]$ oxide-centred triangular units: **2**

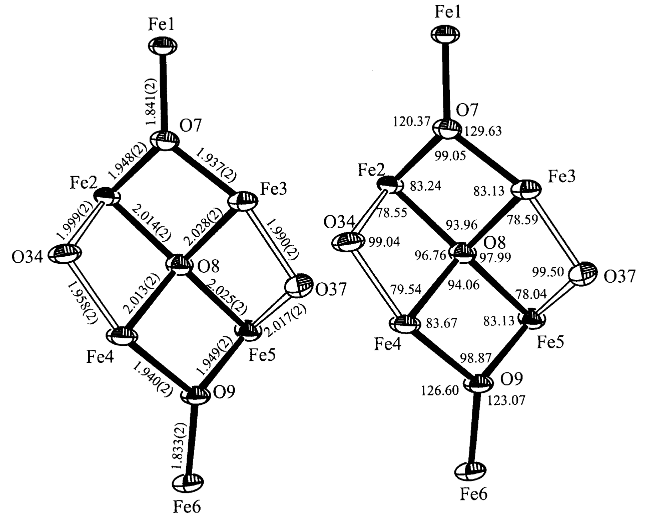
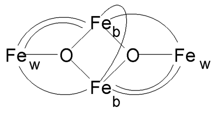


Fig. 2 The $[Fe_6O_3]^{12+}$ core showing interatomic separations (Å) and angles (°).



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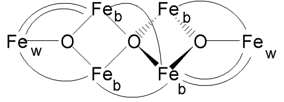


3

contains two edge-fused $[Fe_3O]$ units whereas **3** contains two oxide-bridged $[Fe_3O]$ units.

As in complex **2**, the central iron atoms (Fe_b) in **3** are bridged by two oxide ions, whereas the wingtip ions at the ends (Fe_w) have only a single oxide bridge, resulting in a similar shorter separation between the central iron atoms in the same half of the complex ($Fe_b \cdots Fe_b$ = 2.954 Å in **3** and 2.855 Å in **2**) compared with the body-to-wingtip separation (average $Fe_b \cdots Fe_w$ = 3.351 Å in **3** and 3.372 Å in **2**). The μ_3-O atoms bridge somewhat asymmetrically; the bonds to the wingtip iron atoms (Fe6–O9, 1.833(2) Å and Fe1–O7, 1.841(2) Å) are shorter than the bonds to body iron atoms (Fe5–O9, 1.949(2) Å; Fe4–O9, 1.940(2) Å; Fe3–O7, 1.937(2) Å; Fe2–O7, 1.948(2) Å). The asymmetry in the $Fe \cdots Fe$ distances and Fe–O distances within the Fe_3O unit is paralleled in the Fe–O–Fe angles within this unit: the average internal Fe–O–Fe angle (*e.g.*, Fe5–O9–Fe4) is 99.0°, while the average external Fe–O–Fe angle (*e.g.* Fe1–O7–Fe2) is noticeably larger at 125°. These trends are all similar to those seen in complex **2**, and these structural similarities between **2** and **3** are likely the cause of the similar magnetic properties (*vide infra*).

Not found in the core of complex **2** is the severely distorted tetrahedral oxygen atom that bridges the two halves of the cation of **3**. The Fe–μ_4-O bond distances are all similar, ranging from 2.013 to 2.028 Å (average 2.020 Å), which are significantly greater that the Fe–μ_3-O bond distances, as expected. The distortion from tetrahedral geometry is caused by the bridging EtO^- groups and the unique $MeCO_2^-$ group bridging Fe(3) and Fe(4), and this is reflected in both the $Fe \cdots Fe$ distances and the Fe–O–Fe angles about the μ_4-oxygen atom. The two long $Fe \cdots Fe$ distances correlate with large bond angles ($Fe(2) \cdots Fe(5)$, 3.957 Å and Fe(2)–O(8)–Fe(5), 156.87°; $Fe(3) \cdots Fe(4)$, 3.511 Å and Fe(3)–O(8)–Fe(4), 120.68°), while the two shorter $Fe \cdots Fe$ distances correlate with smaller bond angles ($Fe(2) \cdots Fe(4)$, 3.010 Å and Fe(2)–O(8)–Fe(4), 96.76°; $Fe(3) \cdots Fe(5)$, 3.058 Å and Fe(3)–O(8)–Fe(5), 97.99°). The complete cation has virtual C_2 symmetry.

There are to date no hexanuclear transition metal complexes that contain the same type of $[M_6O_3]$ core that appears in **3**, and in fact, iron complexes with a μ_4-oxide ligand are relatively rare. The oxygen atoms in four such complexes, $[Fe_6(\mu_4\text{-}O)_2(\mu\text{-}OMe)_8(OMe)_4(tren)_2]^{2+}$ [13] (tren = tris(2-aminoethyl)amine), $[Fe_{10}Cl_8O_4(OMe)_{14}(MeOH)_6]$,[17] $[Fe_8(\mu_4\text{-}O)_4(O_2CPh)_{12}(OCH_2Bu^t)_2(Bu^tCH_2OH)_2]$[39] and $[Fe_{10}(\mu_4\text{-}O)_4(OMe)_{10}(dbm)_6]$ (dbm^- is the anion of dibenzoylmethane),[16] are in distorted tetrahedral environments and similarly possess a range of Fe–O–Fe angles about the μ_4-oxide ion. The Fe–μ_4-O bond distances, however, are in a much larger range of 1.9 to 2.2 Å in these complexes, compared with the fairly small deviations in **3**, except for $[Fe_8O_4(O_2CPh)_{12}(OR)_2(ROH)_2]$ for which the range is an intermediate 1.978(2)–2.029(2) Å. In $[Fe_{16}M(\mu_4\text{-}O)_6(\mu_3\text{-}O)_4(OH)_{10}(O_2CPh)_{20}]$,[11] the μ_4-oxide atoms are bound to the central divalent heterometal, and in $[Fe_8(\mu_4\text{-}O)(\mu_3\text{-}O)_4(O_2CMe)_8(tren)_4]^{6+}$, the μ_4-oxide is square planar.[9]

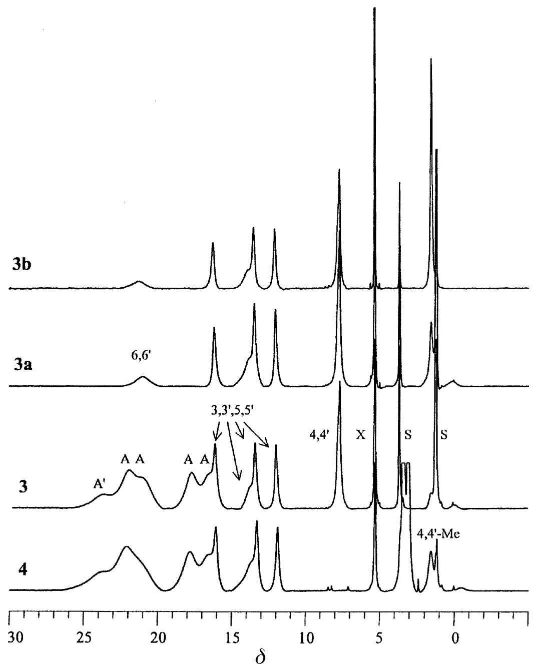


Fig. 3 ^{1}H-NMR spectra of complex **4** (bottom), **3** (second from bottom), **3a** (third from bottom), and **3b** (top). See text for experimental details and assignment of resonances. X = $CHDCl_2$, S = EtOH solvent of crystallization.

^{1}H- and ^{2}H-NMR spectroscopy

An NMR study of complexes **3** and **4** has been carried out in dichloromethane, and these spectra are compared with those previously reported for complex **2**.[33] In Figs. 3 and 4 are shown the spectra recorded for complexes **3**, **3a**, **3b** and **4**; the measured chemical shifts are collected in Table 2. The spectra all display broadened and shifted resonances, features typical of paramagnetic NMR. Nevertheless, all the peaks were located in either the ^{1}H- or ^{2}H-NMR spectra, or both, and all of the peaks were assigned, once all the spectra were compared. The number of resonances expected for complex **3**, based on its virtual C_2 solid-state symmetry, is as follows: eight from the bpy groups, five from the acetate groups, and three from the ethoxide groups. The five acetate peaks are expected to appear in a 1 : 2 : 2 : 2 : 2 ratio; the peaks marked A and A′ in Fig. 3 correspond to the acetate protons, since these peaks do not appear in the ^{1}H spectra of the deuterated analogues **3a** and **3b** (Fig. 3, top two spectra), but do appear in the ^{2}H spectra of the latter (Fig. 4). The peak of lowest intensity at 23.7 ppm (A′) is assigned to the unique acetate group bridging the two central iron atoms, Fe3 and Fe4. The other peaks are all about twice as intense as the single unique acetate resonance, and correspond to the other eight acetate ligands.

The remaining resonances correspond to either the bpy or ethoxide protons. Comparison of the ^{1}H spectra of **3a** (containing resonances from both bpy and ethoxide) and **3b** (with resonances from bpy only) (Fig. 3, top two spectra) shows no

Table 2 ^{1}H- and ^{2}H-NMR data[a] for $[Fe_6O_3(O_2CR)_9(OEt)_2(4,4\text{-}X_2bpy)_2](ClO_4)$

Compound	O_2CR	OCH_2CH_3	bpy
3 $R = CH_3$ $X = H$	23.7, 22.0, 21.1, 17.8, 16.7	—	(3,5): 16.19, 14.05, 13.45, 12.03, (4): 7.70
4 $R = CH_3$ $X = CH_3$	23.6, 21.9, 20.8, 17.7, 16.5	—	(3,5): 16.06, 13.6, 13.29, 11.89; (4,4′-Me): 3.42, 3.09
3a $R = CD_3$ $X = H$	^{2}H: 23.42, 21.67, 20.46, 17.48, 16.25	—	^{1}H: (6): 21.18; (3,5): 16.18, 14.0, 13.45, 12.03; (4): 7.67
3b $R = CD_3$ $X = H$ OCD_2CD_3	^{2}H: 23.34, 21.63, 20.41, 17.44, 16.27	^{2}H: (CD_3): 13.98; (CD_2): 244, 240	^{1}H: (6): 21.02; (3,5): 16.18, 13.8, 13.46, 12.05; (4): 7.79

[a] In dichloromethane at ≈23 °C. All values in ppm.

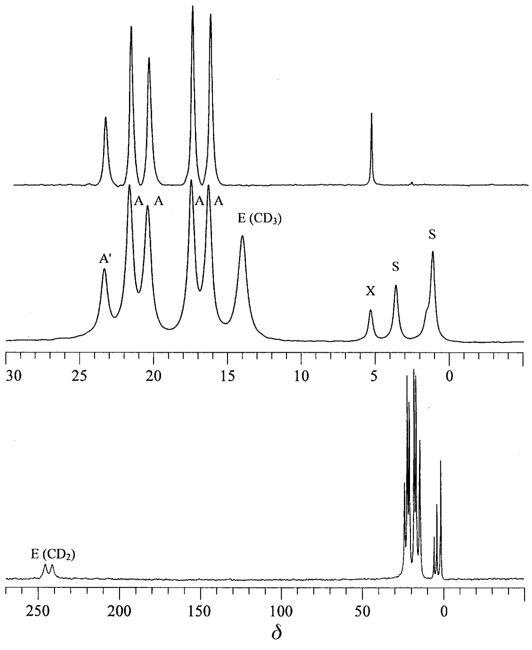


Fig. 4 ^{2}H-NMR spectra of complex **3a** (top), and **3b** (middle and bottom). See text for experimental details and assignment of resonances. $X = CHDCl_2$, $S = CD_3CD_2OD$ solvent of crystallization, E = bound $CD_3CD_2O^-$, $A = CD_3CO_2^-$.

obvious differences. Thus, the six peaks in **3a** must be due to the bpy protons. The peak at 7.70 ppm that is removed in the spectrum of complex **4** (Fig. 3, bottom) is assigned as from the 4,4′ protons, and the new peaks at 3.42 and 3.09 ppm must be from the 4,4′-Me protons. The 7.70 ppm peak corresponds to both 4,4′ protons: it is double the intensity of the smaller signals, and in fact, a shoulder is seen on close inspection, suggesting two separate but poorly-resolved resonances at this position. The four sharper peaks are assigned to the 3, 3′, 5, 5′ protons. These peaks have similar widths, consistent with their similar distances from the metal centers (5.041 to 5.195 Å), making specific assignment of these resonances difficult. The broadest resonance at 21.18 (obscured by the acetate protons in **3**) must be due to one of the 6,6′ protons, since they are the closest to the metal center (3.138 to 3.189 Å). The second resonance from the 6,6′ protons is likely obscured by a bpy resonance.

The resonances from the ethoxide protons are seen only in the ^{2}H-NMR spectrum of **3b** (Fig. 4), where all linewidths are decreased compared with the corresponding ^{1}H-NMR linewidths. The resonance at 13.98 ppm is assigned to the methyl group, since it is of equal intensity to the acetate (A) resonances. This CH_3 signal is obscured by bpy resonances in the ^{1}H-NMR spectra. The CD_2 resonance is observed as two broad signals at 244 and 240 ppm. The presence of two signals correlates with the absence of a mirror plane through O(34), O(8) and O(37), causing these protons to be diastereotopic; the presence of a C_2 rotation axis, however, causes the deuterium atoms on one ethoxide to become equivalent with the deuterium atoms on the symmetry-related ethoxide group. The broadness of these signals is such that the corresponding CH_2 resonances are broadened beyond detection in the ^{1}H-NMR spectra. The source of the extreme broadness and chemical shift is the proximity of these nuclei to all six iron atoms; each proton has two short contacts of 3.5 Å and four long contacts of 5.8 Å.

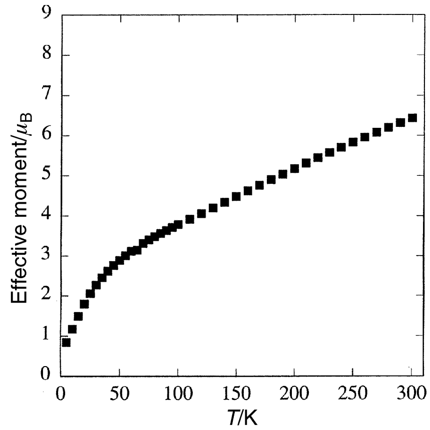
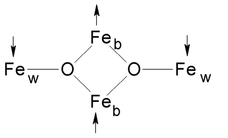


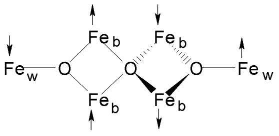
Fig. 5 Plot of the effective magnetic moment of a crystalline sample of $3\cdot H_2O$ as a function of temperature.

Magnetochemistry

The magnetic susceptibility of complex **3** was measured in the range of 5.00–300.0 K. A plot of the effective magnetic moment per molecule is given in Fig. 5. The effective magnetic moment (μ_{eff}) and $\chi_m T$ values per Fe_6 decrease gradually from 6.44 μ_B and 5.18 cm^3 K mol^{-1} at 300 K to 3.31 μ_B and 1.37 cm^3 K mol^{-1} at 70 K, then more dramatically to an essentially diamagnetic value of 0.84 μ_B and 0.09 cm^3 K mol^{-1} at 5 K. The 300 K values are considerably less than the 14.5 μ_B and 26.3 cm^3 K mol^{-1} expected for a hexanuclear species containing non-interacting Fe^{III} ($S = 5/2$) ions, suggesting the presence of relatively strong antiferromagnetic exchange interactions in **3**. The rapidly decreasing shape of the curve at the lowest temperatures is strongly suggestive of an $S = 0$ ground state. The $S = 0$ ground state of the Fe_6 cation in **3** is not unexpected, given that this is the most common ground state for Fe^{III}_x clusters where x is an even number. In fact, the previously characterized cation in **2** was shown to have an $S = 0$ ground state. Some important exceptions, however, include $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ ($S = 10$),[40] $[Fe_4(OMe)_6(dpm)_6]$ ($S = 5$; dpm$^-$ is the anion of dipivaloylmethane)[41] and $[Fe_6O_2(OH)_2(O_2CMe)_{10}(hmp)_2]$ ($S = 5$; hmp is the anion of 2-(hydroxymethyl)pyridine),[42] where the non-zero ground state is caused by spin frustration effects induced by the architecture of these complexes.

The cation of **3** presents an interesting geometry, where two Fe_3O triangular units are intimately connected through a μ_4-oxo bridge, and it is possible to rationalize the magnetic interactions by considering this geometry. Previous studies of $[Fe_3O]^{7+}$ complexes have established that competing antiferromagnetic interactions exist that result in spin frustration and distortions away from equilateral symmetry assignable to the magnetic Jahn–Teller effect.[43–47] The interaction between two such $[Fe_3O]$ triangular units through the μ_4-oxo bridge in **3** results in a system with six non-equivalent J values for the $[Fe_2(\mu_3\text{-}O)(\mu\text{-}MeCO_2)]$, $[Fe_2(\mu_3\text{-}O)(\mu\text{-}MeCO_2)_2]$, $[Fe_2(\mu_3\text{-}O)(\mu_4\text{-}O)]$, $[Fe_2(\mu_4\text{-}O)(\mu\text{-}OEt)(\mu\text{-}MeCO_2)]$, $[Fe_2(\mu_4\text{-}O)(\mu\text{-}MeCO_2)]$ and $[Fe_2(\mu_4\text{-}O)]$ pairwise interactions. Unfortunately, a detailed theoretical analysis of the susceptibility data *via* the Kambe method[48] was not feasible due to the complex architecture of the Fe_6 core, whose virtual C_2 core symmetry still involves six, non-equivalent J values, and a multiplicity of 46,656 for six atoms each of $S = 5/2$. Even assuming D_2 core symmetry simplifies the problem only slightly to four J values. A matrix diagonalization approach would involve a $46{,}656 \times 46{,}656$ matrix, and was not attempted. Qualitatively, however, the $S = 0$ ground state of **3** can readily be rationalized. In fact, given the structural similarity between **2** and **3**, it is instructive to note that **2** also has an $S = 0$ ground state. In the latter, it has been shown that the four antiferromagnetic J_{wb} interactions frustrate the J_{bb} interaction (J_{wb} and J_{bb} are the wingtip–body (Fe_w–Fe_b) and body–body (Fe_b–Fe_b) interactions, respectively) leading to the $S = 0$ ground state *via* the spin alignments shown, *i.e.*, the Fe_b spins are parallel in the ground state even though the J_{bb} parameter is most likely negative (antiferromagnetic).[33] In fact, the precise value of J_{bb} could not be determined in **2** because the energies of spin states populated in the 5–300 K range employed were determined only by J_{wb}. It is likely that a similar frustration of the analogous J_{bb} interactions of the $[Fe_2(\mu_3\text{-}O)(\mu_4\text{-}O)]$ pairs in **3** is occurring, as a result of the many antiferromagnetic J_{wb} interactions and J_{bb} interactions of the $[Fe_2(\mu_4\text{-}O)(\mu\text{-}OEt)]$, $[Fe_2(\mu_4\text{-}O)]$ and $[Fe_2(\mu_4\text{-}O)(\mu\text{-}MeCO_2)]$ pairs. Thus, the $S = 0$ ground state of **3** can be rationalized as shown, where a parallel alignment of central Fe_b–Fe_b spins is enforced, as in **2**, by the many competing antiferromagnetic interactions.





Conclusions

Slow hydrolysis of the butterfly complex $[Fe_4O_2(O_2CMe)_7(bpy)_2]^+$ leads to a low yield of a new Fe^{III} cluster $[Fe_6O_3(O_2CMe)_9(OEt)_2(bpy)_2](ClO_4)$ **3**. As often is the case, once the identity of a product has been obtained, a more rational preparative method can be devised, and this has indeed been accomplished for **3**. The procedure gives the product in good yield and is readily amenable to preparation of derivatives of **3**.

The ^1H- and ^2H-NMR studies confirm that **3** is not merely a solid-state curio, but instead retains its structural integrity on dissolution, in dichloromethane at least, opening up the potential for further reactivity studies. The cluster exhibits a variable-temperature magnetic susceptibility consistent with a singlet spin ground state and thermally-populated $S \neq 0$ excited states in the 5–300 K temperature range. The $S = 0$ ground state is consistent with the expected antiferromagnetic exchange interactions between the Fe^{III} ions and an extended Fe_6 topology that does not introduce large amounts of spin frustration.

The identification of **3** reinforces a belief that, as seen elsewhere, the introduction of alkoxide ligands can lead to new Fe_x topologies not seen or accessible with oxide and carboxylate ligands alone. This has led to further new and novel complexes currently being characterized and which will be reported soon.

Acknowledgements

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