

## A Novel Undecametallic Iron(III) Cluster with an $S = 11/2$ Spin Ground State

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The reaction of  $[\text{NEt}_4]_2[\text{Fe}_2\text{OCl}_6]$  with sodium benzoate, 4,6-dimethyl-2-hydroxypyrimidine (dmhp), and 1,1,1-tris(hydroxymethyl)ethane ( $\text{H}_3\text{thme}$ ) gives the undecametallic compound  $[\text{NEt}_4][\text{Fe}_{11}\text{O}_4(\text{O}_2\text{CPh})_{10}(\text{thme})_4(\text{dmhp})_2\text{Cl}_4]$ . 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  $D = -0.46 \text{ cm}^{-1}$ . Single-crystal magnetic studies show hysteresis of molecular origin at  $T < 1.2 \text{ K}$  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,<sup>1</sup> the study of biomineralization processes that form iron–oxo minerals,<sup>2</sup> and more recently for single-molecule magnetism (SMM) behavior. Although a variety of Mn-containing SMMs have been reported in recent years,<sup>3</sup> fewer Fe SMMs are known.<sup>4–8</sup> 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:  $\text{Fe}_4$ ,  $S = 5$ ;<sup>5</sup>  $\text{Fe}_4$ ,  $S = 8$ ;<sup>8,9</sup>  $\text{Fe}_8$ ,  $S = 10$ ;<sup>4</sup>  $\text{Fe}_{10}$ ,  $S = 11$ ;<sup>6</sup>  $\text{Fe}_7$ ,  $S = 29/2$ ;<sup>10</sup> and  $\text{Fe}_{19}$ ,  $S = 33/2$ ;<sup>11</sup> Following on from our recent success using the ligand 1,1,1-tris(hydroxymethyl)ethane ( $\text{H}_3\text{thme}$ ) in Mn and Fe cluster chemistry,<sup>12,13</sup> 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  $[\text{NEt}_4]_2[\text{Fe}_2\text{OCl}_6]$  (1 equiv) with  $\text{NaO}_2\text{CPh}$  (2 equiv), dmhp (1 equiv), and  $\text{H}_3\text{thme}$  (1 equiv) in MeCN leads to the formation of  $[\text{NEt}_4][\text{Fe}_{11}\text{O}_4(\text{O}_2\text{CPh})_{10}(\text{thme})_4(\text{dmhp})_2\text{Cl}_4]$  **1**<sup>14</sup> in  $\leq 20\%$  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  $\{\text{Fe}_4\text{O}_2\}^{8+}$  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  $\{\text{Fe}_7\text{O}_4\}^{13+}$  unit (Fe1–Fe3–Fe1A =  $180.0^\circ$ ). The two peripheral but-

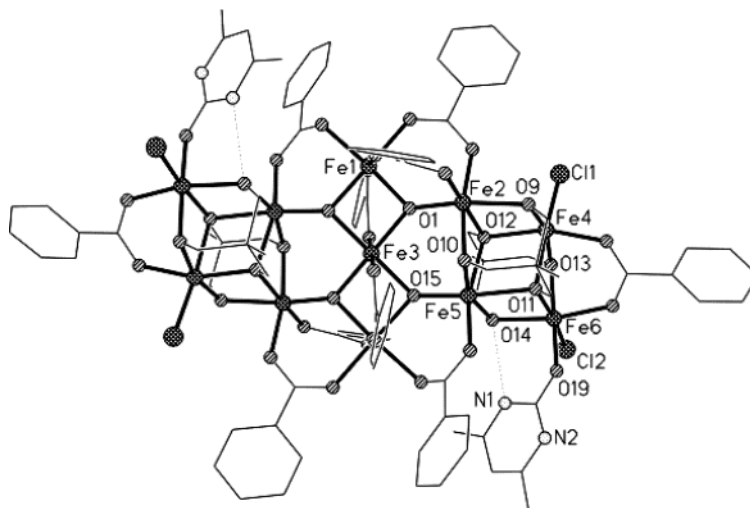
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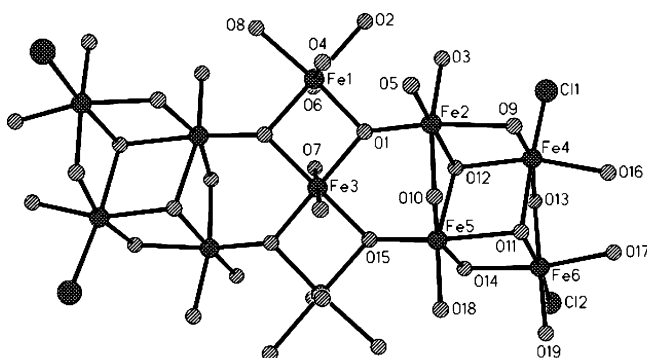
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- Crystal data for **1**:  $\text{C}_{131}\text{H}_{130}\text{Cl}_4\text{Fe}_{11}\text{N}_4\text{O}_{38}$ ,  $M = 3264.64$ , monoclinic, space group  $P2_1/c$ ,  $a = 13.9889(9) \text{ \AA}$ ,  $b = 21.5807(15) \text{ \AA}$ ,  $c = 23.9145(16) \text{ \AA}$ ,  $\beta = 94.753(1)^\circ$ ,  $V = 7194.7(8) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.507 \text{ g cm}^{-3}$ ,  $\mu = 1.229 \text{ mm}^{-1}$  (Mo  $K\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ),  $T = 100(2) \text{ K}$ , CCD diffractometer, 41276 measured, 14643 unique data ( $R_{\text{int}} = 0.0408$ ), 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.



**Figure 1.** The structure of the complex in **1**. Selected interatomic distances (Å): Fe<sup>3+</sup>–O, 1.827(18)–2.182(18), Fe<sup>3+</sup>–Cl, 2.266(8)–2.301(8).

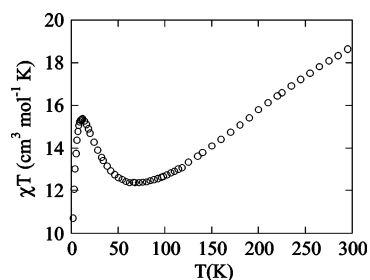


**Figure 2.** The core of the complex in **1**.

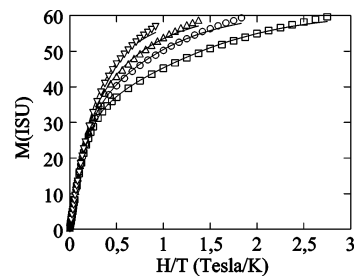
terfly units (Fe2, Fe4, Fe5, Fe6, and symmetry equivalents) are nonplanar and are situated, respectively, above and below the plane of the central {Fe<sub>7</sub>O<sub>4</sub>}<sup>13+</sup> core. The wing tip Fe atoms (Fe2 and Fe6) lie respectively above and below the plane of the body Fe atoms Fe4 and Fe5. The four thme<sup>3-</sup> ligands are found in the peripheral {Fe<sub>4</sub>O<sub>2</sub>} units, with two oxygen atoms acting as μ<sub>2</sub>-bridges, linking the Fe atoms within the {Fe<sub>4</sub>O<sub>2</sub>} unit as well as between the {Fe<sub>4</sub>O<sub>2</sub>} and {Fe<sub>7</sub>O<sub>4</sub>}<sup>13+</sup> units. The third oxygen atom acts as a μ<sub>3</sub>-bridge within the {Fe<sub>4</sub>O<sub>2</sub>} unit. The 10 PhCO<sub>2</sub><sup>-</sup> ligands bridge in their familiar μ<sub>2</sub>-mode, while the Cl<sup>-</sup> ions are all terminal. The neutral dmhp ligands are also terminally bonded, with the nitrogen atom protonated and hydrogen bonding to a μ<sub>2</sub>-oxygen of a thme<sup>3-</sup> ligand (O14–N1, 2.796(8) Å).

{M<sub>4</sub>O<sub>2</sub>} butterfly units are common building blocks in the structures of Fe(III) and Mn(III) clusters. The {M<sub>7</sub>O<sub>4</sub>}<sup>13+</sup> subunit is also a common feature in larger clusters, including Fe<sub>17</sub>/19<sup>11</sup> and Fe<sub>11</sub>.<sup>15</sup> In fact the Fe<sub>11</sub> core is similar to a Mn<sub>11</sub> cluster reported by Christou and co-workers, but in this case the peripheral units are [Mn<sub>4</sub>] cubes not butterflies.<sup>16</sup> **1** is only the second undecametallic Fe complex reported;

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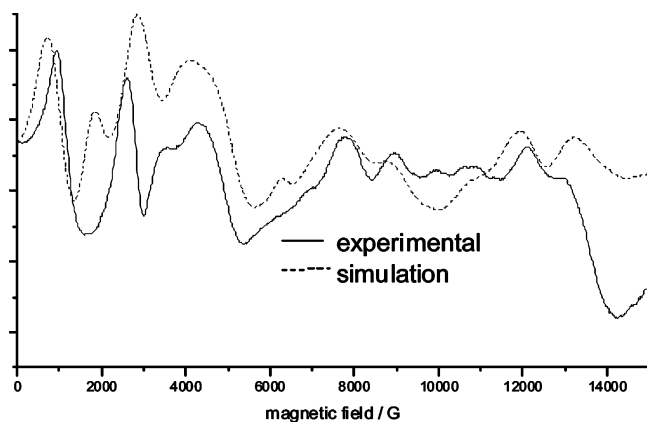
**Figure 3.** Thermal variation of  $\chi_M T$  in the ranges 300–50 K at 0.2 T and 50–2 K at 0.05 T.



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

the original has no structural resemblance to **1**, being based on a pentacapped trigonal prism.

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 2 K. (Figure 3). The room temperature  $\chi_M T$  value of approximately 18.7 cm<sup>3</sup> mol<sup>-1</sup> K decreases to a minimum of 12.4 cm<sup>3</sup> mol<sup>-1</sup> K at 70 K, and then rises to a maximum of 15.4 cm<sup>3</sup> mol<sup>-1</sup> 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<sup>-1</sup>. The maximum value of  $\chi_M T$  at low temperature (15.4 cm<sup>3</sup> mol<sup>-1</sup> 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

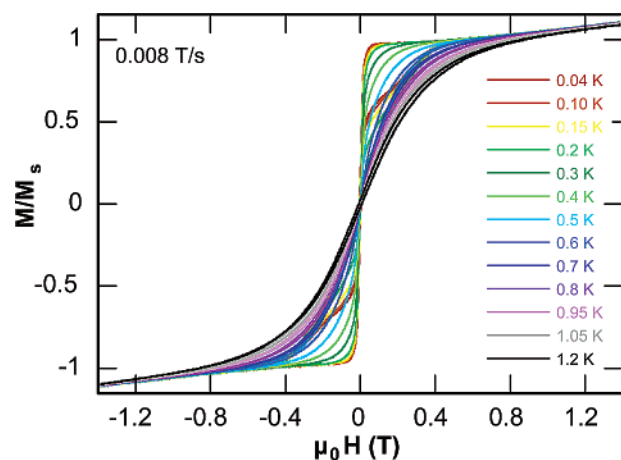


**Figure 5.** Q-band EPR spectrum of **1**. Experimental:  $\nu = 33.9250$  GHz;  $T = 5$  K, power = 1.9 mW; modulation amplitude = 10 G; Simulation:  $g = 2.03$ ;  $D = -0.38$  cm $^{-1}$ ;  $E = 0.055$  cm $^{-1}$ ;  $\Delta B = 1300$  G; Gaussian line shapes were used.

indeed  $S = 11/2$  and that the first excited state is rather high in energy. The previously reported FeII 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.  $2.8 \times 10^{-6}$  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  $S = 9/2$ .<sup>17</sup>



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

Magnetic studies of  $\{\text{Fe}_4\text{O}_2\}^{8+}$  butterflies indicate complexes with  $S = 0$  spin ground states,<sup>18</sup> in contrast to  $\{\text{Mn}_4\text{O}_2\}^{8+}$  complexes which usually exhibit an  $S = 3$  spin ground state.<sup>19</sup> The difference has been explained by considering the different competing exchange interactions present: in  $\{\text{Mn}_4\text{O}_2\}^{8+}$  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  $\{\text{Fe}_4\text{O}_2\}^{8+}$  complexes the body–wing tip exchange interaction dominates, resulting in an  $S = 0$  spin ground state. **1** contains four such  $\{\text{Fe}_4\text{O}_2\}$  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 FeII cluster reported (although various derivatives of the original FeII have been synthesized)<sup>20</sup> 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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