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The First (μ-Oxo)diferric Chain Complex: Structure and Magnetic Properties of $[Fe_2(tren)_2(mtm)O]_n(CF_3SO_3)_nCl_n$

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Oxo-bridged diiron systems have been actively studied owing to their relevance to the active sites of non-heme iron proteins such as hemerythrine, the R2 protein of ribonucleotide reductase and methane monooxygenase.[1] On the other hand, interest in modeling ferritin core or in the magnetic properties of multi paramagnetic metal centers has led to the synthesis of polynuclear iron complexes of Fe_n ($n = 3-6, 8, 10-12, 16, 17, 19$) nuclearity arranged in matrix,[2] short chain,[3] or cyclic type.[4] Particularly, the structural variety and novelty of these polynuclear iron complexes seemed to be determined by types of bridging and end-capping ligands, raising the engaging question as to the role of these ligands in controlling the speciation of iron. As part of pursuing this matter, we have explored the use of [bis(methylthio)methylene]malonate (=mtm) as a bridging ligand in developing one-, two-, or three-dimensional metal complex systems and mtm has led to the formation of a novel heterobimetalic layered compound $[MnCu(mtm)_2(H_2O)_2(CH_3OH)_2]_n$ showing ferrimagnetism.[5] We have also found that by using mtm and tris(2-aminoethyl)amine (=tren) as the bridging and end-capping ligands, respectively, the hitherto unprecedented polymeric (μ-oxo)diferric chain complex $[Fe_2(tren)_2(mtm)O]_n(CF_3SO_3)_n(Cl)_n$ (**1**) can be obtained. We wish to report here accounts of synthesis, structure, and magnetic properties of this molecular "ferric train".

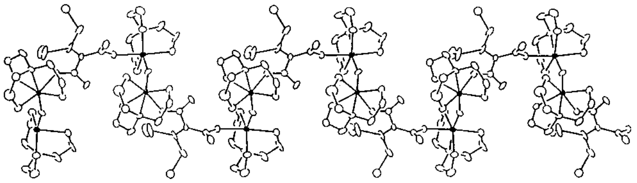

Figure 1. Segment of the molecular chain of **1**.

In a dinitrogen atmosphere, a yellow-brown slurry obtained by adding neat tren (225 μL, 1.5 mmol) dropwise to a solution of $FeCl_3$ (243 mg, 1.5 mmol) in 30 mL of methanol was treated with a solution of the dipotassium salt of mtm (429 mg, 1.5 mmol)[6] in 15 mL of methanol with vigorous stirring, affording a dark brown solution. The reaction mixture was filtered, and a solution of $AgCF_3SO_3$ (387 mg, 1.5 mmol) in 10 mL of methanol was added to the filtrate. After the removal of the AgCl precipitate, a dark red-brown crystalline product was obtained by treating the concentrated filtrate with ether, and recrystallization from methanol/ether gave analytically pure **1** in a yield of 62% (360 mg) based on iron.[7,8]

The crystal structure of **1** reveals that polymeric (μ-oxo)-diferric cationic molecular chains run parallel to the *c* axis and are arranged into an L-shape along the *c* axis. The closest Fe···Fe interchain distance is 8.107 Å. A segment of the molecular chain and the molecular structure of the asymmetric unit are depicted in Figures 1 and 2, respectively, indicating that mtm bridges Fe−O−Fe units via the dicarboxylate oxygen atoms to act as a μ_2-*O*,*O*′ ligand. The repeating unit of the molecular chain consists of two asymmetric units, and the intrachain repeating distance of Fe−O−Fe units is 8.210 Å. The unidentate behavior of each carboxylate group is also confirmed by the value of 217 cm^{-1} for the difference between asymmetric and symmetric carboxylate stretching frequencies in the infrared spectrum.[9] The overall chain structure can be

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[6] (a) Jensen, K. A.; Henrikson, L. *Acta Chem. Scand.* **1968**, *22*, 1167. (b) Preparation of dipotassium [bis(methylthio)methylene]malonate: Ethyl [bis(methylthio)methylene]malonate prepared according to the published procedure[6a] is hydrolyzed in the presence of excess potassium hydroxide in 95% hot ethanol for 1 h, yielding white crystalline precipitate.

[7] Anal. Calcd for $C_{19}H_{42}N_8O_8S_3F_3ClFe_2$: C, 28.1; H, 5.22; N, 13.6; S, 11.9. Found: C, 27.8; H, 5.32; N, 13.6; S, 11.3. IR (KBr, cm^{-1}): 1585, 1560 (ν_a, COO), 1356 (ν_s, COO), 852 (ν_a, Fe−O−Fe). Raman (cm^{-1}): 406 (ν_s, Fe−O−Fe).

[8] Crystal data for **1**: fw 810.94, monoclinic space group $P2_1/c$, $a = 18.031(6)$ Å, $b = 14.480(5)$ Å, $c = 14.722(4)$ Å, $\beta = 112.55(2)°$, $V = 3549.7(18)$ Å^3, $d_{calc} = 1.517$ g cm^{-3}, $Z = 4$. Data were collected at 293 K on a MAC Science MXC3 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) by the $\omega-2\theta$ method. A total of 3310 reflections ($2\theta_{max} = 40.01°$, $\pm h,-k,+l$) were measured, from which 2095 independent reflections with $I > 2\sigma(I)$ were used for calculations, giving $R_1 = 0.0896$ ($wR_2 = 0.228$).

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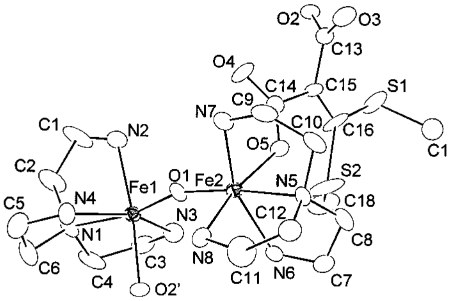

Figure 2. ORTEP drawing of the asymmetric unit of **1** showing the atom-labeling scheme.

mnemonically called a “ferric train” by viewing the Fe−O−Fe unit and mtm as a car and a connector, respectively. The connecting pattern of Fe−O−Fe units is unique such that the dihedral angle between the plane containing the upper two Fe rows in Figure 1 and the plane containing the bottom two Fe rows in Figure 1 becomes 97.2°.

The iron centers have an N_4O_2 coordination environment with distorted octahedral symmetry, and the Fe−O−Fe core shown in Figure 2 is characterized by an Fe1−O1−Fe2 angle of 160.2(6)°, Fe−O1 distances of 1.764(8) and 1.777(8) Å, and an Fe1···Fe2 distance of 3.484 Å. The core parameters are in the usual range of monobridged (μ-oxo)diiron complexes.[10] The estimated values (165 and 163°) for the Fe−O−Fe angle, obtained by the correlation figure[11] and the observed asymmetric (852 cm^{-1}) and symmetric (406 cm^{-1}) stretching frequencies for the Fe−O−Fe unit in **1**, respectively, are in good agreement with the X-ray analysis. The tertiary bridgehead nitrogen atom of the ligand tren forms a longer bonding interaction (average 2.242 Å) with the iron atom than the other three nonbridgehead nitrogen atoms do (average 2.159 Å) presumably owing to its trans position relative to the strong electron-donating μ-oxo ligand.

The magnetic susceptibility data as a function of temperature, measured with an applied field of 1.0 T by using a SQUID magnetometer, are displayed in Figure 3. As the temperature is decreased, $\chi_m T$ approximately decreases from 0.750 cm^3 K mol^{-1} at 300 K to 0.022 cm^3 K mol^{-1} at 5 K. This magnetic behavior is quite similar to those observed in diferric complexes with an oxo bridge,[12] and the susceptibility data can be interpreted in terms of the Heisenberg−Dirac−Van Vleck spin Hamiltonian for isotropic dinuclear magnetic exchange interactions ($H = -2JS_1 \cdot S_2$).[13] The equation used to fit the corrected molar susceptibility data is

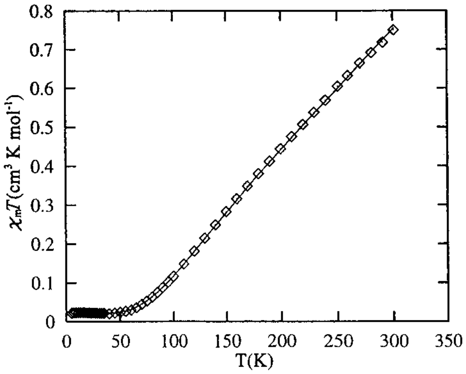

Figure 3. Plot of the temperature dependence of $\chi_m T$. The solid line corresponds to the best data fit.

$$\chi_m = (1 - p)(2Ng_1^{\,2}\beta^2/kT)\{(e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x})/(1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x})\} + p(35Ng_2^{\,2}\beta^2/12kT) + \text{TIP}$$

where x is J/kT, p the paramagnetic impurity with $S = {}^5/_2$, and TIP the temperature-independent paramagnetism. The least-squares fitting of the equation yields $J = -116\ \text{cm}^{-1}$, $p = 0.004\,88$, TIP $= 0$, $g_1 = 2.02$, and $g_2 = 2.00$, indicative of strong antiferromagnetic interactions between the iron atoms of the Fe−O−Fe core.[10] The reliability factor ($R = \sum(\chi_m^{\text{obs}}T - \chi_m^{\text{calc}}T)^2/\sum(\chi_m^{\text{obs}}T)^2$) is 4.91×10^{-5}, implying that the experimental data are well fitted with the isotropic dimer model and thus the Fe−O−Fe cores are magnetically isolated. This assumption concerning the independent magnetic entities seems reasonable because the π-type superexchange pathway of the μ-oxo ligand is expected to dominate any coupling within magnetic centers through space or by the long-range σ-type pathway of the mtm ligand.

In summary, we have demonstrated that the coupled use of mtm and tren afforded the first example of a (μ-oxo)diferric chain complex. In addition to the sterically bulky and coordinatively congested feature of the end-capping ligand tren, the bridging ligand mtm where two carboxylate groups are bonded to the same sp^2-carbon atom also provides a characteristic bridging distance. The discovery of the “ferric train” may spur efforts to search for a variety of structure patterns in iron−oxygen chemistry by tuning the types of bridge and end-capping ligands.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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