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A Novel Undecametallic Iron(III) Cluster with an $S = {}^{11}/_{2}$ Spin Ground State

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The reaction of $[NEt_4]_2[Fe_2OCl_6]$ with sodium benzoate, 4,6-dimethyl-2-hydroxypyrimidine (dmhp), and 1,1,1-tris(hydroxymethyl)ethane (H_3thme) gives the undecametallic compound $[NEt_4][Fe_{11}O_4(O_2CPh)_{10}(thme)_4(dmhp)_2Cl_4]$. X-ray crystallography, EPR spectroscopy, bulk magnetic susceptibility studies, and low-temperature single-crystal magnetic measurements were used to characterize the compound. Magnetic measurements indicate an $S = {}^{11}/_{2}$ ground state with the parameters $g = 2.03$ and $D = -0.46$ cm^{-1}. Single-crystal magnetic studies show hysteresis of molecular origin at $T < 1.2$ K with fast quantum mechanical tunneling at zero field.

Iron−oxo clusters have been investigated for many years for a variety of reasons. These range from biological models for the iron oxo core of the iron storage protein ferritin,[1] the study of biomineralization processes that form iron−oxo minerals,[2] and more recently for single-molecule magnetism (SMM) behavior. Although a variety of Mn-containing SMMs have been reported in recent years,[3] fewer Fe SMMs are known.[4−8] The requirement for SMM behavior is the combination of a large spin ground state with a negative D value, but there are relatively few Fe(III) clusters with large ground spin states: Fe4, $S = 5$;[5] Fe4, $S = 8$;[8,9] Fe8, $S = 10$;[4] Fe10, $S = 11$;[6] Fe7, $S = {}^{29}/_{2}$;[10] and Fe19, $S = {}^{33}/_{2}$;[11] Following on from our recent success using the ligand 1,1,1-tris(hydroxymethyl)ethane (H_3thme) in Mn and Fe cluster chemistry,[12,13] we herein report the synthesis, structure, and magnetic properties of a new undecametallic Fe cluster with an $S = {}^{11}/_{2}$ spin ground state.

Reaction of $[NEt_4]_2[Fe_2OCl_6]$ (1 equiv) with NaO_2CPh (2 equiv), dmhp (1 equiv), and H_3thme (1 equiv) in MeCN leads to the formation of $[NEt_4][Fe_{11}O_4(O_2CPh)_{10}(thme)_4(dmhp)_2Cl_4]$ **1**[14] in ≤20% yield after 1 week. **1** (Figure 1) crystallizes in the monoclinic space group $P2_1/c$.

The core of **1** (Figure 2) consists of four fused butterfly $\{Fe_4O_2\}^{8+}$ motifs. The two butterflies in the center of the core (Fe1, Fe2, Fe3, Fe5, and symmetry equivalents) share a body Fe ion (Fe3) forming a planar central $\{Fe_7O_4\}^{13+}$ unit (Fe1−Fe3−Fe1A = 180.0°). The two peripheral but-

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(14) Crystal data for **1**: $C_{131}H_{130}Cl_4Fe_{11}N_{14}O_{38}$, $M = 3264.64$, monoclinic, space group $P2_1/c$, $a = 13.9889(9)$ Å, $b = 21.5807(15)$ Å, $c = 23.9145(16)$ Å, $\beta = 94.753(1)°$, $V = 7194.7(8)$ Å^3, $Z = 2$, $D_c = 1.507$ g cm^{-3}, $\mu = 1.229$ mm^{-1} (Mo Kα, $\lambda = 0.71073$ Å), $T = 100(2)$ K, CCD diffractometer, 41276 measured, 14643 unique data ($R_{int} = 0.0408$), of which 11583 have $I > 2\sigma(I)$. R ($I > 2\sigma(I)$) $= 0.0400$, $wR2$ (on F^2, all data) $= 0.1105$ with 922 refined parameters, goodness-of-fit $= 1.028$.

10.1021/ic034654v CCC: $25.00

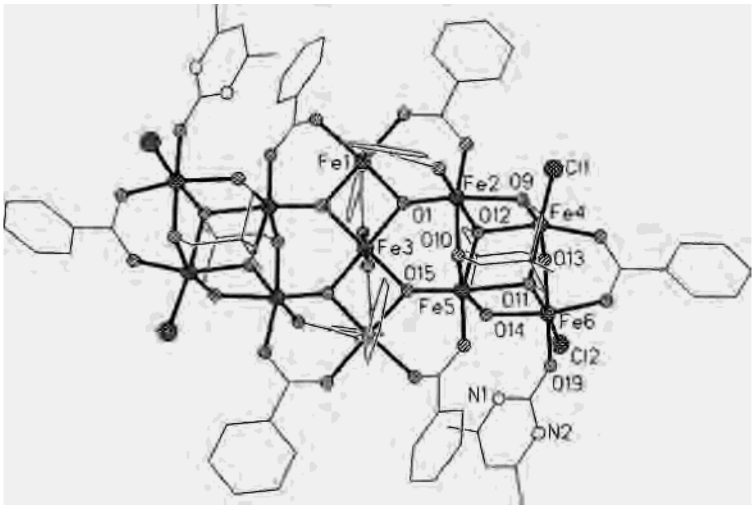

Figure 1. The structure of the complex in **1**. Selected interatomic distances (Å): $Fe^{3+}-O$, 1.827(18)−2.182(18), $Fe^{3+}-Cl$, 2.266(8)−2.301(8).

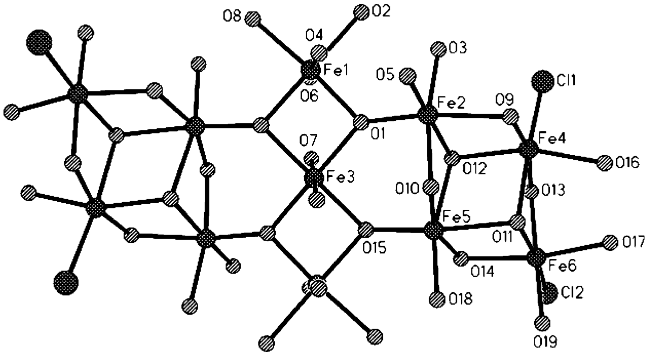

Figure 2. The core of the complex in **1**.

terfly units (Fe2, Fe4, Fe5, Fe6, and symmetry equivalents) are nonplanar and are situated, respectively, above and below the plane of the central $\{Fe_7O_4\}^{13+}$ core. The wing tip Fe atoms (Fe2 and Fe6) lie respectively above and below the plane of the body Fe atoms Fe4 and Fe5. The four $thme^{3-}$ ligands are found in the peripheral $\{Fe_4O_2\}$ units, with two oxygen atoms acting as μ_2-bridges, linking the Fe atoms within the $\{Fe_4O_2\}$ unit as well as between the $\{Fe_4O_2\}$ and $\{Fe_7O_4\}^{13+}$ units. The third oxygen atom acts as a μ_3-bridge within the $\{Fe_4O_2\}$ unit. The 10 $PhCO_2^-$ ligands bridge in their familiar μ_2-mode, while the Cl^- ions are all terminal. The neutral dmhp ligands are also terminally bonded, with the nitrogen atom protonated and hydrogen bonding to a μ_2-oxygen of a $thme^{3-}$ ligand (O14−N1, 2.796(8) Å).

$\{M_4O_2\}$ butterfly units are common building blocks in the structures of Fe(III) and Mn(III) clusters. The $\{M_7O_4\}^{13+}$ subunit is also a common feature in larger clusters, including Fe17/19[11] and Fe11.[15] In fact the Fe11 core is similar to a Mn11 cluster reported by Christou and co-workers, but in this case the peripheral units are [Mn4] cubes not butterflies.[16] **1** is only the second undecametallic Fe complex reported; the original has no structural resemblance to **1**, being based on a pentacapped trigonal prism.

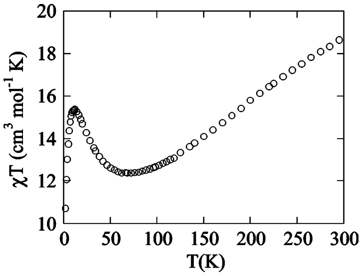

Figure 3. Thermal variation of $\chi_M T$ in the ranges 300−50 K at 0.2 T and 50−2 K at 0.05 T.

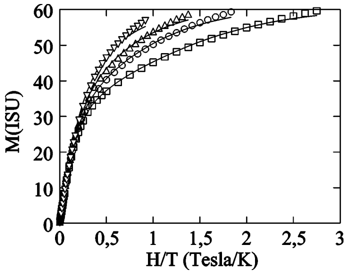

Figure 4. Magnetization vs *H*/*T* plot at 2(□), 3(○), 4(△), and 6(▽) K.

Solid state dc magnetization measurements were performed on **1** in the range 2−300 K in a field of 0.2 T between 300 and 50 K, and 0.05 T between 50 and 2K. (Figure 3). The room temperature $\chi_m T$ value of approximately 18.7 cm^3 mol^{-1} K decreases to a minimum of 12.4 cm^3 mol^{-1} K at 70 K, and then rises to a maximum of 15.4 cm^3 mol^{-1} K at 12 K and then drops. This indicates that **1** has a nonzero spin ground state and that the ground spin state is higher than $^9/_2$. In order to obtain the ground state spin, magnetization data were collected in the ranges 2.0−6.0 K and 0.01−5.5 T (Figure 4). The fits were made simultaneously on the four different temperatures (2, 3, 4, and 6 K), assuming that only the ground state is populated, giving a best fit of $S = {}^{11}/_2$, $g = 2.03$, and $D = -0.46$ cm^{-1}. The maximum value of $\chi_M T$ at low temperature (15.4 cm^3 mol^{-1} K) and the fact that the magnetization data at 2 and 6 K can be fit with one set of parameters strongly indicate that the ground state is

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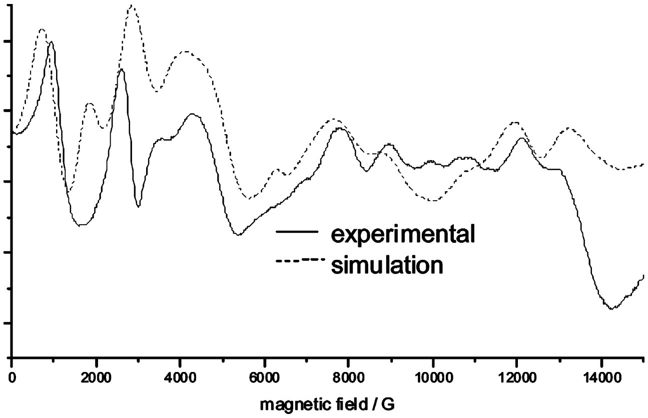

Figure 5. Q-band EPR spectrum of **1**. Experimental: $\nu = 33.9250$ GHz; $T = 5$ K, power = 1.9 mW; modulation amplitude = 10 G; Simulation: $g = 2.03$; $D = -0.38$ cm^{-1}; $E = 0.055$ cm^{-1}; $\Delta B = 1300$ G; Gaussian line shapes were used.

indeed $S = {}^{11}/_2$ and that the first excited state is rather high in energy. The previously reported Fe11 complex has an $S = {}^{1}/_2$ spin ground state.

The polycrystalline EPR spectrum of **1** at Q-band frequency and 5 K (Figure 5) confirmed both the spin state and magnitude and sign of the zero-field splitting deduced from the magnetization curves. Significantly, it was impossible to produce an adequate simulation of the spectrum without inclusion of rhombicity ($E \neq 0$). Given the nature of S and sign of D, measurements were taken to see if **1** acts as a SMM. Low-temperature (1.2−0.04 K) single-crystal magnetic measurements were performed on **1** using a micro-SQUID instrument equipped with three orthogonal fields, allowing the magnetic field to be scanned in all directions.

Below 1.2 K hysteresis loops are seen in magnetization vs field studies whose coercivities increase with decreasing temperature (Figure 6). A detailed study of the field sweep rate dependence of the hysteresis loops showed that the hysteresis at nonzero fields is due not to a phonon bottleneck but to slow relaxation because of the anisotropy barrier. Slow relaxation is seen at $H = 0$, but the presence of strong tunneling does not allow for a reliable Arrhenius plot. For all SMMs the barrier is reduced at $H = 0$ because of the presence of tunneling. Even half-integer spin systems, which in theory should not tunnel, do so because of coupling with the environment: dipolar coupling between molecules, hyperfine coupling, spin−spin cross relaxation, and other multibody quantum processes. For example for a system with $S = {}^{11}/_2$, $D = -0.46$ cm^{-1}, $E = -0.055$ cm^{-1} and assuming an internal transverse field of approximately 10 mT, one can estimate a tunnel splitting of ca. 2.8×10^{-6} K and thus a tunnel probability of $P = 0.68$ for a sweep rate of 0.1 T s^{-1}, in good agreement with our measurements. This has also been observed in a [Mn4] cluster with $S = {}^{9}/_2$.[17]

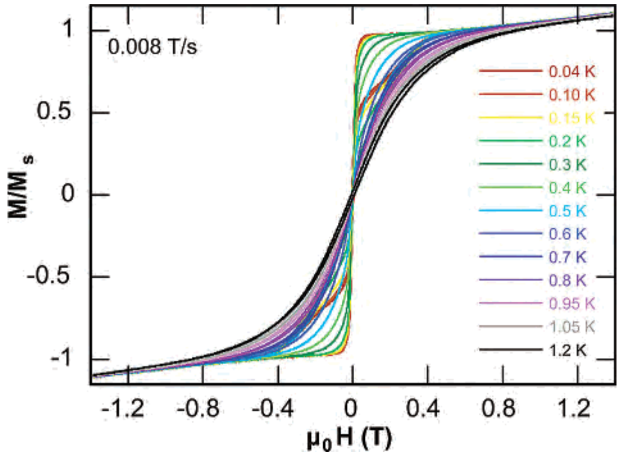

Figure 6. Magnetization of **1** (M) plotted as a fraction of maximum (M_s) vs applied magnetic field ($\mu_0 H$).

Magnetic studies of $\{Fe_4O_2\}^{8+}$ butterflies indicate complexes with $S = 0$ spin ground states,[18] in contrast to $\{Mn_4O_2\}^{8+}$ complexes which usually exhibit an $S = 3$ spin ground state.[19] The difference has been explained by considering the different competing exchange interactions present: in $\{Mn_4O_2\}^{8+}$ complexes the body−body interaction is greater than the wing tip−body interaction, resulting in a “frustrated” spin alignment of the wing tip ions and an $S = 3$ ground state. In $\{Fe_4O_2\}^{8+}$ complexes the body−wing tip exchange interaction dominates, resulting in an $S = 0$ spin ground state. **1** contains four such $\{Fe_4O_2\}$ units fused together, creating a number of competing exchange interactions leading to the stabilization of an intermediate spin ground state of $S = {}^{11}/_2$. **1** is only the second Fe11 cluster reported (although various derivatives of the original Fe11 have been synthesized)[20] and is the first to exhibit an appreciable spin ground state. Combined with a negative D value this leads to **1** being a new example of a SMM.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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