Iron Cluster with High Spin

Solvothermal Synthesis of a Tetradecametallic Fe^{III} Cluster[**]

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Polymetallic cluster complexes of paramagnetic transition-metal ions have attracted intense study since the discovery that such molecules can display the phenomenon of single-

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molecule magnetism (SMM).[1] There is a barrier to relaxation of magnetisation in SMMs due to the combination of a large ground-state spin multiplicity and a significant negative zero-field splitting of that ground state, and this imparts a molecular magnetic memory effect. Unfortunately, all SMMs made to date only exhibit a memory effect at very low temperatures. Therefore, there is a huge effort in synthesizing larger clusters in an attempt to generate larger spin ground states and higher energy barriers to loss of magnetization.

To date, most cluster synthesis has involved "conventional" coordination chemistry techniques, that is, solution chemistry under atmospheric pressure and at temperatures limited to the boiling points of common solvents. We have been investigating the use of solvothermal techniques—chemistry in superheated solvents—towards cluster synthesis.[2] The solvothermal technique allows not only the application of high temperatures to reactions in low boiling solvents but is also a superb technique for crystallizing the products. We previously reported that superheating alcoholic solutions of trimetallic $[Cr_3O(O_2CMe)_6(H_2O)_3]Cl$ yields the decametallic Cr^{III} clusters $[Cr_{10}(OR)_{20}(O_2CMe)_{10}]$ (R = Me, Et).[2] We are now exploring the solvothermal chemistry of other simple basic metal acetates and report herein the isolation of a tetradecametallic Fe^{III} cluster by using the ligand benzotriazole (BtaH). Benzotriazole has previously been used to produce model compounds for corrosion inhibiton studies and in M^{II} cluster chemistry,[3] but until recently never in the synthesis of M^{III} clusters.[4]

A solution of $[Fe_3O(O_2CMe)_6(H_2O)_3]Cl$ in MeOH was superheated at 100 °C for 12 h to give a red solution, from which only insoluble powders could be isolated. However, an analogous reaction in the presence of the potential bridging ligand benzotriazole (BtaH) in MeOH followed by slow cooling gives a red crystalline product, **1**. The equivalent reaction at reflux under atmospheric pressure gives only solutions from which no clean product can be isolated. Single-crystal X-ray diffraction studies[5] of **1** reveals the structure to be the tetradecametallic Fe^{III} cluster $[Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6]$ (Figure 1). Complex **1** has crystallographic C_i symmetry although there is pseudo threefold symmetry down the Fe1–Fe1A vector.

The metallic core of **1** can be described as a hexacapped hexagonal bipyramid with the caps on alternate faces (Figure 2). The three face capping iron ions [Fe2, Fe3, Fe4 and symmetry equivalents] and the apical iron [Fe1 and symmetry equivalents] on either half of the molecule form two $\{Fe_4(bta)_3Cl_3\}$ units each separated by nine μ_2-methoxides and three μ_4-oxides [O1, O2, and O3] from a central $\{Fe_6\}$ ring. The Bta^- ligands bind in a μ_3-fashion to generate $\{Fe_4(bta)_3\}$ fragments: the three "arrowhead" or central nitrogens in each fragment all bond to Fe1 (or symmetry equivalents) and the other two nitrogens on each Bta^- bind two of Fe2, Fe3, Fe4 (and symmetry equivalents). Each of the face caps also has a terminal chloride (Cl1, Cl2, and Cl3), with the coordination sphere of the apical Fe1 completed by three μ_4-oxides [O1,O2,O3] bridging it to each of Fe2, Fe3, and Fe4 and to the central $\{Fe_6\}$ ring [Fe5, Fe6, Fe7, and symmetry equivalents]. Remarkably, there is no carboxylate in the structure.

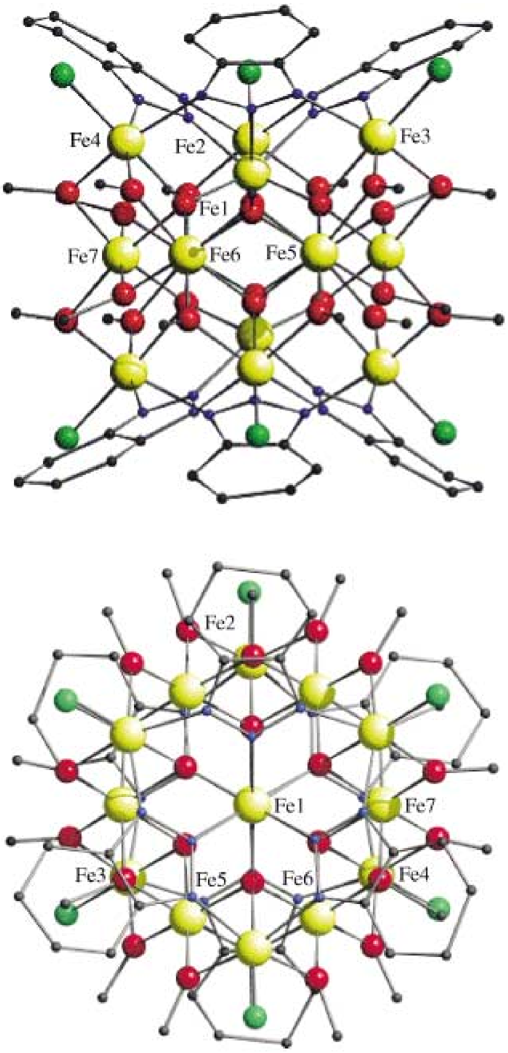

Figure 1. Molecular structure of $[Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6]$ **1**. (top) Viewed perpendicular to the Fe1–Fe1A axis; (bottom) viewed down the Fe1–Fe1A axis. Bond length ranges: Fe-N 2.063–2.183 Å, Fe-Cl 2.235–2.267 Å, Fe-O(Me) 1.949–2.071 Å, Fe-μ_4O 1.935–2.174 Å. Colour scheme: Fe, yellow; O, red; N, blue; Cl, green.

The $\{Fe_6\}$ ring is near planar (0.0066 Å mean deviation from the best least-squares plane) with each iron ion bound to two μ_4-oxides, two μ_2-methoxides bridging to Fe1 and its symmetry equivalents, and two μ_2-methoxides bridging within the $\{Fe_6\}$ ring.

All the iron centers are Fe^{III}, as required by the charge balance of the formula, and the μ_4-oxides preclude any ambiguity of oxide versus hydroxide. This was also confirmed by Bond Valence Sum (BVS) calculations.[6] To our knowledge, complex **1** is the first example of an Fe_{14} cluster[17] and is amongst the highest nuclearity iron clusters reported to date, superseded only by Fe_{16}[7] and Fe_{18} wheels,[8] an Fe_{17} cluster,[9] the "captured rust" Fe_{17}/Fe_{19} clusters reported by Heath and Powell,[10] and a heterometallic species containing thirty Fe^{III} ions.[11]

The $\{Fe_4(bta)_3\}$ moiety resembles that formed between Bta^- and divalent metal cations, in which a centred tetrahedron of metal ions is held together by six μ_3-Bta^- ligands in a

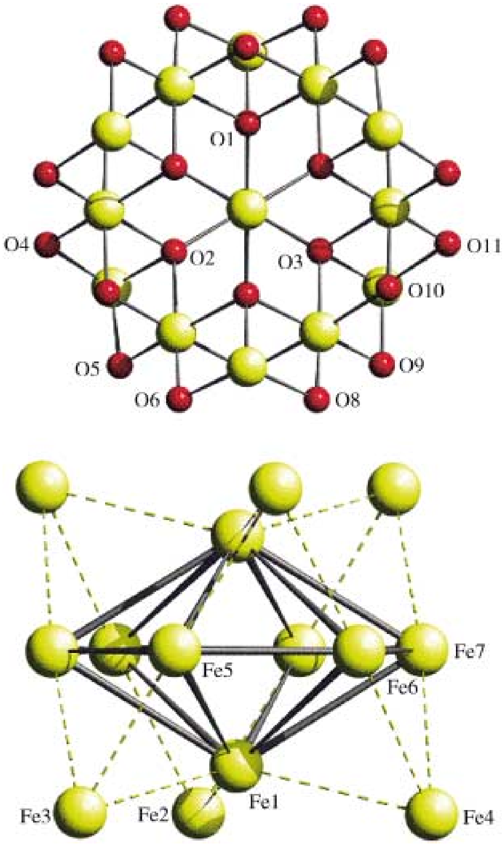

Figure 2. The metal–oxygen core viewed down the Fe1–Fe1A axis (top); The hexacapped hexagonal bipyramidal metallic skeleton (bottom). Fe···Fe distance ranges: Fe(3)···$\{Fe_6\}$ ring 3.543–3.562 Å, Fe(3)···Fe(face caps) 3.147–3.425 Å, adjacent ions within $\{Fe_6\}$ ring 3.023–3.043 Å, Fe(face cap)···$\{Fe_6\}$ ring 3.095–3.129 Å.

similar fashion to give $\{M_5(bta)_6\}$ cores.[12] Nonametallic Ni^{II} and hexaicosametallic Mn^{III} clusters, bound by μ_3-Bta^- type ligands, were also reported.[13,4] The $\{Fe_4(bta)_3\}$ unit is flattened considerably with respect to a fragment of an idealized tetrahedron with Fe(face cap)-Fe(apex)-Fe(face cap) angles in the range 114.9–115.6°.

Solid-state dc magnetization measurements were performed on **1** in the range 2–300 K, in a field of 2.0 kG between 300 and 50 K and 0.5 kG below 50 K. The $\chi_M T$ value is equal to 57 emu mol^{-1} K at 300 K and it then increases steadily with decreasing temperature, reaching a maximum value of 163 emu mol^{-1} K at 17 K, before dropping dramatically below this temperature to a value of approximately 74 emu mol^{-1} K at 2 K (Figure 3). The value of the maximum in $\chi_M T$ suggests that the ground spin state is at least equal to 18. The collapse of $\chi_M T$ below 17 K may be a consequence of either zero-field splitting within the ground state as evidenced from $M = f(H/T)$ data, or of the presence of intermolecular antiferromagnetic interactions between clusters at low temperature.

To determine the value of the spin ground state, magnetization measurements were performed at 3, 4 and 6 K between 0.1 and 5.5 Tesla. We attempted to fit the data assuming different spin states (S) between 21 and 24. The best fit (first made for each temperature independently and second by simultaneously fitting the data for the three temperatures) was obtained for $S = 23$ as the ground state with the following parameters: $g = 1.98$ and $D = 0.08\ cm^{-1}$ (Figure 4; $g = g$ factor, $D =$ zero-field splitting parameter).

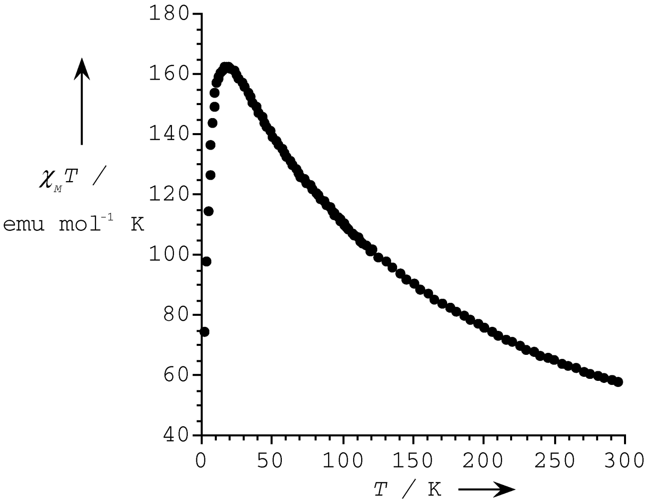

Figure 3. Plot of $\chi_M T$ vs T for **1**.

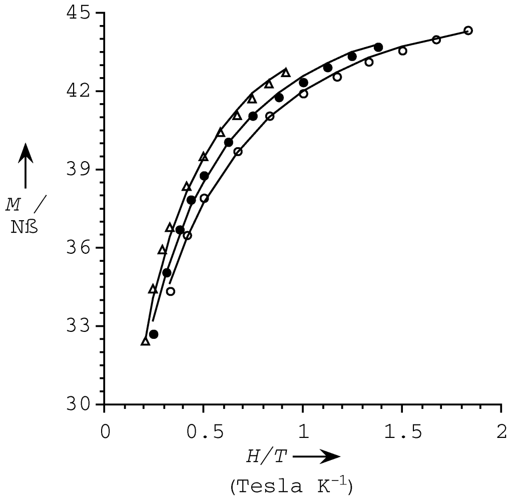

Figure 4. Plot of magnetization (M/Nβ) vs H/T for **1** in the ranges 0.1–5.5 T and 3 (○), 4 (●) and 6 (△) K. The solid lines are fits to $S = 23$, $g = 1.98$ and $D = 0.08\ cm^{-1}$.

This represents only a preliminary assignment of the spin ground state—a more detailed analysis will be reported in a full paper. Presumably the presence of such a large spin ground state is due to the presence of competing antiferromagnetic and ferromagnetic exchange coupling interactions between the Fe^{III} ions. A closer examination of the structure of **1** reveals that the Fe–O–Fe bridges fall into two clear categories: those that connect the apical Fe ions (Fe1 and Fe1A) to the face cap and equatorial Fe ions (through the μ_4-oxides) are characterized by angles of 113–125°, while those that connect all other Fe ions (through the μ_2-methoxides and the μ_4-oxides) are much smaller, characterized by angles less than 102°. If we assume that the larger angles will lead to the strongest antiferromagnetic exchange, thus dominating the other interactions, then we are left with a situation whereby the spins on Fe1 and Fe1A are antiferromagnetically coupled to all the other spins, which leads to twelve "spin up" $S=5/2$ centers and two "spin down" $S=5/2$ centers and an overall $S=25$ ground state. While the best fit to the magnetic data is for an $S=23$ ground state rather than $S=25$, it is clear that a very large spin for this molecule can be rationalized.

Complex **1** would represent not only the highest spin Fe cluster yet reported but possibly the highest spin molecule known. The $S=39/2$ Mn_9W_6 molecule reported by Hashimoto and co-workers[14] and the $S=33/2$ Fe_{19} cluster[10] are the highest spin ground states reported, although an $S=51/2$ ground state was suggested for a Mn_9Mo_6 cluster.[15] Ac susceptibility measurements, single-crystal studies and multi-frequency EPR experiments are currently underway to confirm the precise nature of S and the amplitude and sign of the zero-field splitting parameter D. These results will be reported at a later date.

This work highlights two significant advantages of the solvothermal technique for large paramagnetic cluster synthesis. The first is the synthesis of products different to those available from analogous reactions under conventional conditions—no cluster product was isolated after the reaction mixture had been heated at reflux. Second, solvothermal techniques allow the crystallization of high nuclearity products directly from the reaction mixture in good yield. Solvothermal techniques were originally developed by geochemists to mimic mineral growth, and have long been used for crystallization of inorganic materials.[16] This propensity for crystal growth will be hugely important in cluster chemistry given the reliance of this chemistry on X-ray diffraction for product identification.

Experimental Section

$[Fe_3O(CH_3CO_2)_6(H_2O)_3]Cl$ (0.32 mmol), BtaH (0.32 mmol) and MeOH (9 mL) were placed in a sealed Teflon container and heated for 12 h at 100 °C. X-ray quality crystals of **1** appeared on cooling the MeOH solution, in approximately 40 % yield. Elemental analysis calcd(%)for $Fe_{14}C_{54}H_{78}O_{24}N_{18}Cl_6$: C 27.51, H 3.33, N 10.69, Fe 33.16; found: C 27.65, H 3.55, N 10.78, Fe 32.88. Selected IR data (KBr pellet): $\tilde{\nu}$2924(m), 2820(m) 1573(w), 1442(w), 1273(w), 1222(m), 1055(s), 787(m), 755(m), 573(m), 467 cm^{-1} (m).

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Keywords: cluster compounds · iron · magnetic properties · N ligands · solvothermal chemistry

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[5] Crystal structure data for **1:** $C_{54}H_{78}C_{l6}Fe_{14}N_{18}O_{24}$, $M_r=2357.94$, crystal size $0.05\times0.02\times0.01$ mm^3, monoclinic, space group, $P2(1)/n$ (no. 14) $a=14.2255(6)$, $b=19.4975(8)$, $c=15.5833(7)$ Å, $\beta=110.435(2)°$, $V=4050.2(3)$ $Å^3$, $T=150(2)$ K, $Z=2$, $\rho_{calcd}=1.933$ $g\,cm^{-3}$ $\mu(\lambda=0.6845$ Å$)=2.70$ mm^{-1}, 14319 reflections collected, 4178 unique ($R_{int}=0.0567$), $R(F)=0.0659$ and $wR2=0.1576$ using 3014 reflections with $I>2\sigma(I)$. CCDC-209766 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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