

A New Hexaferrocene Complex with a $[M_3(\mu_3-O)]^{7+}$ CoreValeriu Mereacre,[†] Motohiro Nakano,[‡] Jordi Gómez-Segura,[§] Inhar Imaz,[§] Christian Sporer,[§] Klaus Wurst,^{||} Jaime Veciana,[§] Constantin Turta,^{*,†} Daniel Ruiz-Molina,^{*,§} and Peter Jaitner^{*,||}

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The new hexaferrocene complex **1** has been synthesized and characterized by X-ray diffraction. Its magnetization data were fitted to a detailed theoretical model that considers nonequivalent exchange parameters between Fe ions to yield the magnetic exchange coupling values of $J_1/k_B = -31.5$ K and $J_2/k_B = -25.8$ K. Moreover, the cyclic voltammogram of complex **1** confirmed its redox activity associated with the presence of ferrocene units, with very small or negligible electronic interactions between them.

The design and synthesis of multiferrocene complexes have attracted considerable interest because of their potential applications as electron reservoirs, recognition of anionic species, and/or building blocks for molecular electronic devices, among others.¹ Many examples of multiferrocene systems made of inorganic rings or cages, like borane,² carbalane,³ and mono- and dinuclear organometallic or transition-metal complexes,⁴ have been described. However, examples of polynuclear metal clusters capped by equivalent ferrocenyl ligands whose X-ray structure has been reported

are scarce in spite of their interest.^{5–16} The advantages of using metal clusters for the construction of multiferrocenyl assemblies would be multifold. Besides their tunable composition and geometry, their open-shell electronic structures may lead to the observation of magnetic properties and other interesting phenomena such as intramolecular electron-transfer processes.

In this order, the family of clusters containing the $M_3(\mu_3-O)$ core would be excellent building blocks for the construction of such multiferrocenyl systems. On the one hand, these complexes exhibit a triangular metal ion core with a central μ -oxo bridge stabilized by six carboxylate groups that are susceptible to being replaced by ferrocenecarboxylate groups. On the other hand, this topology has attracted considerable attention within the molecular magnetism community because of the resulting exceptional electron-transfer and magnetic properties, such as spin-frustration behavior.¹⁷ However, to the best of our knowledge, such complexes have never been prepared before with ferrocene carboxylate (FcCOO) ligands. Herein we report the synthesis, X-ray

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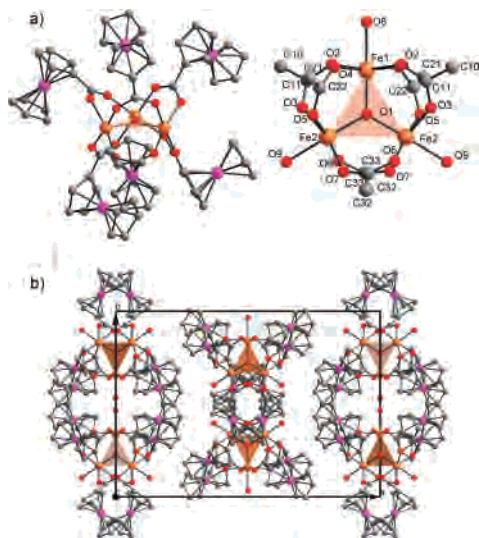


Figure 1. (a) Crystallographic view of the $[\text{Fe}_3\text{O}(\text{FcCOO})_6(\text{DMF})_3]$ cluster (left) and the carboxylate coordination around the Fe_3O core (right). (b) View along the c axis of the crystal packing of compound **1**. Solvent and anion molecules have been omitted for clarity.

structure, electrochemistry, and magnetic characterization of the new complex $[\text{Fe}_3^{\text{III,III,III}}\text{O}(\text{FcCOO})_6(\text{DMF})_3] \cdot \text{ClO}_4$ (**1**; DMF = N,N -dimethylformamide), the first complex with an Fe_3O core bearing Fc-type ligands.

The synthesis of complex **1** was done by the reaction of $[\text{Fe}_3^{\text{III,III,III}}\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ with $\text{C}_5\text{H}_5\text{Fe}^{\text{II}}\text{C}_5\text{H}_4\text{COOH}$ in benzene under argon. The reaction mixture was heated under reflux for 5 h, resulting in the formation of a deep-green precipitate, which was filtered. Crystallization of the precipitate from a Et_2O /hexane (1:1) solution afforded green crystals suitable for X-ray diffraction. The molecular structure and corresponding crystal packing of complex **1** are shown in Figure 1.

As can be seen there, complex **1** exhibits the characteristic $[\text{M}_3^{\text{III,III,III}}(\mu_3\text{-O})]^{7+}$ core consisting of three Fe ions anchored to a $\mu_3\text{-O}$ and six carboxylate groups.¹⁷ However, this cluster deviates from an ideal triangular cationic core because it has a C_2 rotation axis that goes through Fe1, O8, and O1 atoms (the asymmetric unit consists of half a molecule). Each Fc group is connected to two Fe atoms in a bis-monodentate mode (two carboxylates are linked to the same two Fe centers). Thus, each Fe is surrounded by four O atoms coming from carboxylate groups; the octahedral coordination sphere is completed by a N,N -dimethylformamide (DMF) molecule and the central $\mu_3\text{-O}$ (see Figure 1). The ferrocene subunits exhibit average Fe–C (2.034 Å) and Fe–Cp (1.676 Å) distances characteristic of substituted ferrocene. Finally, as far as the supramolecular packing is concerned, molecules are organized in columns (Figure 1b) along the b axis (the same direction of the C_2 axis). Counteranions are located between the clusters and are connected to ferrocene groups

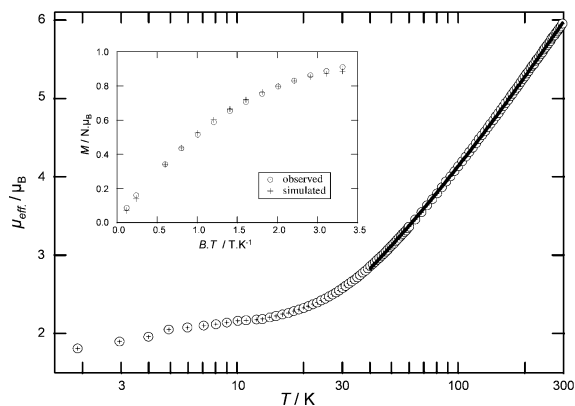


Figure 2. Temperature dependence of the effective magnetic moment of **1** under an external field of 0.1 T. The solid curve stands for a best fit for the data above 40 K by the HDVV model. Inset: Reduced magnetization curves of **1** in the 2.5–4.2 K temperature range under an external field of 0.5–7.0 T. Simulation values (+) were evaluated by the Brillouin function for $S_T = 1/2$ with $g_{\text{av}} = 1.876$.

via H bonds. Ferrocene ligands of different clusters do not exhibit hydrogen bonding or π interaction between them.

The effective magnetic moment μ_{eff} for complex **1** in the temperature range of 2–300 K under an external field of 0.1 T is shown in Figure 2. As can be seen, there is a remarkable decrease on cooling, from $\sim 6 \mu_B$ at room temperature to $\sim 2 \mu_B$ at 10 K, whereupon a plateau is reached. Such a decrease is consistent with the presence of considerable antiferromagnetic intramolecular interactions between the Fe(III) ions mainly through the $\mu\text{-O}$ and, to a lesser degree, through the carboxylate ligands. Low-temperature magnetization curves up to 7.0 T are also shown (inset in Figure 2). Magnetization curves only exhibit a small deviation from a universal Brillouin curve, suggesting a significantly small, if not negligible, overall magnetic molecular anisotropy. Moreover, the saturation value of the magnetization ($\sim 1.0 N\mu_B$) is in agreement with a resulting spin ground state of $S = 1/2$.

Fitting of the magnetization data was done with a Heisenberg–Dirac–Van Vleck (HDVV)-type exchange model, where the intramolecular magnetic exchange path between the Fe ions was considered as an isosceles rather than an equilateral triangle because of the presence of a crystallographic C_2 axis. The spin Hamiltonian of a triangular cluster bearing three high-spin Fe(III) ions was written then as $H = -2J_1(S_1S_2 + S_3S_1) - 2J_2S_2S_3$ by introducing two different exchange coupling parameters (J_1 and J_2).¹⁸ As can be seen in Figure 2, the best simulated fit for the μ_{eff} vs T plot was thus obtained for the $J_1/k_B = -31.5$ K and $J_2/k_B = -25.8$ K values. These parameters result in an $S_T = 1/2$ spin ground state, which is also fully compatible with the magnetization data (see the inset in Figure 2). In a second stage, the exchange parameters J_1/k_B and J_2/k_B previously found were fixed whereas the zero-field-splitting parameter D was varied along the fitting process. The spin Hamiltonian consisting of the HDVV exchange terms and Fe(III) zero-field-splitting terms was numerically diagonalized to provide the effective g value for the spin ground state $S_T = 1/2$. Then,

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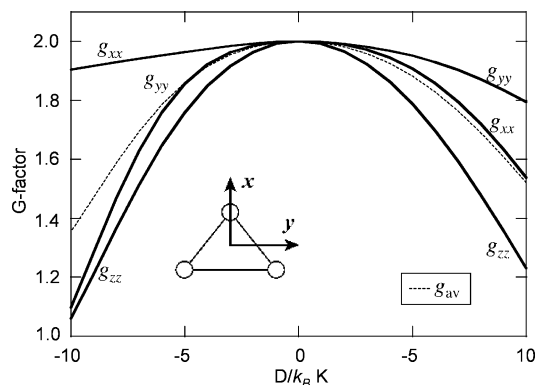


Figure 3. Anisotropic effective g values of the ground-state spin manifold $S_T = 1/2$. The average g value ($g_{av} = (g_{xx} + g_{yy} + g_{zz})/3$) is relevant to powder samples.

by comparison of the simulated and experimental ($g_{av} = 1.876$) powder-averaged g factor (g_{av}), two choices were found feasible for D : (i) $D/k_B = -4.7$ K or (ii) $D/k_B = +5.1$ K (see Figure 3). Because each Fe(III) exhibits a local quasi D_{2h} symmetry (compressed octahedron), the D parameter is expected to be a negative value¹⁹ and, therefore, to be $D/k_B = -4.7$ K.

The reported values of exchange interaction parameters in most of iron(III) basic carboxylate trimers are close to $J \sim 40k_B$ K.^{20,21} The present complex showed slightly small J_1 and J_2 values, but they still remain in the relevant range of exchange interactions. On the other hand, the magnitude of the zero-field-splitting parameter $D/k_B = -4.7$ K seems to be rather large for a high-spin octahedral Fe(III) ion, which usually has less than 1 cm^{-1} .²² Future experiments would be desirable to confirm the consistency between the powder-averaged g value based on the magnetization measurement and the anisotropic g factor determined by low-temperature electron paramagnetic resonance.

Cyclic voltammetric studies in CH_3CN , with TBAPF_6 (0.1 M) as the supporting electrolyte (vs Ag/AgCl) and using a Pt wire as a working electrode, were performed at room

temperature. The cyclic voltammetric response of complex **1** exhibits a reversible oxidation process at $E_{1/2} = +0.23$ V (with an anodic to cathodic peak current relation close to 1) and an irreversible reduction process at approximately -1.1 V, both versus the ferrocene/ferrocenium (fc/fc^+) couple. The oxidation process corresponds to the oxidation of the six ferrocenecarboxylate ligands. The presence of a single redox wave without any further splitting reveals the lack of significant electronic interaction between different Fc ligands along the oxidation process.

In addition to the redox activity of the ferrocene ligands, redox activity centered on the $[\text{M}_3^{\text{III,III,III}}(\mu_3\text{-O})]^{7+}$ core would also be expected. Indeed, different publications have already reported that the reduction from $\text{Fe}^{\text{III}}_3\text{O}$ to the mixed-valence $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$ species occurs at potentials between -640 and $+40$ mV vs fc/fc^+ , varying strongly with the nature of the ligands and the carboxylic acid strength.²¹ However, the cyclic voltammogram of complex **1** does not exhibit any clearly identified redox process within such a range, most likely because it is overlapped with the broad and intense signal of the Fc ligands. It would also be possible that such a redox process is associated with the irreversible peak observed at -1.1 V, although the peak current is much higher than that corresponding to a simple one-electron reduction. Then, the reduction peak could be attributed to (i) the presence of an absorption/desorption process, (ii) decomposition of the complex during the voltammetric scan, although it has already been shown that metal complexes containing Fc's can exhibit strongly reduced redox reversibility, and/or (iii) participation of additional reduction processes to the $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_2\text{O}$ or $\text{Fe}^{\text{II}}_3\text{O}$ species. To share more light into the origin of such electrochemical behavior, reduction of **1** with LiAlH_4 was attempted. In spite of the fact that the reaction was assayed different times, in all of the cases, a dark-brown powder was obtained, from which it was impossible to identify the expected reduced species neither the neutral precursor hexaferrocene species. This can be a confirmation that such an intense reduction peak comes from a decomposition process.

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Supporting Information Available: A detailed experimental section including the synthetic procedure and information of the equipment used, crystallographic information recompiled in two tables (the first one with crystal data and the second one with bond lengths and angles), detailed information on the methodology used for the theoretical fitting of complex **1** and the cyclic voltammetry of complex **1**, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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