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New hexanuclear and dodecanuclear Fe(III) clusters with carboxylate and alkoxide-based ligands from cluster aggregation reactions

Muralee Murugesu, Khalil A. Abboud, George Christou *

Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA

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Dedicated to Malcolm L.H. Green on the occasion of his retirement

Abstract

The syntheses, structures and magnetic properties are reported of three new iron(III) clusters $[Fe_6(\mu_3-O)_2(O_2CH_2)(O_2CC$

Keywords: Fe(III) carboxylate chemistry; Magnetochemistry; Crystal structures; Cluster complexes

1. Introduction

The synthesis of high nuclearity iron(III) clusters is of interest for a number of reasons. These include the desire to understand and model the assembly of the polynuclear Fe/O core of the iron-storage protein ferritin, and the search for molecular species with unusual or novel magnetic properties. The latter encompasses the currently very active efforts to produce new examples of molecular species that can function as nanoscale magnetic particles, or so-called single-molecule magnets (SMMs), especially since the discovery of iron SMMs [1–5]. In such molecules the presence of a large ground state spin (S) combined with an Ising (or easy-axis) type of magnetoanisotropy (negative zero-field splitting parameter, D) leads to superparamagnet-like slow relaxation of the magnetization at low temperatures, and resulting out-of-phase AC magnetic susceptibility signals and magnetization versus applied DC field hysteresis loops [6,7]. Iron(III) is a good choice for the preparation of high nuclearity clusters given its high charge and resulting propensity to favor

^{*} Corresponding author. Tel.: +1 352 392 6737; fax: +1 352 392 8757.

E-mail addresses: christou@chem.ufl.edu, polyhedron@chem.ufl. edu (G. Christou).

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oxide-bridged units, and many large iron clusters have been reported, with nuclearities up to 19 [2,8–11]. Indeed, the formation of the Fe/O/OH core of ferritin relies also on this chemistry, and this protein core is effectively a nanoscale Fe/O particle. Thus, there is a continuing search for new synthetic methods that can yield new polynuclear Fe/O clusters. In this paper, we describe some recent results, two of which have resulted from the use of alcohol-based chelate ligands.

The chelates employed are shown in the scheme. The synthetic strategy was to react these organic molecules with the trinuclear $[Fe_3O(O_2CR)_6(H_2O)_3](O_2CR)$ complexes containing the triangular, oxide-centered $[Fe_3(\mu_3-O)]^{7+}$ core. Such trinuclear species have proven on many occasions to be excellent starting points for the synthesis of higher nuclearity Fe or Mn clusters [12-17]. The 2-methoxyethanol (moeH) [18,19] and syn-2-pyridinealdoxime (pamH) [20–22] ligands have been used on several previous occasions for inorganic synthesis, but there are only a very few examples of cluster compounds having been obtained with them. In particular, we are unaware of their use in reactions with $[Fe_3O(O_2CR)_6L_3]$ complexes. As a result, we felt that this approach could yield some interesting new cluster products. Indeed, this has turned out to be the case. We report that the use of moeH and pamH with $[Fe_3O(O_2CR)_6(H_2O)_3](O_2CR)$ species has led to two new high-nuclearity products, Fe₆ and Fe₁₂, respectively, and we describe the syntheses, crystal structures and magnetic properties of these complexes. In addition, we also describe a second Fe₆ complex, obtained from the reaction of $[Fe_3O(O_2CR)_6(H_2O)_3](O_2CR)$ with pyridine in the presence of MeOH. The combined results continue to demonstrate the flexibility and versatility of iron(III) chemistry for the synthesis of unusual high-nuclearity cluster compounds.



2. Experimental

2.1. Compound preparations

All manipulations were performed under aerobic conditions using materials and solvents as received. $[Fe_3O(O_2CR)_6(H_2O)_3](O_2CR)$ complexes were prepared using the procedure reported previously [23].

2.1.1. $Fe_6O_2(O_2CH_2)(O_2CCH_2Bu^t)_{12}(py)_2$] (1)

Method A. A solution of $[Fe_3O(O_2CCH_2Bu')_6-(H_2O)_3](O_2CCH_2Bu')$ (0.47 g, 0.50 mmol) and pyridine (0.64 ml, 7.80 mmol) in MeCN/MeOH (45/15 ml) was stirred for 30 min to give an orange solution. This was layered with diethyl ether and left undisturbed at room temperature. After several weeks, the orange prism-shaped crystals of **1** that had slowly grown were collected in 25% yield. *Anal.* Calc. for **1** (C₈₃H₁₄₄Fe₆-N₂O₂₈): C, 51.04; H, 7.43; N, 1.43. Found: C, 51.32; H, 7.11; N, 1.55%. Selected IR data (cm⁻¹): 3446 (br), 2955 (s), 1607 (m), 1557 (s), 1455 (m), 1412 (s), 1369 (m), 1061 (w), 898 (w), 643 (w), 562 (w).

Method B. A solution of $[Fe_3O(O_2CCH_2-Bu')_6(H_2O)_3](O_2CCH_2Bu')$ (0.24 g, 0.25 mmol), py (0.64 ml, 7.80 mmol) and 37% formaldehyde (0.50 ml, 6.6 mmol) in MeCN (45 ml) was stirred for 30 min to give an orange solution. This was left undisturbed at room temperature. After one day, the orange prism-shaped crystals of 1 that had slowly grown were collected by filtration in 75% yield. The material was spectroscopically identical (IR) with that from Method A.

2.1.2. $Fe_6O_2(O_2CCH_2Cl)_6(moe)_6](NO_3)_2$ (2)

A solution of $[Fe_3O(O_2CCH_2CI)_6(H_2O)_3]$ (O₂CCH₂ Cl) (0.23 g, 0.25 mmol), Fe(NO₃)₃ · H₂O (0.10 g, 0.25 mmol) and moeH (5 ml, 63 mmol) in MeCN (50 ml) was stirred for 15 min to give a green solution. This was layered with diethyl ether and left undisturbed at room temperature. After 7 days, yellow-green rectangular shaped crystals of **2** were collected in 55% yield based on total Fe. *Anal*. Calc. for **2** (C₃₀H₅₄Cl₆Fe₆N₂O₃₂): C, 23.98; H, 3.62; N, 1.86. Found: C, 23.87; H, 3.53; N, 1.55%. Selected IR data (cm⁻¹): 3436 (br), 2946 (s), 1600 (s), 1432 (s), 1384 (m), 1341 (m), 1265 (m), 1079 (s), 1038 (m), 916 (w), 614 (w), 578 (m), 527 (w).

2.1.3. $[Fe_{12}O_8(OMe)_2(O_2CPh)_{12}(pam)_6]$ (3)

A solution of $[Fe_3O(O_2CPh)_6(H_2O)_3](O_2CPh)$ (0.26 g, 0.25 mmol) in MeCN (30 ml) was added with stirring to a solution of pamH (0.061 g, 0.50 mmol) and NaOMe (0.054 g, 1.00 mmol) in MeCN (20 ml). The resulting dark red solution was left undisturbed at room temperature. After 7 days, dark red rectangular shaped crystals of **3** · 4MeOH · 2MeCN had formed and were collected in 37% yield. *Anal.* Calc. for **3** · 4MeOH (C₁₂₆H₁₁₂Fe₁₂-N₁₂O₄₄): C, 47.76; H, 3.56; N, 5.30. Found: C, 47.51; H, 3.23; N, 5.15%. Selected IR data (cm⁻¹): 3446 (br), 1602(s), 1541 (m), 1404 (s), 1122 (w), 1096 (m), 718 (m), 692 (w), 613 (w), 467 (m), 455 (w).

2.2. General and physical measurements

Elemental analyses (C, H and N) were performed in the in-house facilities of the University of Florida Chemistry Department. Infrared spectra in the 400- 4000 cm^{-1} range were recorded in the solid state (KBr pellets) on a Nicolet Nexus 670 FTIR spectrometer. 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-T dc magnet. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar magnetic susceptibilities (χ_M) . Microcrystalline samples were restrained in eicosane by suspending the solid for 15 min in eicosane maintained at a temperature above its melting point (35-37 °C), and then the temperature was gradually decreased below the melting point to solidify the eicosane.

2.2.1. X-ray crystallography and solution of structures

Data were collected using a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilising Mo Ka radiation ($\lambda = 0.71073$ Å. Suitable crystals of 1, 2 and $3 \cdot 4$ MeOH $\cdot 2$ MeCN 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 monoclinic space group C2/c for complex 1 and triclinic space group $P\overline{1}$ for both 2 and $3 \cdot 4MeOH \cdot 2MeCN$, which 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 ω -scan method $(0.3^{\circ} \text{ frame width})$. 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 SHELXTL-6 [24], and refined on F^2 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.

For complex 1, a total of 557 parameters were included in the structure refinement using 4686 reflections with $I > 2\sigma(I)$. For compound 2, a total of 448 parameters were included in the structure refinement using 12024 reflections with $I > 2\sigma(I)$. For compound 3, a total of 907 parameters were included in the structure refinement using 7761 reflections with $I > 2\sigma(I)$. Unit cell data and the final refinement indices R_1 and wR_2 are listed in Table 1.

3. Results and discussion

3.1. Syntheses

As mentioned earlier, the reaction of a $[M_3O(O_2CR)_6L_3]^{0,+}$ (L = py, H₂O, etc.) complex with a chelating ligand represents a commonly employed and convenient synthetic route to a variety of higher nuclearity clusters of Fe and Mn. For example, the use of 2-(hydroxymethyl)pyridine (hmpH) has led to a large variety of products, depending on the precise reaction conditions and ratios, including Mn₇ [14], Mn₁₀ [15], Mn_{12} [16], and Fe₆ [17] clusters. The alkoxide arm of the hmp⁻ ligand normally adopts a bridging mode, fostering formation of higher nuclearity products, and this was the primary reason for choosing to use moeH and pamH in the present work. However, not all the reactions in the present work involved a chelate; we also investigated the long-term stability of the [Fe₃O $(O_2CCH_2Bu^t)_6(H_2O)_3]^+$ complex to MeOH, in the presence also of py as a proton acceptor, seeking the formation higher nuclearity products via methanolysis. Indeed this reaction led to a nuclearity change, although the isolated product contained no methoxide. The reaction slowly turned orange, and layering with Et₂O deposited orange crystals of $[Fe_6O_2(O_2CH_2)(O_2CCH_2Bu^t)_{12}(py)_2]$ (1) in 25% yield. Its formation is summarised in Eq. (1).

$$2[Fe_{3}O(O_{2}CCH_{2}Bu')_{6}(H_{2}O)_{3}]^{+} + 2py + CH_{3}OH + \frac{1}{2}O_{2}$$

$$\rightarrow [Fe_{6}O_{2}(O_{2}CH_{2})(O_{2}CCH_{2}Bu')_{12}(py)_{2}]$$

$$+ 6H_{2}O + 2H^{+}$$
(1)

When the same reaction in MeCN/MeOH was carried out in the presence of triethanolamine (teaH₃), the product was instead $[Fe_8O_3(O_2CCH_2Bu^t)_9(tea)(teaH)_3]$, structurally analogous to the benzoate complex $[Fe_8O_3(O_2CPh)_9(tea)(teaH)_3]$ reported recently [12].

The most remarkable feature of the reaction and the resulting structure of 1 (vide infra) is the formation of a rare methanediolate ($^{-}OCH_2O^{-}$) group. Such groups are generally unstable but can be formed and trapped in situ [25]. The formation of 1 is not readily amenable to mechanistic studies, but it is reasonable to assume that overall the methanediolate group is formed by iron (III)-promoted oxidation by O₂ of bound MeOH or methoxide, as summarized in Eq. (2), followed by its trapping as a fully deprotonated bridging ligand.

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2(OH)_2 \tag{2}$$

Since *gem*-diols are merely hydrated forms of aldehydes or ketones, we wondered whether a higher yield preparation of **1** might be available via a reaction in which formaldehyde (H₂CO) had been deliberately added. This turned out to be the case (Method B of Section 2). Thus, the reaction of $[Fe_3O(O_2CCH_2-Bu^t)_6(H_2O)_3]^+$, py and H₂CO in a 1:31:26 ratio in MeCN

Table 1 Crystallographic data for complexes $1,\,2$ and $3\cdot 4\text{MeOH}\cdot 2\text{MeCN}$

Compound	1	2	3
Formula	$C_{83}H_{144}Fe_6N_2O_{28}$	$C_{30}H_{54}Cl_6Fe_6N_2O_{32}$	C ₁₃₀ H ₁₁₈ Fe ₁₂ N ₁₄ O ₄₄
Formula weight	1953.10	1502.55	3250.58
Space group	C2/c	$P\overline{1}$	$P\overline{1}$
Unit cell dimensions			
a (Å)	22.8510(16)	11.5721(9)	15.6773(16)
$b(\mathbf{A})$	22.1113(15)	11.8411(94)	15.8373(17)
c (Å)	20.3198(14)	12.0082(90)	16.5046(18)
α (°)	90.00	119.497(2)	115.202(2)
β (°)	98.829(2)	101.521(2)	111.135(2)
γ (°)	90.00	98.926(2)	94.183(2)
$V(\dot{A}^3)$	10145.2(12)	1339.88(18)	3331.9(6)
Z	4	1	1
T (°C)	173(2)	173(2)	173(2)
Radiation	Μο Κα	Μο Κα	Μο Κα
$\rho_{\rm calc} ({\rm g/cm^{-3}})$	1.279	1.862	1.620
$\mu (\mathrm{mm}^{-1})$	0.904	1.975	1.355
$R_1^{a,b}$	6.81	7.72	7.86
$wR_2^{a,c}$	11.68	14.50	15.68

^a $I > 2\sigma(I)$.

$$R_1 = 100 \sum (||F_0| - |F_c||) / \sum |F_0|$$

^c
$$wR_2 = 100 \left[\sum \left[w(F_o^2 - F_c^2)^2 \right] / \sum \left[w(F_o^2)^2 \right] \right]^{1/2}, \ w = 1 / \left[\sigma^2 (F_o^2) + \left[(ap)^2 + bp \right], \ \text{where} \ p = \left[\max(F_o^2, 0) + 2F_c^2 \right] / 2 \right]^{1/2}$$

gave an orange solution from which 1 crystallized and was isolated in 75% yield; the absence of MeOH lowers the solubility of 1, and it crystallizes from MeCN without the addition of Et_2O . This much superior procedure is summarized in Eq. (3).

$$2[Fe_{3}O(O_{2}CCH_{2}Bu')_{6}(H_{2}O)_{3}]^{+} + 2py + H_{2}CO \rightarrow [Fe_{6}O_{2}(O_{2}CH_{2})(O_{2}CCH_{2}Bu')_{12}(py)_{2}] + 5H_{2}O + 2H^{+} (3)$$

The formation of the methanediolate group from formaldehyde is analogous to the more common in situ formation of the *gem*-diol form of di-2-pyridylketone, followed by its trapping as the doubly deprotonated diolate ligand to metal ions [26].

Treatment of an equimolar mixture of $[Fe_3O(O_2CCH_2Cl)_6(H_2O)_3]^+$ and $Fe(NO_3)_3$ in MeCN with an excess of moeH gave a yellow-green solution from which yellow-green rectangular shaped crystals of $[Fe_6O_2(O_2CCH_2Cl)_6(moe)_6](NO_3)_2$ (2) were obtained in 55% yield by layering with Et₂O. This is a more typical type of cluster synthesis reaction than the formation of 1, with no unusual ligand transformations occurring. The formation of the cation of 2 is summarized in Eq. (4).

$$3[Fe_{3}O(O_{2}CCH_{2}Cl)_{6}(H_{2}O)_{3}]^{+} + 3Fe^{3+} + 12moeH$$

$$\rightarrow 2[Fe_{6}O_{2}(O_{2}CCH_{2}Cl)_{6}(moe)_{6}]^{2+} + 6ClCH_{2}CO_{2}H$$

$$+ 8H_{2}O + 8H^{+}$$
(4)

The reaction contained a large excess of moeH over that required by Eq. (4), indicating that the product 2is stable to further incorporation of chelate that might lead to smaller nuclearity products, perhaps even [Fe(moe)₃]. When the reaction was carried out in MeOH instead of MeCN, a mixture of products was obtained, yellow-green complex **2** and golden crystals of known $[Fe_{10}(OMe)_{20}(O_2CCH_2Cl)_{10}]$ [8]. The latter is a member of the 'ferric wheel' family of wheel-like complexes.

The reaction of $[Fe_3O(O_2CPh)_6(H_2O)_3]^+$, pamH and NaOMe in 1:2:4 ratio in MeCN gave a dark red solution from which dark red rectangular shaped crystals of $[Fe_{12}O_8(OMe)_2(O_2CPh)_{12}(pam)_6]$ (3) slowly formed in 37% yield. The reaction is likely a complicated equilibrium involving several species of various nuclearities, and the crystallization of the product directly from the reaction solution is undoubtedly beneficial in providing pure material; the filtrates are still coloured, but we have not pursued isolation of other species. The formation of this novel Fe₁₂ cluster is summarised in Eq. (5).

$$\begin{split} & 4[Fe_{3}O(O_{2}CPh)_{6}(H_{2}O)_{3}]^{+} + 6pamH + 2MeO^{-} \\ & \rightarrow [Fe_{12}O_{8}(\mu\text{-}OMe)_{2}(O_{2}CPh)_{12}(pam)_{6}] + 12PhCO_{2}H \\ & + 8H_{2}O + 2H^{+} \end{split}$$

This reaction ratio and solvent represent the combination that was found to give a pure isolated product in reasonable yield. Small changes to the Fe:pamH ratio still gave the same Fe_{12} product. The NaOMe serves both as a base to deprotonate the pamH and also as a source of MeO⁻ bridges to foster formation of a highnuclearity product. When NEt₃ or NMe₄OH and a mixed MeCN/MeOH reaction solvent were employed, complex **3** was again obtained but only in very poor isolated yields (<5%). This (and the larger but still relatively low yield of **3** using NaOMe) may be due to the fact that pamH is susceptible to hydrolysis [21]; in these cases, it is difficult to isolate such species in good yields.

3.2. Structural description of $[Fe_6O_2(O_2CH_2)(O_2CCH_2-Bu^t)_{12}(py)_2]$ (1)

A labelled ORTEP plot and stereopair of 1 are presented in Fig. 1, and selected bond distances and angles are listed in Table 2. Complex 1 crystallizes in the monoclinic space group C2/c, with the asymmetric unit containing half the Fe₆ molecule.

The Fe₆ core of **1** has a twisted boat-like topology (Fig. 4(a)), comprising two $[Fe_3(\mu_3-O)]^{7+}$ oxide-centered triangular moieties linked between one of their edges (Fe2–Fe3 and the symmetry-related partner) by a μ_4 -O₂CH₂group and two μ -O₂CCH₂Bu^t groups in their familiar *syn*, *syn* binding mode. This edge of both triangular units is also bridged by a μ -O₂CCH₂Bu^t group. The two remaining edges of each $[Fe_3(\mu_3-O)]^{7+}$ unit

are each bridged by two syn, syn μ -O₂CCH₂Bu^t groups. The two pyridine groups complete six-coordination at the end atoms Fe1 and Fe1a. The complex has crystallographic C_2 symmetry, and virtual C_{2v} symmetry if the slight twist in the Fe₆ boat structure is ignored. All Fe atoms are Fe(III) and possess near-octahedral geometries. The overall structure of 1 is similar to those of previously reported $[Fe_6O_2(OH)_2(O_2CBu^t)_{12}]$ [27], $[Fe_6O_2(OH)_2(O_2CPh)_{12}(py)_2]$ [28] and $[Fe_6O_2(OH)_2 (O_2CMe)_{10}(C_7H_{11}N_2O)_2$ [29], but of course differs in possessing the unusual μ_4 -O₂CH₂ bridging group (O13, O13a) at the positions occupied by bridging OH⁻ groups in the above three complexes. The nearest analogue to this μ_4 -O₂CH₂ group is found in [Fe₆O₂- $(O_2)(O_2CPh)_{12}(H_2O)_2$ [30] and $[Fe_6O_2(O_2)(O_2C Bu^{t}_{12}L_{2}$] (L = Bu^{t}_{-} CO₂H or py) [31]. In these



Fig. 1. ORTEP representation and stereopair at the 50% probability level of complex 1, viewed approximately along the crystallographic C_2 symmetry axis. All H atoms and the Bu^t groups of the Bu^tCH₂CO₂⁻ groups have been removed for clarity.

Table 2 Selected bond distances (Å) and angles (°) for complex 1

		0 ()	
Bond distances			
Fe1···Fe2	3.286(6)	Fe2–O6	2.058(4)
Fe1···Fe3	3.301(6)	Fe2–O7	2.042(4)
Fe2···Fe3	3.411(6)	Fe2–O8	2.014(4)
Fe2···Fe3a	3.607(6)	Fe2–O9	2.058(4)
Fe1–O1	1.872(4)	Fe2–O13a	1.979(4)
Fe1–O2	2.021(4)	Fe3–O1	1.956(4)
Fe1–O3	2.022(4)	Fe3-O10	1.990(4)
Fe1–O4	2.024(4)	Fe3011	2.041(4)
Fe1–O5	2.021(4)	Fe3012	2.027(4)
Fe1-N1	2.252(5)	Fe3013	1.975(4)
Fe2–O1	1.945(4)	Fe3–O14	2.037(4)
Bond angles			
Fe1-O1-Fe2	118.84(19)	Fe2-O1-Fe3	121.98(18)
Fe1–O1–Fe3	119.10(19)	Fe3–O13–Fe2a	131.7(2)

complexes, there is a central μ_4 - O_2^{2-} peroxide group bridging analogously to the methanediolate in 1, i.e., without the central CH₂ linker between O atoms O13 and O13a. The unusual μ_4 - O_2 CH₂ group of 1 has itself been seen previously only in a tetranuclear Mo cluster [25], where it bridges the Mo₄ core in the same fashion as that in the central Fe₄ unit of 1.

3.3. Structural description of $[Fe_6O_2(O_2CCH_2Cl)_6-(moe)_6](NO_3)_2$ (2)

A labelled ORTEP plot and stereopair of the cation of **2** are presented in Fig. 2, and selected bond distances and angles are listed in Table 3. Complex **2** crystallizes in the triclinic space group $P\overline{1}$, with the Fe₆ cation lying on an inversion centre.

The cation of 2 consists of two triangular $[Fe_3(\mu_3 -$ O)]⁷⁺ units held together in a face-to-face fashion by six bridging moe⁻ ligands. Each moe⁻ group chelates one Fe atom and bridges with its O atom to another Fe atom in the neighboring $[Fe_3O]^{7+}$ unit. All Fe atoms are Fe(III). Each Fe₂ pair within a trinuclear unit is additionally bridged by a CH2ClCO2⁻ group, completing six coordination at each Fe atom. The cation has crystallographic C_i symmetry but virtual S_6 symmetry, with the S_6 axis passing through the μ_3 -O²⁻ oxygen atoms (O1, O1a). The Fe₆ cation can be also described as an Fe₆ octahedron (Fig. 4(b)) with two opposite faces bridged by μ_3 -O²⁻ ions and six edges bridged by μ -O atoms from moe⁻ ligands. The Fe...Fe separation within the trinuclear [Fe₃O]⁷⁺ units (average 3.311 Å) are only slightly shorter than those between [Fe₃O]⁷⁺ units (average 3.431 Å); thus, the Fe₆ core is almost a regular octahedron. The $Fe \cdot \cdot Fe$ separations on the same axis of the octahedron are much longer (average 4.767 Å).

The cation of **2** is the first such cluster with moe⁻ groups, but the core structure of the cation is similar to those in other Fe_6 species with a recognizable octahedral Fe_6 topology, including $[Fe_6O_2(O_2CCH_2C-$



Fig. 2. ORTEP representation and stereopair of the cation of complex 2 at the 50% probability level, viewed almost along the virtual S_6 symmetry axis. All H atoms and the Cl atoms of CH₂ClCO₂⁻ groups have been removed for clarity.

 $(CH_3)_3)_6(hmp)_6]^{2+}$ [17] and $[Fe_6O(OMe)_3Cl_6(thme)_3]^{2-}$ [32]; the latter also contains a central μ_6 -O²⁻ ion. In contrast, the $[Fe_6O_2(O_2)_3(O_2CMe)_9]^-$ anion contains two face-to-face $[Fe_3(\mu_3-O)]^{7+}$ units in an eclipsed arrangement giving an Fe₆ trigonal prism [33], rather than the

Table 3	
Selected bond distances (Å) and angles (°) for complex	2

		0 () 1	
Bond distances			
Fe1···Fe2	3.310(4)	Fe2–O3	2.000(6)
Fe1···Fe3	3.303(4)	Fe2-O10	1.916(6)
Fe2···Fe3	3.320(4)	Fe2-O11	2.215(7)
Fel-Ol	1.919(4)	Fe2–O12a	2.087(7)
Fel-O6	2.006(6)	Fe3–O1	1.909(4)
Fel-O7	2.013(6)	Fe3–O4	2.009(6)
Fel-O8	1.917(7)	Fe3–O5	2.001(5)
Fe1–O9	2.213(7)	Fe3–O8a	2.089(7)
Fel-Ol0a	2.087(6)	Fe3-O12	1.920(6)
Fe2-O1	1.909(4)	Fe3-O13	2.191(7)
Fe2–O2	2.009(6)		
Bond angles			
Fe1-O1-Fe2	119.7(2)	Fe1–O10–Fe2a	118.22(7)
Fe1-O1-Fe3	119.3(2)	Fe1–O8–Fe3a	118.04(7)
Fe2–O1–Fe3	120.8(2)	Fe2–O12–Fe3a	117.17(7)

more common staggered arrangement that yields an Fe_6 octahedron.

3.4. Structural description of $[Fe_{12}O_8(OMe)_2-(O_2CPh)_{12}(pam)_6]$ (3)

A labelled ORTEP plot and stereopair for complex 3 are presented in Fig. 3, and selected bond distances and angles are listed in Table 4. Complex 3 crystallizes in the triclinic space group $P\bar{1}$, with the Fe₁₂ cluster lying on an

inversion centre. The unprecedented core of this complex can be described in different ways. The central Fe₆ portion of the core (Fe4, Fe4a, Fe5, Fe5a, Fe6, Fe6a) can be considered as (i) comprising four face-sharing partial cubanes lacking an Fe atom at one vertex; or (ii) as a skewed Fe₆ ladder with μ_3 -O atoms of O²⁻ (O4, O4a) or MeO⁻ (O5, O5a) ions alternately above and below the plane of the ladder; or (iii) as four edge-sharing [Fe₃(μ_3 -O)]⁷⁺ triangular units. A similar planar [Fe₆O₄]¹⁰⁺ unit has been reported in the cation of



Fig. 3. Labelled ORTEP plot and stereopair at the 50% probability level of complex **3**. H atoms and benzoate phenyl groups have been removed for clarity.

[Fe₆O₄Cl₄(O₂CPh)₄L₂][FeCl₄]₂ [31], where however the Fe(III) ions are bridged exclusively via oxide ions. Attached to the central Fe₆ core of **3** by four O²⁻ bridges (O2, O3, O2a, O3a) are two triangular [Fe₃(μ_3 -O)]⁷⁺ units (Fe1, Fe2, Fe3 and symmetry equivalents), disposed above and below the central Fe₆ plane. The resulting [Fe₁₂O₁₀] core has an overall chair conformation, as is best seen in Fig. 4(c) where the three cores of **1–3** are compared. As is usually the case [2,17], the Fe–O²⁻ bonds (1.853–2.083 Å) are significantly shorter than the Fe–OMe bonds (2.112–2.168 Å). Ligation around the core is provided by the PhCO₂⁻ and pam⁻ groups, and every Fe atom consequently has octahedral coordination.

Complex 3 is one of only a very small number of known dodecanuclear iron clusters. Other examples include $[Fe(OMe)_2(dbm)]_{12}$ with a wheel-like structure [37], and $[Fe_{12}O_2(OMe)_{18}(O_2CMe)_6(MeOH)_{4.67}]$ [9], which is mixed-valence 4Fe(III), 8Fe(II).

For all three compounds 1-3, the oxidation states of the Fe atoms and the degree of protonation of O atoms were confirmed by bond valence sum (BVS) calcula-

Table 4

Selected bond distances (Å) and angles (°) for complex $3\cdot 4MeOH\cdot 2MeCN$

Bond distances			
Fe1···Fe2	3.284(4)	Fe2–O2	1.861(5)
Fe1···Fe3	3.241(4)	Fe2–O9	2.086(6)
Fe2···Fe3	3.410(4)	Fe2-O10	2.100(5)
Fe2···Fe4	3.367(2)	Fe2-O11	2.054(4)
Fe2···Fe5	3.565(4)	Fe2-O16	2.069(5)
Fe3···Fe5	3.540(4)	Fe3–O1	1.938(4)
Fe3···Fe6	3.381(3)	Fe3–O3	1.916(5)
Fe4···Fe5	2.843 (2)	Fe3–O12	2.091(5)
Fe4···Fe6a	3.302 (4)	Fe3–O13	2.069(5)
Fe5···Fe6	3.067 (4)	Fe3–O14	2.099(4)
Fe5···Fe5a	3.328 (4)	Fe3–O15	2.012(5)
Fe5···Fe6a	3.172 (5)	Fe4–O2	1.961(4)
Fe1-O1	1.853(5)	Fe4–O4	1.889(5)
Fe1–O6	2.006(5)	Fe4017	2.079(5)
Fe1–O7	2.004(5)	Fe4–O20a	1.991(5)
Fe1–O8	2.028(5)	Fe4–N3	2.192(5)
Fe1-N1	2.222(7)	Fe4–N4	2.148(6)
Fe1-N2	2.149(6)	Fe5–O2	1.920(4)
Fe2-O1	1.956(4)	Fe5–O3	1.950(4)
Fe5–O4	2.083(4)	Fe6–O4a	1.879(5)
Fe5–O5	2.112(4)	Fe6-O19	1.999(4)
Fe5–O5a	2.143(5)	Fe6–O5	2.168(4)
Fe5-O18	2.048(5)	Fe6–N5	2.273(6)
Fe6–O3	1.935(4)	Fe6–N6	2.201(6)
Bond angles			
Fe1-O1-Fe2	119.1(2)	Fe4-O2-Fe5	94.2(2)
Fe1-O1-Fe3	117.5(2)	Fe4–O4–Fe5	91.26(19)
Fe2-O1-Fe3	122.2(2)	Fe4–O4–Fe6a	122.4(2)
Fe2-O2-Fe4	123.5(2)	Fe5-O3-Fe6	104.3(2)
Fe2–O2–Fe5	141.1(2)	Fe5–O4–Fe6a	106.3(2)
Fe3–O3–Fe5	132.6(2)	Fe5–O5–Fe5a	102.90(18)
Fe3–O3–Fe6	122.8(2)	Fe6–O5–Fe5a	94.73(18)

tions, leading to the conclusions described above that all metal centers are Fe(III) and all inorganic O atoms are O^{2-} rather than OH⁻. The BVS values obtained were in the 3.05–3.15, 3.10–3.28 and 2.88–3.09 for complexes **1–3**, respectively.

The above structural descriptions of 1–3 emphasize that the three clusters can all be structurally related to the parent $[Fe_3O(O_2CR)_6(H_2O)_3]^+$ complexes and can thus all be said to be represent different ways of linking or edge-fusing a number of $[Fe_3(\mu_3-O)]^{7+}$ triangular units, with the additional incorporation of other bridges such as MeO⁻. This point is emphasized by the structural comparison of the three cores provided in Fig. 4.

3.5. Magnetochemistry

Variable-temperature, solid-state magnetic susceptibility $(\chi_{\rm M})$ studies were performed on microcrystalline samples of 1-3 in a 1-kG applied DC magnetic field in the 5.0 - 300 K range. The obtained data for 1 (O), 2 (\bullet) and 3 (\blacktriangle) are plotted as $\chi_M T$ versus T in Fig. 5. The $\chi_{\rm M}T$ value for 1 decreases steadily with decreasing temperature from $11.42 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to $0.14 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ 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 26.3 cm³ mol⁻¹ K for six non-interacting Fe(III) ions, indicating strong antiferromagnetic interactions between the Fe(III) centers to give a singlet spin ground state. For complex 2, the $\chi_{\rm M}T$ value again decreases steadily with decreasing temperature from 7.13 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to 0.11 $cm^{3}mol^{-1}$ K at 5.0 K, consistent with an S = 0 ground state. The $\chi_M T$ value at 300 K is far below the spinonly value of 26.3 cm³ mol⁻¹ K for six non-interacting Fe(III) ions, indicating even stronger antiferromagnetic interactions between the Fe(III) centers in 2 than in 1, and again giving an S = 0 spin ground state. Similarly, the $\chi_{\rm M}T$ value for 3 decreases steadily from 12.69 $cm^{3} mol^{-1} K$ at 300 K to 0.19 $cm^{3} mol^{-1} K$ at 5.0 K, again indicating an S = 0 spin ground state. Furthermore, the 300 K $\chi_{\rm M}T$ value is very far below the spin-only value of 52.5 cm³ mol⁻¹ K for 12 non-interacting Fe(III) ions, which is indicative of very strong antiferromagnetic exchange interactions within this molecule.

The three complexes all thus have S = 0 ground states. This is by far the most common ground state for Fe_x clusters with x an even number [10,17,34– 36], and is primarily the result of strong antiferromagnetic exchange interactions between Fe(III)₂ pairs. Although competing exchange antiferromagnetic interactions and spin frustration effects in higher nuclearity species can occasionally lead to non-zero ground state spins [2,10,29], this is clearly not the case in the present complexes. The S = 0 ground states for 1 and 2 can readily be rationalized on the basis of two



Fig. 4. Comparison of the cores of complexes: 1 (a), 2 (b) and 3 (c), emphasizing the presence of recognizable [Fe₃O] oxide-bridged triangular subunits, and the overall structure of the cores as a twisted boat (a), an octahedron (b), and a chair (c).

 $S = 5/2 [\text{Fe}_3(\mu_3-\text{O})]^{7+}$ triangular units antiferromagnetically coupled to each other through the bridging ligands connecting them. The ground state for **3** is not so easily rationalized, but the spin of the central Fe₆



Fig. 5. Plot of $\chi_M T$ vs. T for complexes 1 (O), 2 (\bullet) and 3 (\blacktriangle).

unit is likely S = 0, as found for other compounds with such a planar, ladder-like Fe₆ topology [38,39], and then the S = 5/2 spins of the two $[Fe_3(\mu_3-O)]^{7+}$ triangular units on the flanks would be coupled antiferromagnetically through the central unit to give an overall S = 0 ground state.

4. Conclusions

Synthetic methods have been identified that can convert the triangular $[Fe_3O(O_2CR)_6(H_2O)_3]^+$ complexes to new Fe₆ and Fe₁₂ products. The structures of the latter can be described as aggregates of Fe₃ triangular units. These results continue to emphasize the utility of small nuclearity clusters as stepping-stones to higher-nuclearity products through the use of alcoholcontaining chelate ligands such as the moeH and pamH used in this work, or even by incorporation of methoxide bridges. The magnetic properties of the three complexes described indicate that they all possess S = 0 ground states, and this is not surprising given the dominance of antiferromagnetic interactions in highspin Fe(III) chemistry. Nevertheless, iron(III) carboxylate chemistry continues to surprise with the structural variety and aesthetic beauty of its molecular complexes.

5. Supplementary material

Full crystallographic details have been deposited in CIF format with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336408, e-mail: deposit@ccdc.cam.ac.uk or www at http://www.ccdc.cam.ac.uk) quoting the deposition numbers CCDC 237027 (1), 237028 (2) and 237029 (3).

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