Iron–Oxo Aggregates: Synthesis, Structure, and ^{1}H NMR of the Octanuclear Hexacation $[Fe_8O_5(OAc)_8(tren)_4]^{6+}$, Containing a Square-Planar Oxide Bridge

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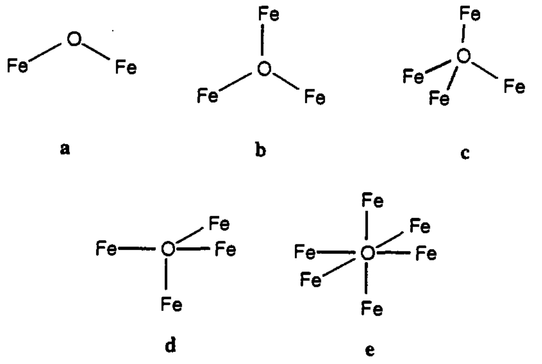
The importance of iron–oxo interactions in chemistry and biochemistry has generated a considerable effort to develop the chemistry of polynuclear iron–oxo aggregates.[1] We have undertaken a study of the formation of possible model compounds in order to understand the nucleation and propagation of the high-nuclearity iron–oxo–hydroxo aggregates of the iron storage protein ferritin.[2] A series of iron(III)–oxo aggregates with $Fe_2(\mu\text{-}O)$,[3] $Fe_3(\mu_3\text{-}O)$,[4] $Fe_3(\mu\text{-}O)_2(\mu\text{-}OH)$,[5] $Fe_4(\mu_3\text{-}O)_2$,[6] $Fe_4(\mu\text{-}O)_2(\mu\text{-}OH)_4$,[7] $Fe_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_2$,[8] $Fe_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_6$,[9] $Fe_6(\mu_4\text{-}(O_2))(\mu\text{-}OH)_2$,[10] $Fe_6(\mu_6\text{-}O)$,[11] $Fe_8(\mu_3\text{-}O)_2(\mu\text{-}OH)_{12}$,[12] $Fe_{10}(\mu\text{-}OCH_3)_{20}$,[13] $Fe_{11}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6$,[14] $Fe_{16}M(\mu_4\text{-}O)_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_8(\mu\text{-}OH)_2$,[15] $Fe_{17}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{10}$,[16] and $Fe_{19}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_8$[16] cores have been isolated. Those with multiple O^{2-} and/or $OH(R)^-$ bridges have the possibility of four-membered Fe_2O_2 rhombs and are therefore more highly condensed than those also bridged by the three atoms of carboxylato ligands.[5] The variable bridging modes **a**–**e** adopted by the O^{2-} and/or $OH(R)^-$ bridges are found in the above cores and are central to the aggregation process. We report here the octanuclear iron–oxo–carboxylato aggregate $[Fe_8(\mu_4\text{-}O)(\mu_3\text{-}O)_4(OAc)_8(tren)_4]^{6+}$ ($\mathbf{1}(CF_3SO_3)_6\cdot 5CH_3CN$), which is the first iron–oxo aggregate with a square-planar oxide and which exhibits an unusual ^{1}H NMR spectrum for an iron(III)–oxo aggregate.



Our initial synthetic approach to new iron–oxo cores was the reaction of dioxygen with Fe(II) starting materials. The ^{1}H NMR spectrum of an air-oxidized acetonitrile solution of $[Fe(tren)(O_2CCH_3)](CF_3SO_3)$[17] reveals a set of considerably narrower resonances with greater contact shifts than those normally observed for Fe(III) oxo-bridged dimers.[3,18] A crystalline material which exhibits the same solution spectrum between 10 and 160 ppm (Figure 1) can be isolated as the solvated triflate salt by air oxidation of a 2:2:2:1 molar ratio of Fe(II), $CD_3CO_2^-$, $CF_3SO_3^-$, and tren in butyronitrile. A convenient preparative procedure involves passing O_2 through a colorless slurry prepared from 0.17 g (0.50 mmol) of $Fe(tren)(O_2CCH_3)_2$[17] and 0.22 g (0.50 mmol) of $Fe(CF_3SO_3)_2\cdot 2MeCN$ in 10 mL of butyronitrile to form an orange-brown solution from which a greenish-brown crude microcrystalline product is isolated (0.28 g, 86% yield). Pure crystals of **1**,[19] suitable for diffraction measurements,[20] were grown by diffusing diethyl ether into a solution of the crude product in an acetonitrile/butyronitrile mixture. To ensure that **1** is not a mixed-valence Fe(II)/Fe(III) aggregate, the triflate salt of **1** has subsequently been isolated by starting from an iron(III) salt.[21]

The remarkable octairon hexacation **1** (Figure 2) has no crystallographically imposed symmetry yet belongs to an idealized S_4 point group, a rare occurrence for a multinuclear aggregate.[22] Four central irons (Fe_c) and a μ_4-O ligand make up a planar

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(19) Anal. Calcd for $\mathbf{1}(CF_3SO_3)_6\cdot 1.5CH_3CN$, $C_{49}F_{18}Fe_8H_{100.5}N_{17.5}O_{39}S_6$: C, 23.17; H, 3.99; N, 9.65; S, 7.57. Found: C, 23.22; H, 4.03; N, 9.27; S, 7.18.

(20) X-ray analysis (−100 °C): $\mathbf{1}\cdot 5CH_3CN$ crystallizes in the triclinic space group $P\bar{1}$, with α = 15.951(10) Å, b = 16.432(12) Å, c = 20.840(16) Å, α = 99.31(b)°, β = 90.55(6)°, γ = 94.87(6)°, V = 5369 (4) Å^3, and Z = 2. With the use of 6478 unique reflections (3° < 2θ < 45°, Mo Kα radiation) on a single-crystal X-ray diffractometer, the structure was solved by Patterson synthesis interpretation followed by expansion, Fourier syntheses, and refinement to an R index of 0.069.

(21) An acetonitrile solution of $Fe(CF_3SO_3)_3\cdot 6DMF$, tren, acetic acid, water, and triethylamine in an 8:4:8:5:18 mole ratio afforded crystals of **1** in 27% yield following ether diffusion.

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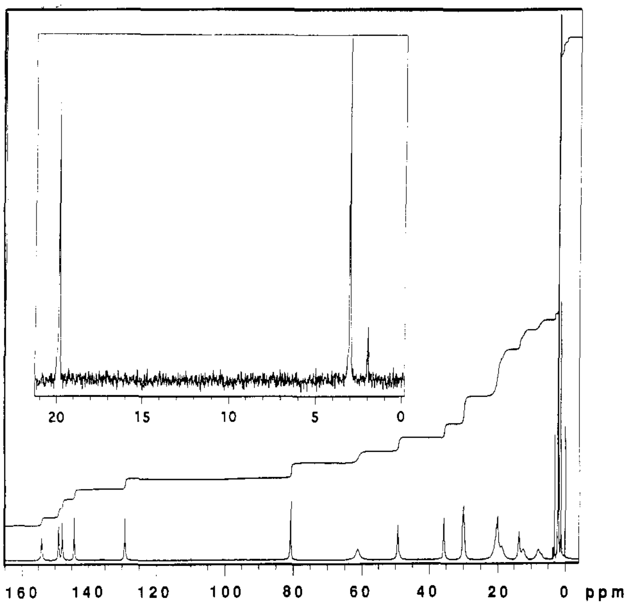

Figure 1. ^{1}H NMR of $[Fe_8O_5(O_2CCD_3)_8(tren)_4](CF_3SO_3)_6$ (in CD_3CN at 21 °C and 600 MHz): CH at 153.5, 148.4, 147.4, 143.8, 128.8, 80.4, 49.1, 35.6, 30.0, 29.7, 19.9, 13.6 ppm, NH at 60.9, 20.3, 18.7, 13.6, 80 ppm, and CH_3 at 19.9, 3.0 ppm downfield of TMS. Inset: ^{2}H NMR (92 MHz) of the same sample showing the labeled acetate resonances at 19.9 and 3.0 ppm.

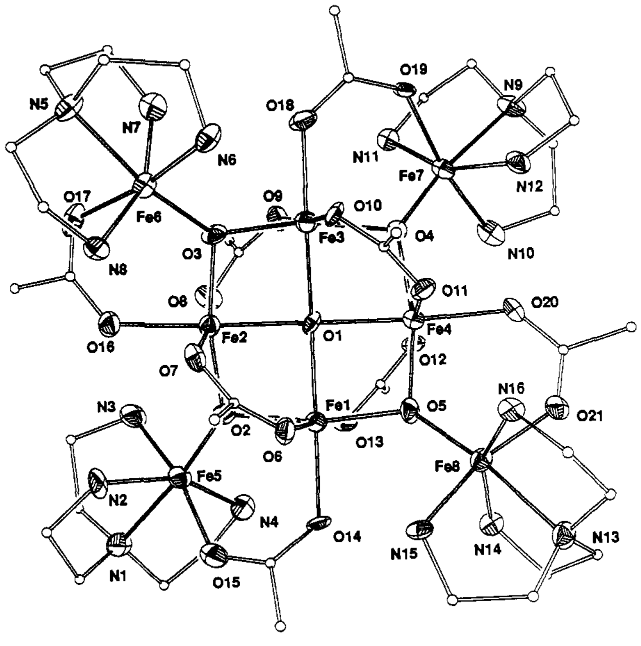

Figure 2. Structure of **1** depicting 30% ellipsoids. Carbons are an arbitrary size, and hydrogens have been omitted for clarity. Metrical averages under S_4 point group and representative interatomic distances (Å) and angles (deg): $Fe_c\cdots Fe_c$, 2.889(9); Fe(1)···Fe(2), 2.887(3); $Fe_c\cdots Fe_o$ (across μ-O_2CCH_3), 3.34(1); Fe(1)···Fe(5), 3.35; $Fe_c\cdots Fe_o$, 3.52(2); Fe(1)···Fe(8), 3.54; Fe_c–O(1), 2.043(11); Fe(2)–O(1), 2.044(10); Fe_c–(μ_3-O) (across μ-O_2CCH_3), 1.94(1); Fe(1)–O(2), 1.949(9); Fe_c–(μ_3-O), 1.94(1); Fe(1)–O(5), 1.945(10); Fe_o–(μ_3-O), 1.822(15); Fe(5)–O(2), 1.819(9); Fe–(μ-O_2CCH_3), 2.04(2); Fe–3°N(av), 2.22(2); Fe–1°N(av), 2.15(2); Fe–O(1)–(μ_3-O)(av), 93.3; Fe_c–(μ_3-O)–Fe_o (across μ-O_2CCH_3), 125.4(9); Fe_c–(μ_3-O)–Fe_o, 138.4(14).

Fe_4O unit[23] with four acetate ligands, each bridging two Fe_c alternately above and below the Fe_4O plane and perpendicular to it. Four additional iron atoms (Fe_o) are connected to the central core by four μ_3-O ligands, each bridging two Fe_c and one Fe_o, and four additional acetate ligands, each bridging one Fe_c and one Fe_o. The Fe_o are alternately displaced above and below the central plane.[23] The Fe–O distances are typical of iron(III) in other carboxylate complexes. The aggregate can be constructed from either four dimers (Fe_2O, structure **a**) brought together by the central oxo, a fusion of three trimers (Fe_3O, **b**) by the central oxo, or a fragment of the hexamethalate (Fe_6O, **e**) in which coordination of two of the *trans* Fe is prevented by the four carboxylates that are perpendicular to the plane.

The Fe_c are coordinated solely to six oxygen donor ligands, whereas the Fe_o are ligated by two oxygen ligands and the four nitrogen donors of the ligand tren. This is reflected in the Mössbauer spectrum which is fit to two equal-intensity, overlapping doublets[24] which are consistent with high-spin iron(III). The variable-temperature behavior of the magnetic moment of a solid sample indicates antiferromagnetic coupling between Fe(III) atoms but with a paramagnetic ground or low lying state.[25] This is supported by structure observed in preliminary Mössbauer measurements in an applied field at 4 K.

The solution magnetic moment (Evans method 2.45 μ_B/Fe) is similar to that of the solid, suggesting that the structure is maintained in solution. The ^{1}H NMR spectrum (Figure 1) provides further evidence of this. The narrowest two resonances are assigned (by deuteration) to the acetate ligands, whereas 12 resonances arise from the methylene hydrogens of tren, while the remaining broader resonances are D_2O-exchangeable amine protons. The solution structure is thus consistent with S_4 point group and is stable in aprotic but not protic solvents.

Complex **1** is the first iron aggregate to have a planar quadruply bridging oxo ligand, the only others being the recently discovered V_4,[26] Nb_4,[27] and Cu_4[28] oxo aggregates. The Fe_4O_5 core may occur in the polymerization of iron(III) in aqueous or alcoholic media and can be considered the central fragment of the hexametalate $M_6O_{19}^{n-}$, which is common to early transition metals and whose iron–oxo–alkoxo analog was recently reported.[11] The structural features of a compact Fe_4O_5 core loosely capped by four FeL units through oxo and carboxylato bridges render **1** a good model for the biomineralization of iron oxides, which probably involves the nucleation of compact, regular FeO(OH) cores from amorphous iron sources. Similar features are observed in the largest iron–oxo aggregate crystallized to date, in which $Fe_7(OH)_{12}$ cores are surrounded by Fe_{10} and Fe_{12} caps.[16]

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Supplementary Material Available: Textual details of the X-ray experimental work and tables of crystallographic data, atomic positional and isotropic thermal parameters, anisotropic thermal parameters, and bond lengths and angles for **1** (20 pages). Ordering information is given on any current masthead page.

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(23) Displacements from the unweighted least-squares plane defined by Fe_c and O(1): Fe_c, –0.007 to 0.010 Å; O(1), –0.005 Å; Fe_o, –1.441 to 1.348 Å; O_o, –0.560 to 0.579 Å. Angles at Fe_c defining the square range from 89.6 to 90.3°.

(24) For measurements made at 4.2 K and referenced to iron metal at room temperature: $\Delta E_Q(F_c)$ = 1.37 mm/s, $\delta(Fe_c)$ = 0.45 mm/s and $\Delta E_Q(Fe_o)$ = 1.04 mm/s, $\delta(F_o)$ = 0.49 mm/s.

(25) The magnetic moment per Fe_8 decreases nonlinearly from 6.6 μ_B at 300 K to 5.56 μ_B at 200 K to 2.65 μ_B at 20 K. A more detailed analysis is in progress.

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