Iron Oxo Aggregation: Fe_3 to Fe_6. Synthesis, Structure, and Magnetic Properties of the Hexanuclear Dication $[Fe_6(\mu_4\text{-}O)_2(\mu_2\text{-}OMe)_8(OMe)_4(tren)_2]^{2+}$, a Soluble, Crystalline Model of Iron Oxo Hydroxo Nanoparticles, the Core of Ferritin and Rust Formation

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Hydrolytic polymerization of iron results in soluble nanoparticles averaging 70 Å in diameter,[1-3] followed by precipitation of hydrous oxide (FeO(OH)) commonly known as ferrihydrite or rust. This process is especially relevant to life forms where solubilization and storage of iron occur in ferritin, a multisubunit protein that provides a hollow "molecular flask" with an internal diameter of approximately 70 Å capable of storing up to 4500 iron atoms.[4,5] Our interests lie in the formative process of the large iron oxo hydroxo aggregates, especially those in ferritin, some forms of which are crystalline and resemble the layered structure of the mineral ferrihydrite.[5,6] The facile hydrolytic aggregation of such species makes this process difficult to control. Yet, with suitable "capping" ligands to prevent polymerization, the following polyoxo Fe(III) and related Mn(III)–Mn(IV) core structures[7] have been obtained: $[Fe_4O_2(OH)_4]^{4+}$,[8] $[Fe_4O_2(OH)_2(OR)_2]^{4+}$,[10] $[Mn_4O_6]^{4+}$,[11] $[Fe_6O(OR)_{18}]^{2-}$,[12] $[Fe_8O_2(OH)_{12}]^{8+}$,[13] and $[Mn_{10}O_{14}]^{8+}$.[14] Central to this research endeavor is an analysis of the bridging modes for the oxo ligand. Our initial efforts in this area involved a trinuclear aggregate $[Fe_3O_2(OH)(tren)_3]^{4+}$ (**1**),[9,15] which contains only oxo and hydroxo bridges and is formed by way of the dimeric oxo-bridged intermediate $[Fe_2O(CF_3SO_3)_2(tren)_2]^{2+}$ (**2**). Herein we report the synthesis and structure of a hexanuclear aggregate $[Fe_6(\mu_4\text{-}O)_2(\mu_2\text{-}OMe)_8(OMe)_4(tren)_2]^{2+}$ (**3**), which forms by solvolytic aggregation in methanol and contains the first example of a μ_4-O^{2-} ion ligated to four iron atoms.

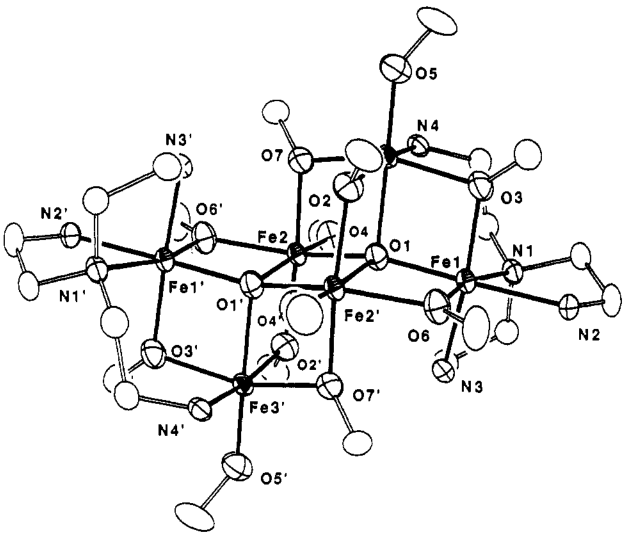

Figure 1. Structure of $[Fe_6O_2(OMe)_{12}(tren)_2]^{2+}$ depicting 30% ellipsoids. Selected interatomic distances (Å) and angles (deg):[17] Fe(1)···Fe(2′), 3.055; Fe(1)···Fe(3), 3.025; Fe(2)···Fe(3), 3.128; Fe(2)···Fe(2′), 3.170; Fe(2)···Fe(3′), 3.239; Fe(1)···Fe(2), 3.818; Fe(1)–O(1), 1.911; Fe(2)–O(1), 1.985; Fe(2)–O(1′), 2.196; Fe(3)–O(1), 2.125; Fe(2′)–O(2), 2.201; Fe(1)–O(2), 1.945; Fe(1)–O(3), 1.996; Fe(2)–O(2′), 2.035; Fe(2)–O(4), 2.074; Fe(2)–O(5′), 2.014; Fe(2)–O(6), 1.853; Fe(3)–O(3), 2.015; Fe(3)–O(4), 1.972; Fe(3)–O(5), 2.011; Fe(3)–O(7), 1.863; Fe(1)–N(1), 2.269; Fe(1)–N(2), 2.172; Fe(1)–N(3), 2.120; Fe(3)–N(4), 2.404; Fe(1)–O(1)–Fe(2), 157.0; Fe(1)–O(1)–Fe(3), 96.9; Fe(2)–O(1)–Fe(3), 99.0; Fe(2)–O(1)–Fe(2′), 98.5; Fe(2′)–O(1)–Fe(3), 97.1.

The synthesis of **3**$(CF_3SO_3)_2\cdot 2MeOH$ was accomplished by allowing a solution of **1** (1.0 mmol, 1.25 g) in 50 mL of MeOH to stand overnight, whereupon 0.17 g of analytically pure,[16] X-ray-quality,[17] orange crystals was deposited (27% yield). Alternatively, exposure of a methanol solution (10 mL) of 1 mmol of $Fe(CF_3SO_3)_2\cdot 2MeCN$ and 1 mmol of tren to air afforded large, orange crystals of **3**$(CF_3SO_3)_2\cdot 2MeOH$ in 40% yield over the course of a few days. The crystals are sparingly soluble in methanol but dissolve in DMF, from which they were crystallized as a DMF solvate by addition of ether.[18]

The centrosymmetric structure of **3** consists of two each of FeO_6, FeO_5N, and FeO_3N_3 octahedra, which share four, three, and two edges, respectively, with neighboring octahedra. Three

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(7) Only aggregates bridged by O^{2-}, OH^-, or OR^- and having nuclearity greater than 2 are listed here. The simplest unit, Fe_2O, is reviewed in: Kurtz, D. M., Jr. *Chem. Rev.* **1990**, *90*, 585–606.

(8) Sources for $[Fe_4O_2(OH)_4(tacn)_4]^{4+}$ [9] are as follows. (a) From $Fe(tacn)Cl_3$: Drueke, S.; Wieghardt, K.; Nuber, B.; Weiss, J.; Bominaar, E. L.; Sawaryn, A.; Winkler, H.; Trautwein, A. X. *Inorg. Chem.* **1989**, *28*, 4477–4483. (b) From $Fe(tacn)_2^{2+}$: Hagen, K. S. Unpublished work.

(9) Abbreviations used: tacn, 1,4,7-triazacyclononane: tren, 2,2′,2″-triaminotriethylamine; TIEO, 1,1,2-tris(*N*-methylimidazole-2-yl)-1-hydroxyethane; L^1, 2-hydroxy-1,3-xylylenediaminetetraacetate; L^2, 1,1-bis(*N*-methylimidazol-2-yl)-1-hydroxyethane.

(10) $[Fe_4O_2(OH)_4(L^1)]$: (a) Murch, B. P.; Boyle, P. D.; L. Que, J. *J. Am. Chem. Soc.* **1985**, *107*, 6728. (b) Murch, B. P.; Bradley, F. C.; Boyle, P. D.; Papaefthymiou, V.; Que, L., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 7993–8003.

(11) $[Mn_4O_6(tacn)_4]^{4+}$: (a) Wieghardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328–329. (b) Hagen, K. S.; Westmoreland, T. D.; Scott, M. J.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1907–1909.

(12) (a) $[Fe_6(\mu_6\text{-}O)((OCH_2)_3CCH_3)_6]^{2-}$: Hegetschweiler, K.; Schmalle, H.; Streit, H. M.; Schneider, W. *Inorg. Chem.* **1990**, *29*, 3625–3627. (b) $[Fe_6O(OCH_3)_{18}]^{2-}$: Hegetschweiler, K.; Schmalle, H.; Streit, H. M.; Gramlich, V.; Hund, H.-U.; Erni, I. *Inorg. Chem.* **1992**, *31*, 1299–1302.

(13) $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$: Wieghardt, K.; Pohl, K.; Jibril, I.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 77–78.

(14) $[Mn_{10}O_{14}(tren)_6]^{8+}$: Hagen, K. S.; Armstrong, W. H.; Olmsted, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 774–775.

(15) Hagen, K. S.; Nair, V. S. To be submitted for publication.

(16) Anal. Calcd for **3**·2MeOH, $C_{28}F_6Fe_6H_{80}N_8O_{22}S_2$: C, 24.12; H, 5.78; N, 8.04. Found: C, 23.99; H, 5.76; N, 8.01.

(17) X-ray analysis: **3**$(CF_3SO_3)_2\cdot 2MeOH$ crystallizes in the monoclinic space group $P2_1/n$; a = 14.188 (7) Å, b = 12.637 (6) Å, c = 15.577 (11) Å, β = 94.02 (5)°, V = 2786 (3) Å^3, T = 21 °C, ρ(calcd/obsd) = 1.66/1.65 g cm^{-3}, Z = 2; 3477 reflections ($I \geq 3\sigma_I$); Mo Kα (λ = 0.710 73 Å, $3 \leq 2\theta \leq 52°$); Patterson interpretation and expansion (SHELXS-86) and full-matrix refinement to R (R_w) = 5.4% (6.0%). Standard deviations: distances, 0.001–0.002 Å for Fe–Fe, 0.003–0.005 Å for Fe–O(N); angles, 0.1–0.2°.

(18) Cell dimensions at –70 °C: a = 13.74 (1) Å, b = 12.138 (8) Å, c = 17.68 (1) Å, α = 90°, β = 99.62 (7)°, γ = 90°, V = 2906 Å^3. ρ(calcd/obsd) = 1.68/1.65 g cm^{-3}, for **3**$(CF_3SO_3)_2\cdot 2DMF$ and Z = 2.

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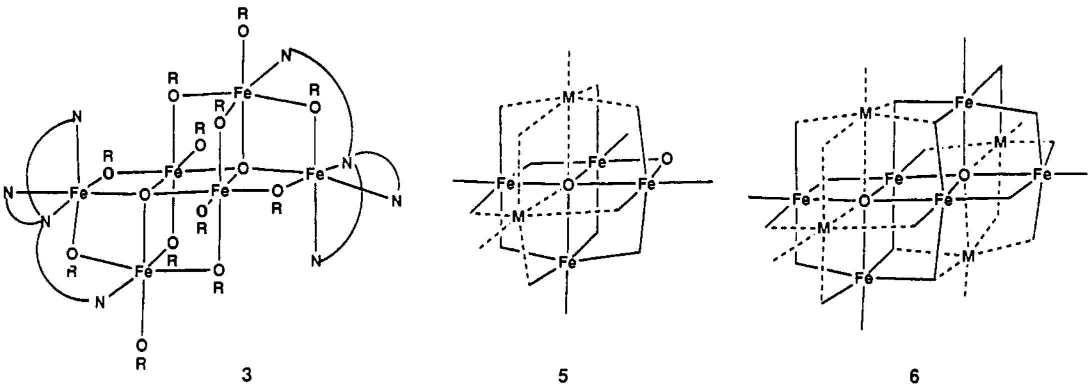
Chart I



nitrogen donors of the tetradentate ligand tren coordinate to Fe(1), while the fourth coordinates to Fe(3). Similar ligation of tren was observed in Mn_2 and Mn_{10} complexes.[14,19] A progression from μ_3- to μ_4-bridging modes can be formally constructed by dimerization of $(\mu_3\text{-O})Fe_3$ units through the center of symmetry to form the central Fe_2O_2 rhomb and new methoxide bridges. One arrangement of Fe_3 involves a "T-shaped" μ_3-O in a $Fe_3O(OMe)_2$ fragment (Fe(1), Fe(2), Fe(3), O(1), O(3), and O(7)) which is structurally very similar to the core of $[Fe_3O(TIEO)_2(O_2CPh)_2Cl_3]$ (**4**).[7,20] These two Fe_3O moieties lie in parallel planes (2.19 Å apart). Complex **3** can also be considered a fusion of two Fe_4 units (Fe(1), Fe(2), Fe(3), Fe(2′)) which are recognizable fragments of the more common group 5 and 6 isopolyanion hexametalates ($[M_6O_{19}]^{n-}$ (**5**, Chart I)) and decametalates ($[M_{10}O_{28}]^{n-}$ (**6**)).[21]

The methoxide oxygens and two nitrogen donors form two close-packed layers of donor atoms with iron atoms in octahedral holes. The remaining two iron atoms are above and below the O–Fe–O layers and are terminally ligated by amine ligands, which prevent further aggregation or the formation of $\mu_5\text{-O}^{2-}$ and subsequently $\mu_6\text{-O}^{2-}$, as is found in $[Fe_6O(OR)_{18}]^{2-}$.[12] The structure thus resembles a fragment of the layered structure common to iron oxides[5,6] and is considerably more compact than the oxohydroxo(carboxylato)hexairon(III) complexes.[22]

The Mössbauer spectrum at 190 K is consistent with high-spin Fe(III), and high-field data (40 and 80 kG at 4.2 K) indicate a paramagnetic ground state for an exchange-coupled Fe_6 unit with three distinguishable sites.[23] Very small zero-field splitting and an $S = 5$ ground state are suggested for **3** by the nested reduced magnetization curves at four fields and saturation at 11 μ_B (Figure 2). The three irons, distinguishable by crystallography and Mössbauer spectroscopy, may experience antiferromagnetic exchange interactions and spin frustration, resulting in a $^5/_2$ spin state. The room-temperature effective magnetic moment (8.61 μ_B/Fe_6 at 299.6 K as a solid and 8.67 μ_B/Fe_6 at 294.6 K in DMF solution) is consistent with two such noninteracting Fe_3 units with individual $\mu_{eff} \sim 6\ \mu_B$. An increase in the magnetic moment at low temperature (inset of Figure 2) is characteristic of ferromagnetic behavior. The $S = 5$ ground state may thus be a result of weak intramolecular ferromagnetic coupling of two $S = {}^5/_2$ Fe_3 moieties. The magnetism of **3** is remarkably similar to that of **10**, for which an $S = 5$ ground state has been determined from the saturation of the reduced magnetization at 9.2 μ_B.

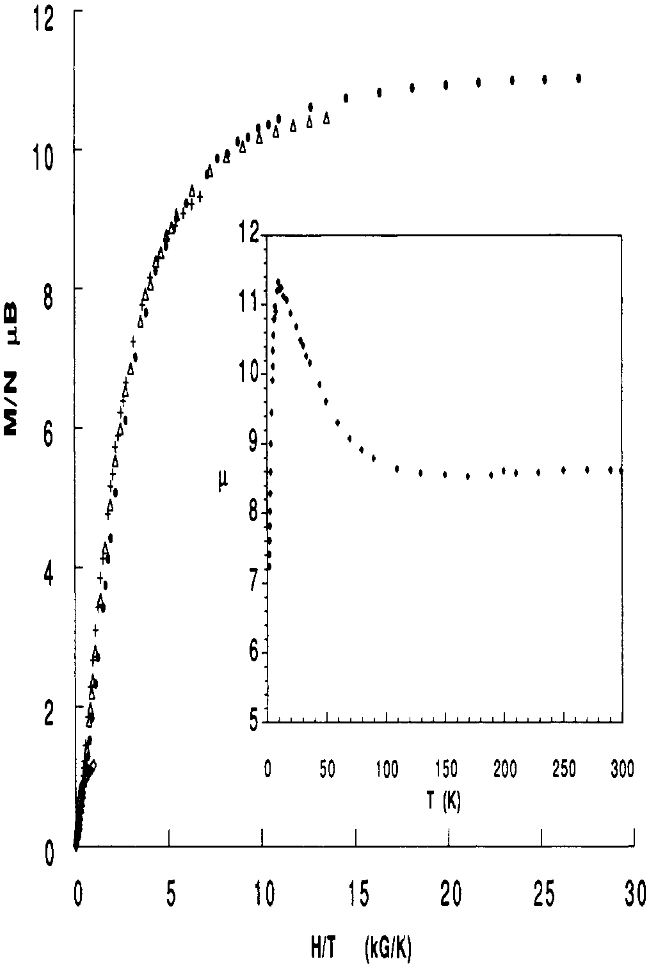


Figure 2. Plot of reduced magnetization ($M/N\mu_B$) of $3(CF_3SO_3)_2 \cdot 2MeOH$ versus H/T at fields of 2 kG (◇), 55 kG (●), 27.5 kG (△), and 13.75 kG (+). The inset shows a plot of μ_{eff} per molecule versus temperature at an applied field of 2 kG.

We have shown here that intermediate-spin ground states can occur in highly condensed polyiron structures. Complex **3** contains only single-atom bridges and is related to polyoxoanions, which have long been considered models of metal oxides.[21]

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(22) (a) $[Fe_6O_2(OH)_2(O_2CCMe_3)_{12}]$: Batsanov, A. S.; Struchkov, Y. T.; Timko, G. A. *Koord. Khim.* **1988**, *14*, 266. (b) $[Fe_6O_2(OH)_2(O_2CPh)_{12}(1,4\text{-dioxane})(OH_2)]$: Micklitz, W.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 3067–3069. (c) Micklitz, W.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372–374. (d) $[Fe_6O_2(OH)_2(O_2CCH_3)_{10}(L^2)_2]$: Harvey, D. F.; Christmas, C.; McCusker, J. K.; Hagen, P. M.; Chadha, R. K.; Hendrickson, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 598–600. (e) McCusker, J. K.; Christmas, C.; Hagen, P. M.; Chadha, R. K.; Harvey, D. F.; Hendrickson, D. *J. Am. Chem. Soc.* **1991**, *113*, 6114–6124.

(23) For measurements made at 190 K and referenced to iron metal at room temperature: three-site fit, $\Delta E_Q = 0.82$, 0.55, and 0.51 mm/s and $\delta =$ 0.42, 0.43, and 0.45 mm/s, respectively, with $\Gamma = 0.32$ mm/s.

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Supplementary Material Available: Text describing the X-ray experimental work and tables of crystallographic data, atomic positional and thermal parameters, and bond lengths and angles for **3** (10 pages). Ordering information is given on any current masthead page.