J. Am. Chem. Soc. **1990**, *112*, 9629-9630 9629

Synthesis and Structure of $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, a Molecular Ferric Wheel

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Received September 26, 1990

Compounds of high nuclearity, symmetry, and architectural beauty have long fascinated chemists. Although such molecules are prominent in organic chemistry, cubane, dodecahedrane, and buckminsterfullerene illustrating the point, fewer examples of inorganic complexes that fall into this category are well-known. In the present communication we describe such a compound, $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$ (**1**), a decanuclear molecule that forms a nearly perfect circle. This molecular "ferric wheel" assembles in methanolic solutions of diiron(III) oxo complexes currently being studied in our laboratory[1] as part of a broad program to elucidate the chemistry of polyiron oxo protein cores such as occur in the proteins hemerythrin, ribonucleotide reductase, methane monooxygenase, and ferritin.

Compound **1** was prepared by allowing the monochloroacetate analogue of basic iron acetate,[2] $[Fe_3O(O_2CCH_2Cl)_6(H_2O)_3](NO_3)$ (0.315 g, 0.366 mmol), to react with 3 equiv of $Fe(NO_3)_3{\cdot}9H_2O$ (0.444 g, 1.10 mmol) in 65 mL of methanol. Diffusion of ether into the green-brown solution gave a yellow solution, from which both gold-brown crystals of **1** and a yellow precipitate deposited after several days. The crystals, which hydrolyze slowly in air to give a red solid, proved suitable for X-ray diffraction analysis.[3] Pure samples of **1** for elemental analysis and spectroscopic and magnetic measurements were obtained by decanting a 1,2-dichloroethane mixture of the crystals and powder several times to remove the latter, which was suspended in the solution. The crystals were subsequently washed with methanol, water, acetone, and ether and vacuum-dried to give 0.069 g of **1** (89% based on μ-oxo anions, which afford two base equivalents used to deprotonate methanol; 15% based on iron).[4]

The structure of **1**, shown in Figure 1, consists of 10 ferric ions in a circular array. In the solid state, **1** resides on an inversion center so that only half of the molecule is crystallographically unique. The 10 iron atoms are essentially coplanar, with an average deviation of only ±0.005 Å from the best least-squares plane through them. Each iron atom has a distorted octahedral geometry and is joined to its neighbors by edge-sharing methoxide and *cis*-carboxylate bridges, forming a molecular ferric wheel of ~12 Å in diameter. Ignoring the chlorine atoms of the bridging carboxylates, the molecule has idealized D_{5d} symmetry.

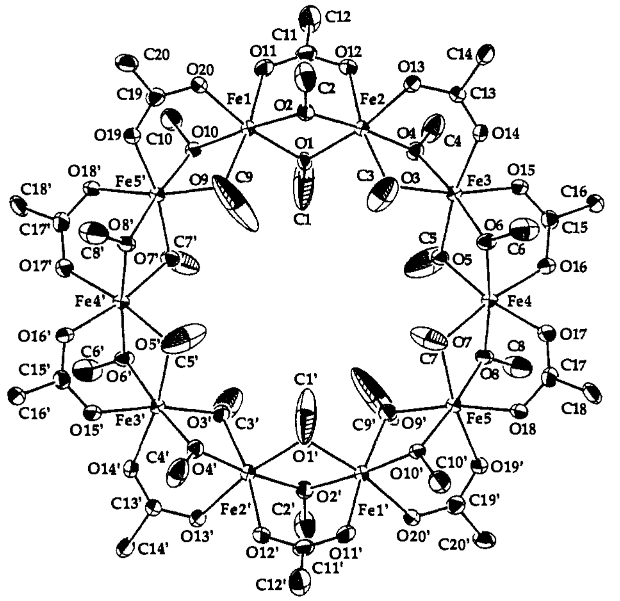

Figure 1. ORTEP drawing of the planar projection of **1** with 50% probability thermal ellipsoids and atom labels; primed and unprimed atoms are related by a center of inversion. Chlorine and hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg) were averaged over the entire molecule for each unique value and are as follows (the Fe1, Fe2 core was used to identify the specific distances and angles): Fe1–O1, 1.975 (4); Fe1–O2, 1.987 (4); Fe1–O11, 2.057 (4); O1–C1, 1.39 (1); O2–C2. 1.420 (8); O11–C11, 1.259 (8); O1–Fe1–O2, 77.9 (2); O1–Fe1–O9, 97.9 (2); O1–Fe1–O10, 98.4 (2); O1–Fe1–O11, 88.6 (2); O1–Fe1–O20, 169.4 (2); O2–Fe1–O11, 91.1 (2); O2–Fe1–O20, 92.9 (2); O2–Fe1–O10, 174.5 (2); O11–Fe1–O20, 86.3 (2); Fe1–O1–Fe2, 100.1 (2); C1–O1–Fe1, 125.3 (5); Fe1–O2–Fe2, 99.3 (2); C2–O2–Fe1, 126.3 (4); Fe1–O11–C11, 127.2 (4); O11–C11–O12, 127.0 (6); O11–C11–C12, 116.5 (6). Numbers in parentheses are averages of the estimated standard deviations in the last digit for individual values. The Fe···Fe distance for adjacent irons averages 3.028 Å. No corrections were made for thermal motion.

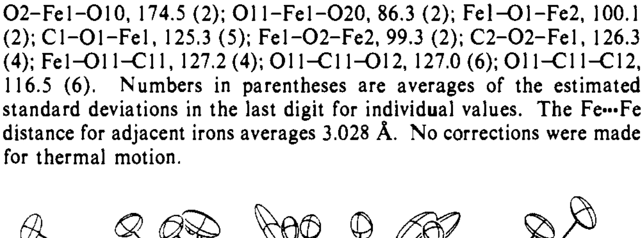

Figure 2. ORTEP drawing of side-on view of **1** with 50% probability thermal ellipsoids. Chlorine and hydrogen atoms were omitted for clarity.

The bridging methoxide ligands can be subdivided into two distinct sets by their orientation with respect to the ring of iron atoms. One set points into the center of the circle while the second grouping is directed outward from the rim of the wheel. The carbon atoms of the interior bridging methoxides have oblong thermal ellipsoids, indicative of relatively unrestricted vibrational motion through the center of the wheel and/or unresolved disorder. Side-to-side motion is limited by steric interactions with the adjacent μ-methoxide ligands. Both sets of bridging methoxide ligands are positioned alternatively above and below the plane of the circle in a staggered manner. The bridging monochloroacetate ligands exhibit a similar alternating orientation around the rim of the wheel. The repeated motifs afforded by the disposition of the ligands in **1** generate a structure composed of layers of iron, oxygen, and carbon atoms when viewed parallel to the plane of the metal atoms (Figure 2).[5]

The interior cavity of **1** has a diameter of approximately 2–3 Å, accounting for the van der Waals radii of the methyl groups. The negligible amount of residual electron density (0.8 e/Å^3) located on the special position in the center of the ring indicates that **1** does not harbor a guest molecule in its cavity. The decamers are stacked along the *c* axis in the crystal lattice to produce an infinite channel passing through the interior holes.

As expected from the high symmetry of the molecule, the geometry about the five unique iron sites is well-conserved (Figure 1, caption). The repeating bis(μ-alkoxo)(μ-carboxylato) unit has not been previously observed in iron chemistry, although such species occur in manganese compounds.[6] A related bis(μ-phenoxo)(carboxylato)diiron(III) complex has been structurally

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(3) Crystal data for **1**: $Fe_{10}C_{40}H_{80}O_{40}Cl_{10}$, M_r = 2114.06, monoclinic, space group $P2_1/c$ (No. 14), a = 11.106 (3) Å, b = 15.958 (3) Å, c = 22.938 (5) Å, β = 97.34 (1)°. Z = 2, V = 4032 (1) Å^3, ρ_{calcd} = 1.74 g cm^{-3}. For 5043 unique observed reflections collected at −47 °C with $F^2 > 3\sigma(F^2)$, R = 0.048 and R_w = 0.060. Full details will be reported elsewhere.

(4) Anal. Calcd for $Fe_{10}C_{40}H_{80}O_{40}Cl_{10}$ (**1**): C, 22.73; H, 3.81; Fe, 26.42. Found: C, 22.67; H, 3.82; Fe, 26.14. IR (KBr, cm^{-1}): 2926, 2824, 1561 (ν_{as}, COO), 1419 (ν_s, COO), 1255, 1034, 794, 708, 508, 444.

(5) Average distance from the plane of the iron atoms for the different ligand atom classes found in **1** (the value in parentheses is the standard deviation of the average): inner μ-O*Me*, 0.93 (3) Å; C*OO*, 1.10 (7) Å; outer μ-O*Me*, 1.22 (2) Å; O*Me*, 2.26 (9) Å.

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characterized[7] and has bond distances and angles similar to those in **1**. Other diferric compounds with two alkoxo,[8] phenoxo,[9] or hydroxo[10] bridges (or different combinations),[11] but lacking the bridging carboxylate ligand, have similar core geometries. From temperature-dependent magnetic susceptibility studies, compound **1** was found to be antiferromagnetically exchange coupled with a singlet ground state.[12] Such behavior is typical for complexes with a $\{Fe_2(OR)_2\}^{4+}$ or $\{Fe_2(OR)_2(O_2CR)\}^{3+}$ core, with one notable exception.[9c] The Mössbauer spectrum of a polycrystalline sample at 4.2 K revealed a single quadrupole doublet with an isomer shift of 0.52 mm/s and a quadrupole splitting of 0.62 mm/s. Taken together, the geometry, Mössbauer, and magnetic properties of **1** are characteristic of high-spin iron(III) and do not appear to be significantly affected by the novel ring structure of the molecule.

A growing number of polynuclear iron and manganese compounds with predominantly oxygen donor ligands have been synthesized and structurally characterized as interest in related biological units, particularly those in ferritin[1,13] and the oxygen-evolving complex of photosystem II,[14] has increased. Included[15] are a variety of M_4,[15b] M_6,[15c] M_8 (M = Fe, Mn[15d]), Mn_9, Mn_{10}, Fe_{11}, Mn_{12}, and $Fe_{16}M'$ (M' = Fe[15e], Mn, Co) complexes. The present molecule, $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, is distinguished from this set by its high symmetry, simple empirical formula, and aesthetically pleasing circular structure. The last property is reminiscent of a cyclic toroidal iron-sulfur cluster having the formula $[Na_2Fe_{18}S_{30}]^{8-}$.[16] Other ligand-bridged polynuclear compounds with ring structures have been characterized, including M_4 (M = Ti, Ni, W),[17] M_5 (M = Cu, Ag),[18] M_6 (M = Ni, Cu, Mo),[19] and M_8 (M = V, Ni, Cu, Mo).[20] Of these, the iron decamer most closely resembles the recently reported octanuclear cluster, $[Cu_8(3,5\text{-dimethylpyrazolate})_8(OH)_8]$.[20d]

The nature of the soluble complexes formed by the polymerization of iron in aqueous or alcoholic media has remained obscure despite numerous studies. The novel arrangement of $\{Fe(OR)_2(O_2CR)\}$ units in **1** suggests new possible structural motifs for several such species.[21] A cyclic hexanuclear complex $[Fe_6(OH)_{12}](OH)_6$ has been postulated to exist in solution,[22] and a series of compounds having the same general empirical formula as **1** have been reported but not structurally characterized.[23] Efforts to prepare and elaborate further the structural patterns found in this interesting class of polynuclear iron compounds are continuing.

Acknowledgment. This work was supported by grants from the National Institutes of Health and the National Science Foundation. K.L.T. also thanks the National Science Foundation for a predoctoral fellowship. We are grateful to Drs. P. Poganiuch and S. Liu for assistance with the magnetic and X-ray structural studies and to Dr. G. C. Papaefthymiou for obtaining the Mössbauer spectrum.

Supplementary Material Available: Tables of atomic positional and thermal parameters for **1** (5 pages). Ordering information is given on any current masthead page.

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Genomic Direction of Synthesis during Plasmid-Based Biocatalysis

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Received June 27, 1990

Plasmid-based biocatalysis[1] potentially requires the preparation of a single plasmid in order to synthesize all the enzyme substrates intermediate in a biosynthetic pathway. The plasmid contains extrachromosomal copies of genes which encode enzymes that influence commitment of carbon resources in the cell. Elevated concentrations of these enzymes direct a surge of carbon flow into the targeted pathway. Which enzyme substrate is synthesized once plasmid-based biocatalysis has created a surge of carbon flow? If the plasmid is introduced into a microbial strain devoid of a particular catalytic activity due to a genomic mutation, the substrate synthesized may correspond to the substrate of the missing enzyme.[1] Alternatively, elevated carbon flow through the pathway may lead to synthesis of the substrate of a rate-determining enzyme intermediate in the biosynthetic pathway.

This report examines the substrate(s) synthesized by *aro*E mutants of *Escherichia coli* following transformation with plasmids which drastically increase the flow of carbon into the common

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