

# Preparation and properties of new Fe<sub>6</sub> and Fe<sub>8</sub> clusters of iron(III) with tripodal ligands

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The syntheses, structures and magnetic properties are reported of new iron(III) complexes with Fe<sub>6</sub> wheel and Fe<sub>8</sub> cage topologies, and containing tripodal ligands. The compound [Fe<sub>8</sub>O<sub>3</sub>(O<sub>2</sub>CPh)<sub>9</sub>(tea)(teaH<sub>3</sub>)<sub>3</sub>]·MeCN (**1**·MeCN), where teaH<sub>3</sub> is triethanolamine, was obtained from the reaction of two equivalents of teaH<sub>3</sub> with [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](O<sub>2</sub>CPh) in MeCN. Similarly, the compound [Fe<sub>6</sub>(bic)<sub>6</sub>]·4H<sub>2</sub>O·4MeOH (**2**·4H<sub>2</sub>O·4MeOH), where bicH<sub>3</sub> is bicine, was prepared by the analogous reaction but with two equivalents of bicine. Variable-temperature solid-state magnetic susceptibility studies of **1** and **2** in the temperature range 5.00–300 K reveal that both complexes possess *S* = 0 ground state spins, consistent with the expected antiferromagnetic exchange interactions between the constituent iron(III) ions.

## Introduction

There continues to be a great interest in the synthesis and study of polynuclear metal clusters containing paramagnetic metal ions. There are various reasons for this, not least of which is the aesthetically pleasing nature of many of these species. But from an applications point of view, efforts in this area are part of the continuing search for new examples of molecular species that can function as nanoscale magnetic particles, or so-named single-molecule magnets (SMMs).<sup>1</sup> These zero-dimensional systems display slow relaxation of their magnetisation vector as a result of the combination of a large ground state spin (*S*) and an Ising (or easy-axis) type of magnetoanisotropy.<sup>1a</sup> Thus, such molecules exhibit magnetization hysteresis loops, the classical behaviour of a magnet. The most famous and well-studied examples of SMMs are the [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] complexes with *S* = 10.<sup>1</sup> We and others have developed many methods in the past that allow the synthesis of 3d metal clusters of various nuclearities,<sup>2</sup> and some of these have proven to be SMMs.<sup>1,2g-n</sup>

As part of our continuing search for new preparative routes to high nuclearity species, we have recently turned our attention to polydentate, tripodal ligands. Among the various such organic species we are employing are triethanolamine (teaH<sub>3</sub>) and bicine (bicH<sub>3</sub>), whose structures are shown in Scheme 1. Tripodal ligands with a central nitrogen atom such as deprotonated nitrilotriacetic acid (ntaH<sub>3</sub>)<sup>3</sup> and triethanolamine (teaH<sub>3</sub>)<sup>4</sup> have been used previously on several occasions in inorganic synthesis, whereas there are only a very few examples of compounds obtained with bicH<sub>3</sub>.<sup>5</sup> Notwithstanding these previously published compounds, we believed that both teaH<sub>3</sub> and bicH<sub>3</sub> still possessed great potential as a route to new and potentially interesting new metal cluster compounds.

In iron(III) chemistry, we have in the past found that a convenient route to cluster products has been to react the trinuclear

[Fe<sub>3</sub>O(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub>]<sup>6</sup> complexes containing the triangular, oxide-centred [Fe<sub>3</sub>(μ<sub>3</sub>-O)] core with a suitably chosen chelate ligand. For example, with 2-(hydroxymethyl)pyridine (hmpH), this leads cleanly to Fe<sub>6</sub> clusters of formula [Fe<sub>6</sub>O<sub>2</sub>(O<sub>2</sub>CR)<sub>6</sub>(hmp)<sub>6</sub>].<sup>7</sup> The reactions of teaH<sub>3</sub> and bicH<sub>3</sub> with [Fe<sub>3</sub>O(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub>] complexes have never been reported to our knowledge, and this thus seemed an attractive potential route into new iron(III) cluster chemistry. This has proven to be the case. We herein report the syntheses, structures and magnetic properties of two new hexanuclear and octanuclear iron(III) complexes that represent the initial products of our efforts in this area.

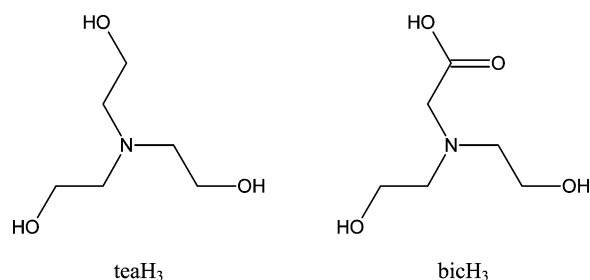
## Experimental

### Syntheses

All reagents were used as received (Aldrich). [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](O<sub>2</sub>CPh) was prepared using the procedure previously reported.<sup>8</sup>

**[Fe<sub>8</sub>O<sub>3</sub>(O<sub>2</sub>CPh)<sub>9</sub>(tea)(teaH<sub>3</sub>)<sub>3</sub>] (**1**).** To an orange solution of [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](O<sub>2</sub>CPh) (0.27 g, 0.25 mmol) in MeCN (25 ml) was added with stirring a solution of teaH<sub>3</sub> (0.075 g, 0.50 mmol) in MeCN (25 ml). The resultant solution was stirred for a further 15 min, filtered, and the filtrate left undisturbed at ambient temperature. After two weeks, the X-ray quality red-orange crystals of **1**·MeCN that had formed were collected by filtration, washed with MeCN, and dried *in vacuo*. Yield 45%. Calc. (Found) for **1**·MeCN: C, 48.29 (48.61); H, 4.51 (4.82); N, 3.16 (2.82)%. Selected IR data (cm<sup>-1</sup>): 3414 (br), 2856 (s), 1600 (m), 1566 (m), 1403 (w), 1341 (m), 1166 (s), 1070 (m), 913 (s), 715 (m), 670 (w).

**[Fe<sub>6</sub>(bic)<sub>6</sub>] (**2**).** To an orange solution of [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](O<sub>2</sub>CPh) (0.27 g, 0.25 mmol) in MeCN (25 ml) was added with stirring a solution of bicine (0.082 g, 0.50 mmol) in MeCN (25 ml). The resulting pale yellow solution slowly produced a precipitate as it was stirred overnight at ambient temperature. The precipitate was collected by filtration, washed with MeCN, and then redissolved in MeOH–CH<sub>2</sub>Cl<sub>2</sub> (1 : 1). The resulting clear solution was layered with Et<sub>2</sub>O and left at ambient temperature. After one week, the X-ray quality yellow-green crystals of **2**·4H<sub>2</sub>O·4MeOH that had slowly formed were collected by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub>, and dried *in vacuo*. The yield was 38%. Calc. (Found) for **2**·4H<sub>2</sub>O·4MeOH: C, 32.11 (31.80); H, 5.65 (5.39); N, 5.61 (5.48)%. Selected IR data



Scheme 1

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**Table 1** Crystallographic data for **1**·MeCN and **2**·4H<sub>2</sub>O·4MeOH

Empirical formula	C <sub>89</sub> H <sub>99</sub> Fe <sub>8</sub> N <sub>5</sub> O <sub>33</sub>	C <sub>40</sub> H <sub>84</sub> Fe <sub>6</sub> N <sub>6</sub> O <sub>32</sub>
<i>M<sub>r</sub></i>	2213.53	1496.23
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2/c</i>
<i>a</i> /Å	18.1207(10)	11.5538(6)
<i>b</i> /Å	27.2142(14)	11.5495(6)
<i>c</i> /Å	19.3376(10)	22.3761(12)
$\beta$ /°	105.881(2)	104.724(2)
<i>V</i> /Å <sup>3</sup>	9172.2(8)	2887.8(3)
<i>Z</i>	4	2
<i>T</i> /K	173(2)	173(2)
Radiation	Mo-K $\alpha$	Mo-K $\alpha$
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.603	1.721
$\mu$ /mm <sup>-1</sup>	1.316	1.566
<i>R</i> <sub>1</sub> <sup>a,b</sup>	5.18	3.31
<i>wR</i> <sub>2</sub> <sup>a,c</sup>	9.08	8.51

<sup>a</sup>  $I > 2\sigma(I)$ . <sup>b</sup>  $R_1 = 100\sum(|F_o| - |F_c|)/\sum|F_o|$ . <sup>c</sup>  $wR_2 = 100[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]]$ , where  $p = [\max(F_o^2, 0) + 2F_c^2]/3$ .

(cm<sup>-1</sup>): 3416 (br), 2930 (m), 2880 (m), 1652 (m), 1464 (m), 1344 (m), 1080 (m), 1014 (s), 910 (m), 458 (w).

### X-Ray crystallography and solution of structure

Data were collected using a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilising Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Suitable crystals of **1**·MeCN and **2**·4H<sub>2</sub>O·4MeOH were attached to glass fibres using silicone grease and transferred to a goniostat where they were cooled to 173 K for data collection. An initial search of reciprocal space revealed a monoclinic cell group for both **1** and **2**; the choices of space group *P2<sub>1</sub>/n* and *P2/c*, respectively, were confirmed by the subsequent solution and refinement of the structures. Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the  $\omega$ -scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on *I* was <1%). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structures were solved by direct methods in SHELXL<sup>9a</sup> and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. The asymmetric units consists of the complete Fe<sub>8</sub> cluster and one MeCN molecule of crystallisation for compound **1**, and half the Fe<sub>6</sub> cluster, two MeOH and two H<sub>2</sub>O molecules for compound **2**. For compound **2**, all solvent molecules were badly disordered and could not be modeled properly, thus the SQUEEZE program, a part of the PLATON<sup>9b</sup> package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

For compound **1**, a total of 1220 parameters were included in the structure refinement on *F*<sup>2</sup> using 80936 reflections with  $I > 2\sigma(I)$  to yield *R*<sub>1</sub> and *wR*<sub>2</sub> of 5.18 and 9.08%, respectively. For compound **2**, a total of 325 parameters were included in the structure refinement on *F*<sup>2</sup> using 24572 reflections with  $I > 2\sigma(I)$  to yield *R*<sub>1</sub> and *wR*<sub>2</sub> of 3.31 and 8.51%, respectively. Unit cell data and details of the structure refinements are listed in Table 1.

CCDC reference numbers 217872 and 217873 for **1**·MeCN and **2**·4H<sub>2</sub>O·4MeOH, respectively.

See <http://www.rsc.org/suppdata/dt/b3/b310030h/> for crystallographic data in CIF or other electronic format.

### Other studies

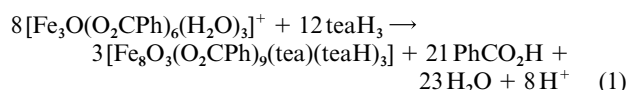
Elemental analysis (C, H and N) were performed by the in-house facilities of the University of Florida Chemistry Department. Infrared spectra were recorded in the solid state

(KBr pellets) on a Nicolet Nexus 670 FTIR spectrometer in the 400–4000 cm<sup>-1</sup> range. Variable-temperature dc magnetic susceptibility data down to 5.0 K were collected using a Quantum Design MPMS-XL SQUID susceptometer equipped with a 7 Tesla dc magnet at the University of Florida. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibility to give the molar magnetic susceptibility ( $\chi_M$ ).

## Results and discussion

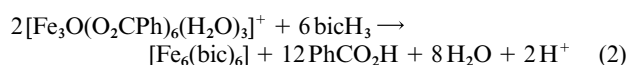
### Syntheses

A convenient synthetic procedure that we have used on a regular basis to prepare higher nuclearity clusters of Fe or Mn has been the reaction of the trinuclear [M<sub>3</sub>O(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub>]<sup>0,+</sup> compounds, containing the [M<sub>3</sub>( $\mu_3$ -O)] triangular core, with a bidentate chelate. For example, the use of 2-(hydroxymethyl)pyridine (hmpH) has led to a large variety of products depending on the precise reaction conditions, including Mn<sub>7</sub>,<sup>10</sup> Mn<sub>10</sub>,<sup>11</sup> Mn<sub>12</sub>,<sup>12</sup> and Fe<sub>6</sub><sup>7</sup> clusters. The alkoxide arm of the hmp<sup>-</sup> ligand normally adopts a bridging mode, fostering formation of higher nuclearity products. Thus, a similar reaction using the triol teaH<sub>3</sub> was explored. Treatment of [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](O<sub>2</sub>CPh) with two equivalents of teaH<sub>3</sub> in MeCN gave a red-orange solution from which the new octanuclear cluster [Fe<sub>8</sub>( $\mu_4$ -O)<sub>3</sub>(O<sub>2</sub>CPh)<sub>9</sub>(tea)(teaH<sub>3</sub>)] **1** was obtained in 45% yield. Its formation can be summarised in eqn. (1).



The reaction procedure employed thus contained an excess of teaH<sub>3</sub> over that required by eqn. (1), and this might have proven beneficial in providing H<sup>+</sup> acceptors to help formation of O<sup>2-</sup> groups. Reactions with small variations in the Fe<sub>3</sub>:teaH<sub>3</sub> ratio gave the same Fe<sub>8</sub> compound **1**.

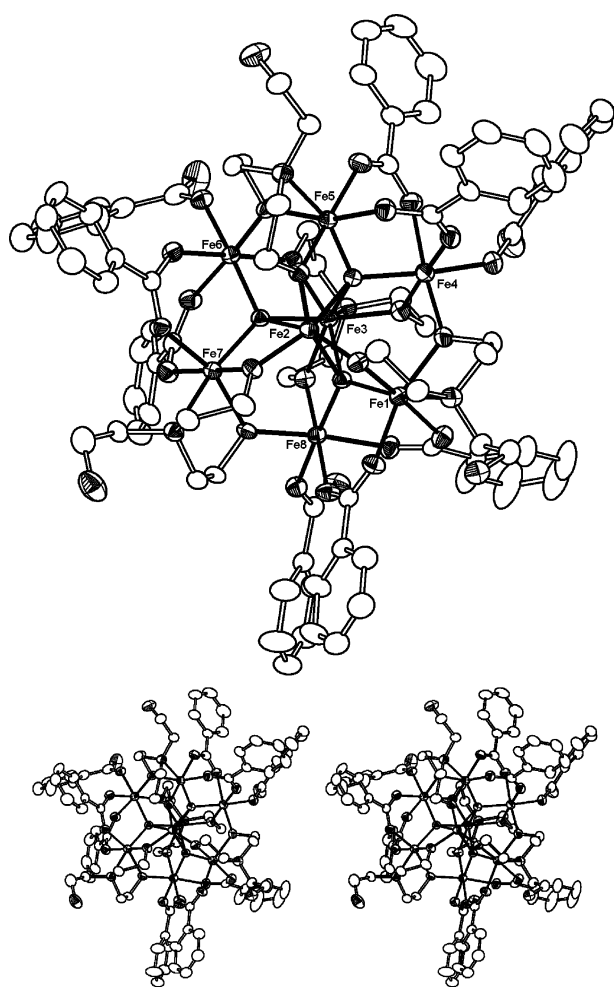
The same reaction as above was also explored with the related chelate bicH<sub>3</sub>. This differs from teaH<sub>3</sub> in that one of the alcohol groups is now a carboxylic acid group. Treatment of [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](O<sub>2</sub>CPh) with two equivalents of bicH<sub>3</sub> in MeCN gave a yellow solution that slowly gave a precipitate. Recrystallization from MeOH–CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O gave the new hexanuclear cluster [Fe<sub>6</sub>(bic)<sub>6</sub>] **2** in 38% yield. Its formation is summarised in eqn. (2).



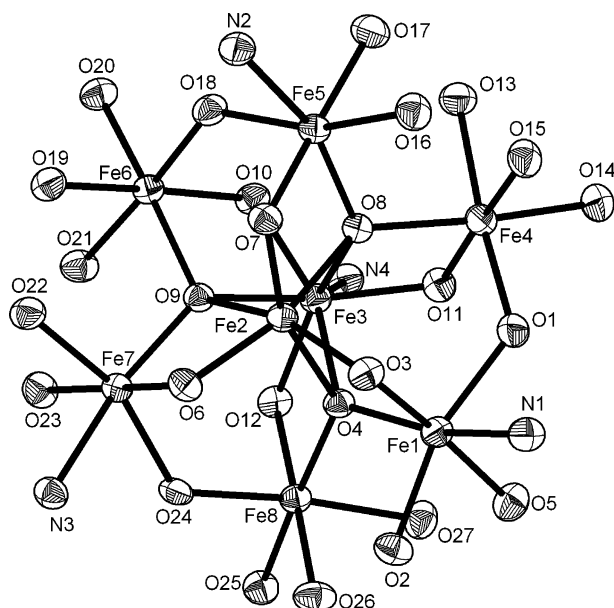
Again, small changes to the Fe<sub>3</sub> : bicH<sub>3</sub> ratio still gave the same Fe<sub>6</sub> compound **2**. After the wheel structure of **2** had been determined by crystallography (*vide infra*), we repeated the reaction but with added sources of Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> or Cs<sup>+</sup> to investigate whether any of these cations would be incorporated into the wheel, and if so, even perhaps alter its nuclearity (size). In every case, however, the isolated product was **2**. This is probably due to the low solubility and precipitation of **2** from MeCN, since species with an additional M<sup>+</sup> would be charged and thus likely more soluble.

### Structural description of [Fe<sub>8</sub>O<sub>3</sub>(O<sub>2</sub>CPh)<sub>9</sub>(tea)(teaH<sub>3</sub>)] **1**

A labelled ORTEP<sup>13</sup> plot and stereopair of complex **1** are presented in Fig. 1, and a fully labelled view of the central part of the molecule is shown in Fig. 2. Selected bond distances and angles are listed in Table 2. Complex **1**·MeCN crystallises in the monoclinic space group *P2<sub>1</sub>/n* with the asymmetric unit containing a complete Fe<sub>8</sub> cluster and one MeCN of crystallisation.



**Fig. 1** Structure and stereopair of  $[\text{Fe}_8\text{O}_3(\text{O}_2\text{CPh})_6(\text{tea})(\text{teaH})_3]$  **1**, with the atoms drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.



**Fig. 2** Fully labelled central portion of complex **1**.

The structure of **1** consists of a core of eight Fe(III) ions bridged by four  $\mu_4\text{-O}^{2-}$  ions. The resulting structure of this unit is unusual: it can be described as a central  $\text{Fe}_2$  pair (Fe2 and Fe3) bridged by three oxide ions (O4, O8 and O9), each of which also bridges an outer  $\text{Fe}_2$  pair. These outer  $\text{Fe}_2$  pairs are not coplanar and thus the outer six Fe ions do not form a flat wheel. Instead, the three outer  $\text{Fe}_2$  pairs are arranged like the

**Table 2** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1**·MeCN

Fe1 $\cdots$ Fe2	2.9909(6)	Fe2–O7	1.952(2)
Fe1 $\cdots$ Fe4	3.6083(6)	Fe2–O8	2.065(2)
Fe1 $\cdots$ Fe8	3.3174(6)	Fe2–O9	2.040(2)
Fe2 $\cdots$ Fe3	2.9093(6)	Fe3–O4	2.238(2)
Fe2 $\cdots$ Fe4	3.7586(6)	Fe3–O8	2.254(2)
Fe2 $\cdots$ Fe5	2.9701(6)	Fe3–O9	2.234(2)
Fe2 $\cdots$ Fe6	3.7008(6)	Fe3–O10	1.929(2)
Fe2 $\cdots$ Fe7	2.9758(6)	Fe3–O11	1.934(2)
Fe2 $\cdots$ Fe8	3.1377(6)	Fe3–O12	1.939(2)
Fe3 $\cdots$ Fe4	3.1274(6)	Fe3–N4	2.527(2)
Fe3 $\cdots$ Fe5	3.8766(6)	Fe4–O1	1.997(2)
Fe3 $\cdots$ Fe6	3.1438(6)	Fe4–O8	1.991(2)
Fe3 $\cdots$ Fe7	3.8271(6)	Fe4–O11	1.954(2)
Fe3 $\cdots$ Fe8	3.1377(6)	Fe5–O7	1.986(2)
Fe4 $\cdots$ Fe5	3.3129(6)	Fe5–O8	1.946(2)
Fe5 $\cdots$ Fe6	3.5944(6)	Fe5–O18	1.981(2)
Fe6 $\cdots$ Fe7	3.3713(6)	Fe6–O9	2.012(2)
Fe7 $\cdots$ Fe8	3.5690(6)	Fe6–O10	1.968(2)
Fe1–O1	2.011(2)	Fe6–O18	1.984(2)
Fe1–O3	1.975(2)	Fe7–O6	1.980(2)
Fe1–O4	1.938(2)	Fe7–O9	1.952(2)
Fe2–O3	1.939(2)	Fe7–O24	1.993(2)
Fe2–O6	1.941(2)	Fe8–O12	1.968(2)
Fe2–O4	2.095(2)	Fe8–O4	1.985(2)
		Fe8–O24	1.992(2)
Fe1–O3–Fe2	99.68(9)	Fe1–O4–Fe2	95.65(8)
Fe1–O4–Fe3	132.75(10)	Fe2–O4–Fe8	134.82(10)
Fe1–O1–Fe4	128.37(11)	Fe3–O8–Fe4	94.71(8)
Fe1–O4–Fe8	115.46(10)	Fe3–O11–Fe4	107.12(10)
Fe2–O4–Fe3	84.28(7)	Fe3–O8–Fe5	134.61(10)
Fe2–O8–Fe3	84.56(7)	Fe3–O9–Fe6	95.39(8)
Fe2–O9–Fe3	85.67(7)	Fe3–O10–Fe6	107.56(9)
Fe2–O8–Fe4	135.85(10)	Fe3–O9–Fe7	132.10(10)
Fe2–O7–Fe5	97.91(9)	Fe3–O4–Fe8	95.78(8)
Fe2–O8–Fe5	95.50(8)	Fe3–O12–Fe8	106.83(9)
Fe2–O9–Fe6	131.90(10)	Fe4–O8–Fe5	114.62(10)
Fe2–O6–Fe7	98.76(9)	Fe5–O18–Fe6	130.10(11)
Fe2–O9–Fe7	96.37(8)	Fe6–O9–Fe7	116.51(10)
		Fe7–O24–Fe8	127.17(10)

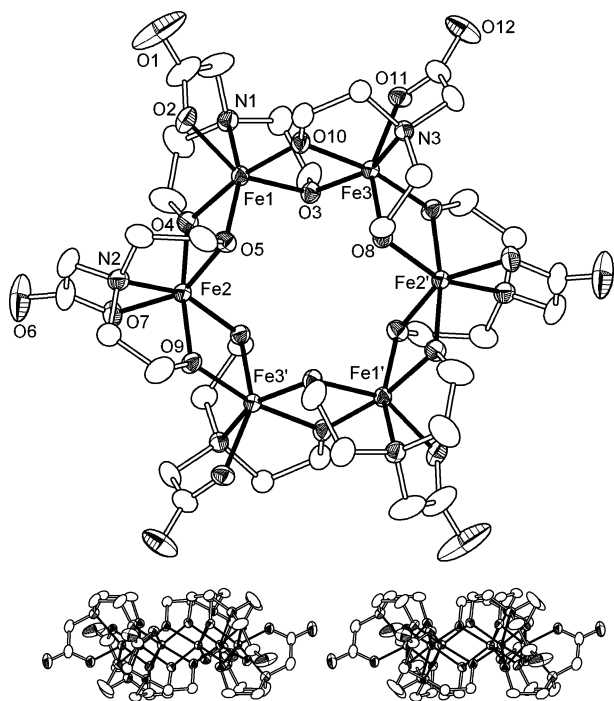
blades of a propeller. In fact, this analogy is quite useful, because the central  $\text{Fe}_2$  pair can then be considered the axis of the propeller. Alternatively, the core can instead be described as three  $[\text{Fe}_4(\mu_4\text{-O})]$  tetrahedra sharing the common  $\text{Fe}_2\text{--Fe}_3$  edge. The  $C_3$  symmetry of the propeller-like core is maintained by the location of the peripheral ligands, and thus the molecule has overall  $C_3$  virtual symmetry. The single triply-deprotonated  $\text{tea}^{3-}$  ligand is tridentate through its three alkoxide O atoms (O10, O11, O12), each one bridging central Fe3 to one of the outer Fe atoms (Fe4, Fe6, Fe8). In fact, this  $\text{tea}^{3-}$  group is better described as tetradentate, because it forms a long, very weak, but undoubtedly real bond to Fe3 (Fe3–N4 2.527(2)  $\text{\AA}$ ). If this contact is included, then Fe3 is seven-coordinate, with a capped-octahedral geometry. All the other Fe atoms have octahedral geometry. The three  $\text{teaH}^{2-}$  groups are tridentate, binding through two alkoxide O atoms and their central N atom; the remaining O atom is protonated (*i.e.* an alcohol group) and unbound. One of the  $\text{teaH}^{2-}$  alkoxide O arms bridges from an outer Fe atom (Fe1, Fe5, or Fe7) to central Fe2, whereas the other arm bridges from the same Fe atom (Fe1, Fe5, or Fe7) to another outer Fe atom, Fe4, Fe6, or Fe8, respectively. Finally, the benzoate groups, which all bind in their common *syn-syn*,  $\mu$ -mode, bridge only between outer Fe atoms and complete the peripheral ligation.

### Structural description of $[\text{Fe}_6(\text{bic})_6]\mathbf{2}$

A labelled ORTEP plot and stereopair viewed along the  $\text{Fe}_6$  edge of complex **2** are presented in Fig. 3. Selected bond distances and angles are listed in Table 3. Complex **2** crystallises in the monoclinic space group  $P2_1/c$ , with the asymmetric unit containing half the  $\text{Fe}_6$  cluster, two MeOH and two  $\text{H}_2\text{O}$  molecules of crystallisation.

**Table 3** Selected bond distances (Å) and angles (°) for 2·4H<sub>2</sub>O·4MeOH

Fe1...Fe2	3.1162(4)	Fe2–O5	2.0152(16)
Fe1...Fe3	3.1235(5)	Fe2–O9	2.0007(15)
Fe2...Fe3	3.1169(4)	Fe2–N2	2.1996(19)
Fe1–O2	1.9915(17)	Fe2–O8'	1.9634(15)
Fe1–O3	2.0067(15)	Fe3–O3	1.9716(15)
Fe1–O4	2.0020(16)	Fe3–O8	2.0037(15)
Fe1–O5	1.9724(15)	Fe3–O9'	1.9695(15)
Fe1–O10	1.9722(15)	Fe3–O10	1.9974(15)
Fe1–N1	2.2039(19)	Fe3–O11	1.9853(16)
Fe2–O4	1.9657(15)	Fe3–N3	2.2134(18)
Fe1–O4–Fe2	103.51(7)	Fe1–O10–Fe3	103.74(7)
Fe1–O5–Fe2	102.79(7)	Fe2–O8'–Fe3'	103.56(7)
Fe1–O3–Fe3	103.42(7)	Fe2–O9–Fe3'	103.45(7)

**Fig. 3** Structure and stereopair viewed along the Fe<sub>6</sub> edge of [Fe<sub>6</sub>(bic)<sub>6</sub>] **2**, with the atoms drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

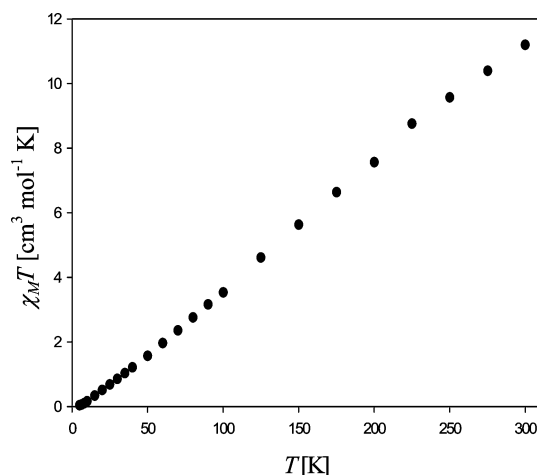
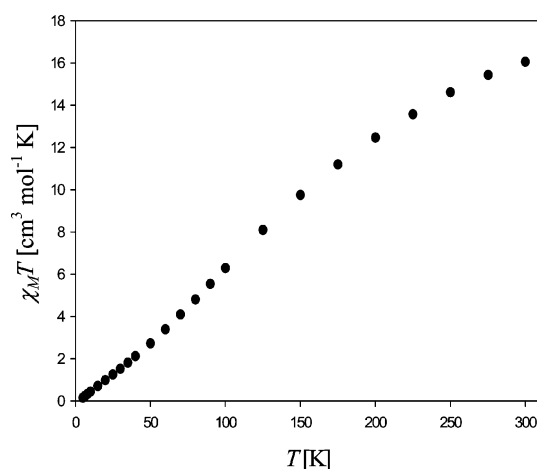
The structure of **2** consists of a wheel of six Fe(III) ions and six bic<sup>3-</sup> ligands. The molecule lies on an inversion centre at the middle of the wheel. All Fe atoms are octahedral. Each bic<sup>3-</sup> group is tetradentate: the N and carboxylate O form a five-membered chelate ring at each Fe atom, and the two alkoxide arms bridge between this Fe atom and the neighbouring Fe atom on each side. Thus, two alkoxide groups bridge each Fe<sub>2</sub> pair (Fe...Fe ≈ 3.1 Å). It is interesting to note that the centre of the wheel is empty, not even containing, for example, a capping water molecule. The distance between diagonally opposite Fe atoms is ~6.2 Å. Since each Fe<sub>2</sub> pair is bridged by two alkoxides, with one O above the Fe<sub>6</sub> plane and the other below, the [Fe<sub>6</sub>O<sub>12</sub>] core has a distinct O/Fe/O layered structure, as can clearly be seen in the side-view in Fig. 3. The molecules pack in the crystal in layers, within which the molecules are all parallel, but between which they are perpendicular.

There are only a few Fe<sub>6</sub> wheels known in the literature. The reaction of teaH<sub>3</sub> with a mixture of FeCl<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and NaH in THF yielded the Fe<sub>6</sub> wheel complex [Fe<sub>6</sub>(tea)<sub>6</sub>], which is similar to complex **2**; it has been obtained containing either a central Li<sup>+</sup> or Na<sup>+</sup> ion, and also without a guest ion.<sup>14</sup> It is interesting that using our synthetic routes, we obtained an Fe<sub>6</sub> with bic<sup>3-</sup> but with teaH<sub>3</sub> obtained the non-wheel complex **1**. Perhaps the latter was due to the additional presence of carboxylate groups in the reaction, but these were also present in the bicH<sub>3</sub> reaction

that gave a benzoate-free Fe<sub>6</sub> wheel. This emphasizes the complicated nature of these reactions and the sensitivity of the resulting product to many factors and conditions. The reactions of the diols *N*-(methyl)diethanolamine (L1) and *N*-(2,5-dimethylbenzyl)iminodiethanol (L2) with FeCl<sub>3</sub> and CaH<sub>2</sub> under similar conditions gave the Fe<sub>6</sub> wheels [Fe<sub>6</sub>Cl<sub>6</sub>(L1)<sub>6</sub>] and [Fe<sub>6</sub>Cl<sub>6</sub>(L2)<sub>6</sub>], respectively.<sup>14</sup> Like complex **2**, these wheels have no guest ion or group at their center. Finally, the Fe<sub>6</sub> wheel compounds [NaFe<sub>6</sub>(OMe)<sub>12</sub>(dbm)<sub>6</sub>]<sup>+</sup> (dbmH is dibenzoylmethane) and [NaFe<sub>6</sub>(OMe)<sub>12</sub>(pmdbm)<sub>6</sub>]<sup>+</sup> (pmdbmH is 4,4'-(MeO)<sub>2</sub>dbmH) are structurally very similar and contain a central Na<sup>+</sup> guest.<sup>15</sup> In all these cases, the Fe<sub>6</sub> wheel is held together by two alkoxide bridges between each Fe<sub>2</sub> pair.

### Magnetochemistry

The magnetic susceptibilities of **1** and **2** were measured on microcrystalline samples in a 1 T field in the 5.0–300 K range. The obtained data for **1** and **2** are plotted as  $\chi_M T$  vs.  $T$  in Figs. 4 and 5, respectively. The  $\chi_M T$  value for **1** decreases steadily with decreasing temperature from 11.19 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K to 0.04 cm<sup>3</sup> mol<sup>-1</sup> K at 5.0 K, consistent with an  $S = 0$  ground state. The  $\chi_M T$  value at 300 K is well below the spin-only ( $g = 2$ ) value of 35.0 cm<sup>3</sup> mol<sup>-1</sup> K expected for eight non-interacting high-spin ( $S = 5/2$ ) Fe(III) ions. This behaviour is clearly indicative of strong antiferromagnetic interactions between the Fe(III) centres to give an overall  $S = 0$  spin in the ground state.

**Fig. 4** Plot of  $\chi_M T$  vs.  $T$  for complex **1**.**Fig. 5** Plot of  $\chi_M T$  vs.  $T$  for complex **2**.

Complex **2** exhibits a similar behaviour. In this case, the  $\chi_M T$  value decreases steadily with decreasing temperature from 16.06 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K to 0.15 cm<sup>3</sup> mol<sup>-1</sup> K at 5.0 K, again indicating an  $S = 0$  ground state. The 300 K value is significantly

below the spin-only value  $26.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for six non interacting Fe(III) ions, again indicating strong antiferromagnetic exchange interactions. This result is fully in agreement with those previously reported for  $\text{Fe}_6$ , and indeed other  $\text{Fe}_x$  ( $x = \text{even}$ ) wheels, which also have spin singlet ground state as a result of antiferromagnetic exchange interactions between adjacent Fe(III) ions and resulting antiparallel arrangement of spin around the ring.

## Conclusions

The reactions of the tripodal ligands  $\text{teaH}_3$  and  $\text{bicH}_3$  with the Fe(III) carboxylate sources  $[\text{Fe}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]$  have provided clean access to two new polynuclear iron(III) aggregates. One is an octanuclear species with an unprecedented  $[\text{Fe}_8(\mu_4\text{-O})_3]$  propeller-like core, and the other a new hexanuclear wheel complex to join the few other examples of this type in the literature. The exchange interactions in Fe(III) complexes are expected to be antiferromagnetic, and as is usually the case in the absence of spin frustration effects, the ground states of both complexes reported here are  $S = 0$ .

The present work extends the body of results that emphasise the ability of tripodal ligands such as  $\text{teaH}_3$  and  $\text{bicH}_3$  to form a variety of new structural types in both iron and manganese chemistry. More new species with these metals are currently under investigation and will be reported in due course.

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