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Octametallic and Hexadecametallic Ferric Wheels[**]

Leigh F. Jones, Andrei Batsanov, Euan K. Brechin,[*] David Collison,[*] Madeleine Helliwell, Talal Mallah, Eric J. L. McInnes, and Stergios Piligkos

The synthesis of paramagnetic molecular clusters has become an area of intense research since the discovery that such molecules can act as nanoscale magnets below a critical temperature.[1,2] Such single-molecule magnets (SMMs) are promising new materials for data storage and quantum computing, which exhibit not only magnetization hysteresis but also display quantum tunneling of magnetization and quantum phase interference.[3,4] In order to function as a SMM a molecule must possess the combination of a large spin and large, easy-axis-type anisotropy. The first SMM was $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ ("Mn12"), and since its preparation a number of molecules have been reported as new members of this family.[5–9] An intriguing class of cluster in this respect is the "molecular wheel". Most even-membered wheels are antiferromagnetic and characterized by $S = 0$ ground states, however, this is not the case for the reported "Ni12" and "Cr10" wheels.[10,11] Indeed "Ni12" was recently reported as the first example of a Ni SMM.[10] Although compounds with $S = 0$ ground states cannot function as SMMs, they represent ideal model systems for the study of 1D magnetic materials, quantum effects, and magnetic anisotropy. To this end, molecular wheels and metallocycles with 6, 8, 10, 12, 18, and 24 metal ions have been reported.[12] We have chosen to investigate the use of the pro-ligand 1,1,1-tris(hydroxymethyl)ethane (H_3thme) in the synthesis of novel transition metal clusters, and herein report the synthesis and initial magnetic properties of two new Fe^{III} clusters, the first unsupported octametallic and hexadecametallic ferric wheels (unsupported in the sense that there are no central metal ions present). The H_3thme ligand has been successfully used in vanadium chemistry[13] but has been sparingly employed for other transition metal complexes.[14]

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[*] Dr. E. K. Brechin, Dr. D. Collison, L. F. Jones, Dr. M. Helliwell, Dr. E. J. L. McInnes, S. Piligkos
Department of Chemistry
The University of Manchester
Oxford Road, Manchester, M13 9PL (UK)
Fax: (+44) 161-275-4616
E-mail: euan.k.brechin@man.ac.uk
david.collison@man.ac.uk

Dr. A. Batsanov
Department of Chemistry
University Science Laboratories
South Road, Durham DH1 3LE (UK)

Prof. T. Mallah
Université Paris-Sud, Bat. 420
Laboratoire de Chimie Inorganique, UMR CNRS 8613
91405 Orsay (France)

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Treatment of the triangular iron complex $[\mathrm{Fe_3O(PhCOO)_6(H_2O)_3}](\mathrm{NO_3})$ with $\mathrm{H_3}$thme in acetonitrile yields a precipitate that can be recrystallized from $\mathrm{CH_2Cl_2/Et_2O}$ to give the octametallic complex $[\mathrm{Fe_8(PhCOO)_{12}(thme)_4}]\cdot 2\,\mathrm{Et_2O}$ (**1**, see Experimental Section). Complex **1** crystallizes in the monoclinic $P2_1$ space group.[15] The structure (Figure 1) can be described as a wheel of eight $\mathrm{Fe^{III}}$ ions bridged by a combination of $\mathrm{PhCOO^-}$ and $\mathrm{thme^{3-}}$ ligands. The $\mathrm{PhCOO^-}$ groups bridge neighboring $\mathrm{Fe^{III}}$ ions in the usual μ_2-manner, while the triply deprotonated $\mathrm{thme^{3-}}$ ligands show much greater flexibility in each bridging four iron centers, with each arm providing a μ_2-oxygen atom for adjacent iron centers. The Fe ions all lie in distorted octahedral geometries, and are of three distinct types: Fe1, Fe3, Fe5, and Fe7 are bridged to three $\mathrm{PhCOO^-}$ and two $\mathrm{thme^{3-}}$ ligands (Figure 1) and have single and double 2-bond bridges through an oxygen atom to neighboring iron ions (that is, that each of these metal centers is coordinated to one oxygen atom from one $\mathrm{thme^{3-}}$ ligand, and two oxygen atoms from the other); Fe2 and Fe6 are bound to four $\mathrm{PhCOO^-}$ and two $\mathrm{thme^{3-}}$ ligands with 2 single 2-bond bridged oxygen atoms; Fe4 and Fe8 are bound to two $\mathrm{PhCOO^-}$ and two $\mathrm{thme^{3-}}$ ligands with 2 double 2-bond bridges fulfilling the coordination at these centers. The single and double 2-bond bridges are characterized by Fe-O-Fe angles of 118.3(7)–121.3(7) and 98.0(7)–103.0(7)°, respectively. The "Fe8" wheel is nonplanar and is perhaps best described as ladle-shaped. The plane defined by the rectangular array {Fe2, Fe4, Fe6, Fe8} lies between, and effectively coparallel to the approximately mutually perpendicular vectors defined by Fe1–Fe5 and Fe3–Fe7, which are themselves nearly parallel to the sides of the rectangle. The ring is approximately 8 Å in diameter.

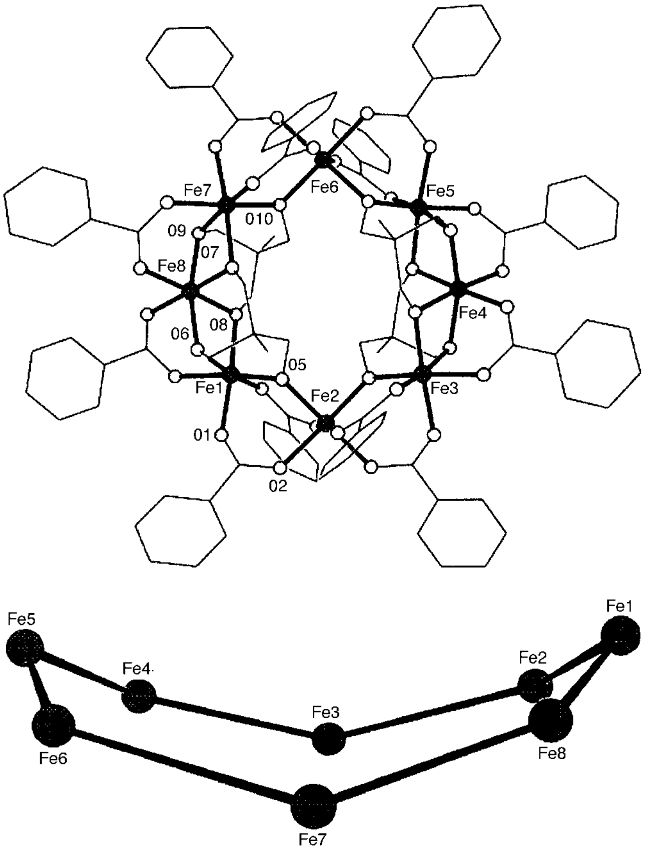

Figure 1. The molecular structure (top) and the arrangement of metal centers (bottom) of **1**. Selected interatomic distances [Å]: Fe-O 1.847(19)–2.054(12), Fe3···Fe7 7.997(7), Fe1···Fe5 7.971(7).

The size of the wheel is doubled by the addition of a coordinating alcohol group in the crystallization step. A similar procedure to that for **1**, but using $\mathrm{EtOH/CH_2Cl_2}$ for recrystallization, produces the hexadecametallic wheel $[\mathrm{Fe_{16}(EtO)_4(PhCOO)_{16}(Hthme)_{12}}](\mathrm{NO_3})_4\cdot 4\,\mathrm{CH_2Cl_2}\cdot 10\,\mathrm{H_2O}$ (**2**, see Experimental Section). Complex **2** (Figure 2) crystallizes in the tetragonal $P4_2/n$ space group [15] and is isolated in good yield after 2 days. It can be described as a wheel of sixteen $\mathrm{Fe^{III}}$ ions bridged by $\mathrm{PhCOO^-}$, $\mathrm{Hthme^{2-}}$ and $\mathrm{EtO^-}$ ligands. The $\mathrm{PhCOO^-}$ ligands again bridge in their familiar μ_2-mode, and are located above, below and in the "plane" of the wheel. The $\mathrm{Hthme^{2-}}$ ligands are of two types. Eight ligands use their two deprotonated arms as μ_2-bridges to form a near-linear chain of three metal centers, with the third protonated arm bonded only to the middle ion these three. Four $\mathrm{Hthme^{2-}}$ ligands occupy the central cavity of the wheel, with the

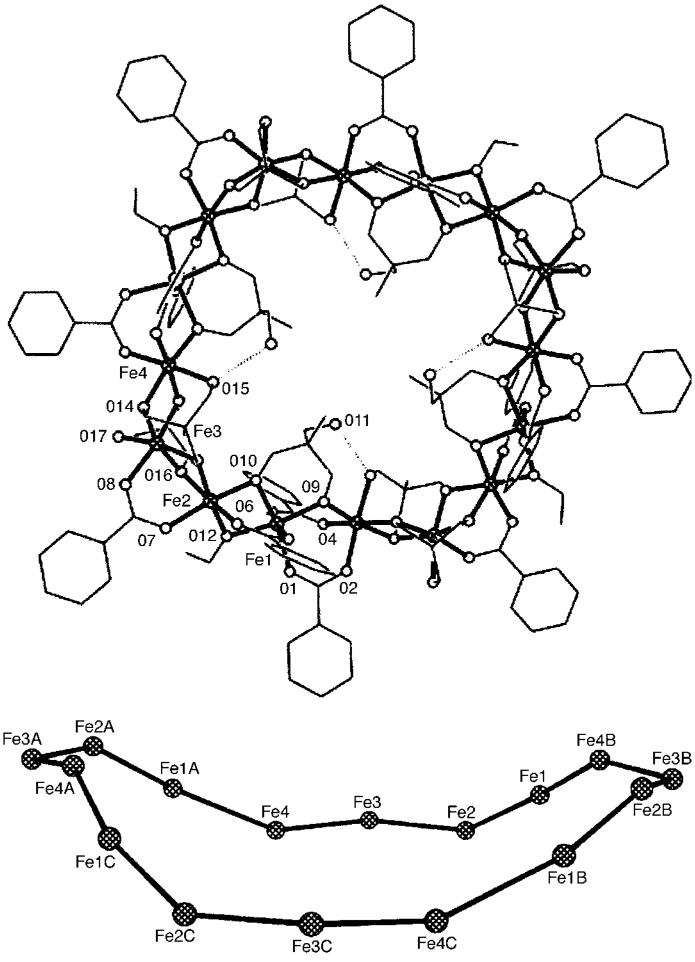

Figure 2. The cation (top) and the arrangement of metal centers (bottom) of **2**. Selected interatomic distances [Å]: Fe-O, 1.962(6)–2.072(6); Fe3A···Fe3B 15.999(6).

deprotonated arms again acting as μ_2-bridges and the protonated arm hydrogen bonding to the monodentate arm of an adjacent $Hthme^{2-}$ ligand (for example, O11–O15B 2.591(6) Å) and to a water molecule above the central cavity of the wheel (O11-O1S 2.804(6) Å). The four EtO^- ligands each bridge two iron centers on the outside edge of the wheel. The iron centers are all bound to six oxygen atoms in a distorted octahedral geometry; for Fe1, the coordination is derived from one EtO^-, three $PhCOO^-$, and two $Hthme^{2-}$ ligands, whereas Fe2 is coordinated to one EtO^-, two $PhCOO^-$, and three $Hthme^{2-}$ ligands. The Fe3 center is coordinated to one $PhCOO^-$ and five $Hthme^{2-}$ ligands, and Fe4 is bonded to two $PhCOO^-$ and four $Hthme^{2-}$ ligands. As for complex **1**, the wheel is nonplanar (Figure 2) and is best described as bowl-shaped, with an approximate diameter of 16 Å. Fe2, Fe3, Fe4, Fe2C, Fe3C, and Fe4C form the basal "plane"; the four symmetry equivalent Fe1 ions form the next plane up, with Fe2A, Fe3A, Fe4A Fe2B, Fe3B, and Fe4B constituting the upper plane. The arrangement of 2-bond oxygen-atom bridges between iron centers in this complex is different from that in **1**. Connections between Fe1 and Fe2, Fe2 and Fe3, and Fe3 and Fe4 are made by two 2-bond oxygen-atom bridges (Fe-O-Fe, 97.9(3)–100.7(3)°), whereas the connections between Fe4 and Fe1′, and Fe1 and Fe4′ are from only one 2-bond oxygen-atom bridge (Fe-O-Fe, 117.8(3)°).

Initial magnetic studies of both **1** and **2** indicate that antiferromagnetic exchange exists between the metal centers. For both complexes the value of $\chi_M T$ declines rapidly from room temperature (approximately 19 and 28 emu K mol^{-1}, respectively) to a value approaching 0 emu K mol^{-1} at 1.8 K, indicative of $S=0$ ground states for both complexes. The values of $\chi_M T$ at room temperature are approximately half of the expected values for eight or sixteen noninteracting iron centers (approximately 35 and 70 emu K mol^{-1}, respectively), which indicates the existence of strong antiferromagnetic interactions, even at room temperature. This behavior is commonly found for iron–oxo clusters with Fe-O-Fe angles between 100–120°.[12] The EPR spectrum of a polycrystalline powder of **1**, measured at the Q-band frequency, increases in intensity between 5 and 50 K and comprises a series of very broad resonances separated by approximately 2500 G, which start at 2000 G and exhibits a more intense derivative-shaped broad resonance centered around 12000 G. This spectrum has maximum intensity and resolution at 20 K. These data are consistent with the observation of an $S=2$ excited state with a zero-field splitting ($|D_2|$) of approximately 0.23 cm^{-1}. Further measurements will be required to confirm this tentative assignment. Note that the population of an $S=2$ state at these temperatures is consistent with the preliminary modeling of the magnetic susceptibility behavior for both **1** and **2**. In contrast, under the same recording conditions, **2** has a relatively well-resolved EPR spectrum at 5 K (see Figure 3) dominated by resonances in the "$g=2$" region and with much weaker features to lower field. By raising the temperature, the signals broaden and at 30 K a much broader feature starts to grow at around 0 G. A plausible interpretation of the low-temperature spectrum is an $S=2$ state with a $|D_2|$ value of around 0.1 cm^{-1}, although the profile of the signal implies a somewhat rhombic character.[16] In common with the situation for **1**, further measurements will be required to produce more definitive values of the spin-Hamiltonian parameters. For comparison, estimated values of $|D_2|$ have been reported for other ferric wheels from cantilever torque measurements, such as $[LiFe_6(OMe)_{12}(dbm)_6][PF_6]$ (0.295 cm^{-1}, dbm = 1,3-diphenyl-1,3-propanedionato),[12] $[Fe_{10}(OMe)_{20}(O_2CCH_2Cl)_{10}]$ (0.540 cm^{-1}),[17] and $[CsFe_8\{N(CH_2CH_2O)_3\}_8]Cl$ (0.315 cm^{-1}).[12] However, there is a clear distinction between the zero-field splitting parameters of **1** and **2**. Furthermore, we have now demonstrated that minor modifications to the coordination sphere in ferric wheels of different iron content, whilst using the same type of ligand donor function, can produce different values of $|D_2|$ within the same excited state spin multiplicity, which has presumably derived from a substantially different magnetic coupling composition. Interestingly, this observed change in $|D_2|$ is in agreement with our observations concerning monomeric, high-spin tris-malonato complexes of Fe^{III}, $[Fe(O_2CCR_2CO_2)_3]^{3-}$, in which $|D_2|$ ranged from 0.04 to 0.2 cm^{-1} for the same coordination sphere as R was varied between H, Me, and Et.[18]

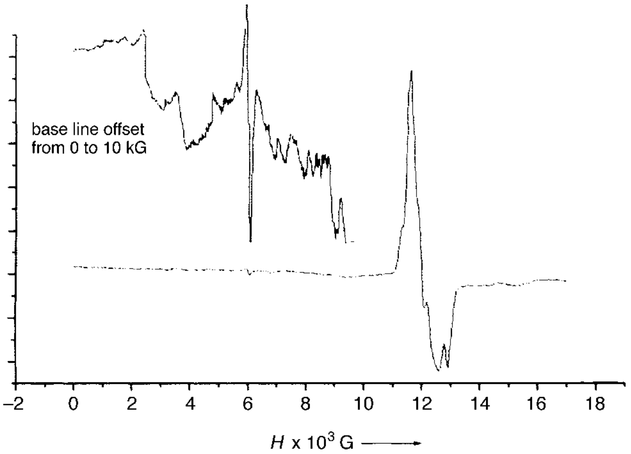

Figure 3. Q-band EPR spectrum of a polycrystalline sample of **2** at 5 K.

In summary, the use of the pro-ligand H_3thme has led to two new structural types: unsupported octametallic[19] and hexadecametallic iron wheels. Previously reported cyclic Fe_8-compounds have contained alkali-metal ions within the central cavity of the wheel, and the Fe_{16} complex is unprecedented. The effect of the coordinating alcoholate groups is remarkable and prompts further investigation.

Experimental Section

1: $[Fe_3O(PhCOO)_6(H_2O)_3](NO_3)$ (0.5 mmol) and H_3thme (0.5 mmol) were stirred in MeCN (30 mL) for 4 h. The resulting precipitate was filtered, air-dried, and redissolved in CH_2Cl_2. Crystals were formed in 2 days after diffusion of diethyl ether into the solution, in approximately 30% yield. Elemental analysis calcd (%) for $Fe_8C_{92}H_{104}O_{36}$: C 52.74, H 4.09; found: C 52.68, H 4.01; selected IR data (KBr pellet): $\tilde{\nu} = 1601$ (s), 1561 (s), 1519 (s), 1493 (m), 1409 (s), 1307 (w), 1176 (m), 1158 (w), 1117 (w), 1069 (m), 1045 (m), 1025 (m), 877 (w), 717 cm^{-1} (s).

2: $[Fe_3O(PhCOO)_6(H_2O)_3](NO_3)$(0.5 mmol) and H_3thme (0.5 mmol) were stirred in MeCN (30 mL) for 4 h. The resulting precipitate was filtered, air-dried, and redissolved in a 1:1 mixture of CH_2Cl_2 and EtOH. Crystals formed after 2 days in approximately 40% yield. Elemental analysis calcd

(%) for $Fe_{16}C_{180}H_{216}O_{84}N_4$: C 46.22, H 4.74, N 1.20; found: C 46.08, H 4.41, N 1.14; selected IR data (KBr pellet): $\tilde{\nu} = 1554$(s), 1528(s) 1493(m), 1409(s), 1307(w), 1176(m), 1158(w), 1069(w), 1045(m), 1025(m), 877(w), 717 cm^{-1}(s).

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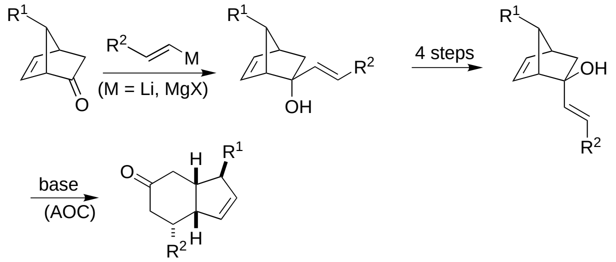
[19] The same molecular product may also be obtained using the mixed-valent triangular complex $[Fe_3O(PhCOO)_6(H_2O)_2(MeCN)]$. This has been confirmed by determination of the complete crystal and molecular structure: orthorhombic, space group Fddd, $a = 20.9903$, $b = 25.4990$, $c = 46.6602$ Å.

A Radical Alternative to the Anionic Oxy-Cope Rearrangement**

Rachel Chuard, Anne Giraud, and Philippe Renaud*

The anionic oxy-Cope rearrangement has emerged as a highly useful tool for organic synthesis.[1,2] Various 1,5-dien-3-ols readily undergo this electronic reorganization, and the usually easy preparation of the precursors contributes to the popularity of this reaction. However, a limitation of this sigmatropic rearrangement is the requirement of proximal double bonds. Indeed, the distance and the angular relationship between the two double bonds should be close to optimal values in order to achieve the rearrangement.[2,3] For example, with 1,5-dien-3-ols that result from the addition of alkenyl anions to 2-norbornenones, the double bonds are not proximal and therefore anionic sigmatropy is not possible. Two protocols that allow the inversion of the configuration of the quaternary center have been developed to remedy this problem. However, both are lengthy (four steps) and not high-yielding (Scheme 1).[4,5]



Scheme 1. Inversion of the stereogenic center of the alcohol is required prior to anionic oxy-Cope rearrangements (AOC) of norbornenone derivatives.[4,5]

We report herein a mechanistically different approach to solve this problem: a radical alternative to the oxy-Cope rearrangement. A cascade reaction that involves the fragmentation of an alkoxyl radical followed by a 6-*endo*-cyclization process leads to the oxy-Cope product (Scheme 2). According to this mechanism, the relative configuration of the alcohol has no influence on the efficacy of the rearrangement. Related anionic stepwise mechanisms have been observed for anionic amino-Cope rearrangements[6] as well as for oxy-Cope rearrangements of 4-phenylthio-1,5-dien-3-alkoxides.[7,8]

We investigated several methods to generate the desired alkoxyl radical **A**, starting from 2-norbornenone. Treatment

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[*] Prof. P. Renaud, R. Chuard
Department of Chemistry and Biochemistry, University of Bern
Freiestrasse 3, 3000 Bern 9 (Switzerland)
Fax: (+41)31-631-4359
E-mail: philippe.renaud@ioc.unibe.ch

A. Giraud
Department of Chemistry, University of Fribourg
Pérolles, 1700 Fribourg (Switzerland)

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