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Syntheses, Structures, and Magnetic Properties of Two Dinuclear Iron(III) Citrate Complexes

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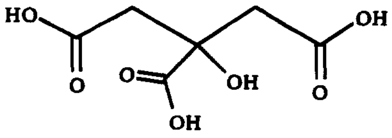
The mobilization of iron in living cells requires a complex array of biological molecules in order to overcome the formation of insoluble, polymeric iron oxide/hydroxide species at physiological pH.[2,3] Among the natural products involved in this process are the storage protein ferritin, the transport protein transferrin, and several low molecular weight molecules, including enterobactin and citric acid. Examples where iron citrate complexes have been postulated to be involved include the biological mobilization of iron, its extraction by plants from the rhizosphere,[4] and transport across the cell membrane by a specific receptor system in *Escherichia coli*.[5,6] Iron citrate preparations are also used to enhance iron bioavailability in the diet of mammals.[7] Although polymeric ferrous and ferric citrate complexes are known,[8,9] no discrete iron citrate compound has been isolated and structurally characterized. In the present report we describe the syntheses, structures, and solid state magnetic properties of two well-defined, dinuclear ferric citrate complexes.


citric acid

From an aqueous solution containing equimolar quantities of ferric nitrate, sodium citrate, and pyridine were obtained large yellow-green crystals of $(Hpy)_2[Fe_2(cit)_2(H_2O)_2]\cdot 2H_2O$, **1**, in 78% yield.[10] As shown in Figure 1, the complex has a centrosymmetric structure in which the two iron atoms are bridged by two alkoxide oxygen atoms of the fully deprotonated

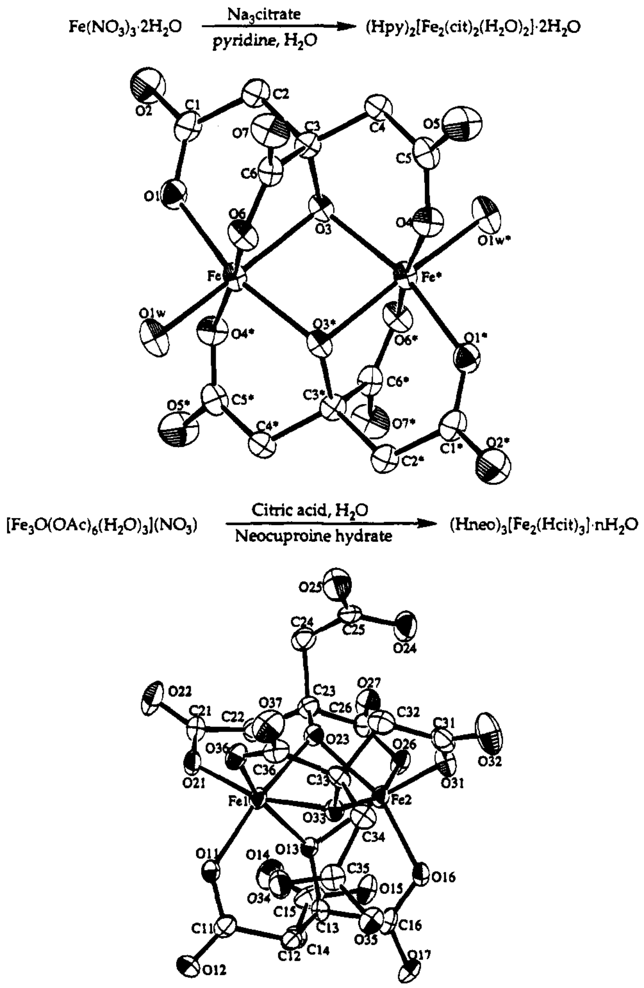


Figure 1. Syntheses and structures of two dinuclear ferric citrate complexes, **1** (top) and **2** (bottom). The ORTEP diagrams depict the 50% (**1**) and 35% (**2**) probability thermal ellipsoids. Only the anions are shown. Hydrogen atoms have been omitted for clarity.

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citrate ligands. All of the carboxylate groups coordinate in a monodentate fashion to terminal positions, and two water molecules complete the slightly distorted octahedral coordination spheres. The Fe−O bond lengths range from 1.987(3) to 2.038(3) Å, the nonbonded Fe••Fe distance is 3.120(1) Å, and the O−Fe−O angle in the four-membered Fe_2O_2 ring is 78.7(1)°.

The second complex, $(Hneo)_3[Fe_2(Hcit)_3]\cdot nH_2O$, **2**, is also dinuclear but contains three bridging citrate ligands, each of which uses its alkoxide functionality to link the two ferric ions while also contributing a monodentate carboxylate to each (Figure 1). The remaining carboxylate group on each of the citrate ligands is protonated and noncoordinating, conveying an overall 3− charge to the complex. The $[Fe_2(Hcit)_3]^{3-}$ anion was prepared by allowing basic iron acetate, $[Fe_3O(O_2CCH_3)_6(H_2O)_3](NO_3)$, citric acid, and neocuproine hydrate to react in water in a 1:4.3:4.6 ratio, respectively. Light green crystals of the neocuproinium salts $(Hneo)_3[Fe_2(Hcit)_3]\cdot nH_2O$, $n = 8$ (**2a**) or 14 (**2b**), were obtained, both of which analyzed as the hexahydrate after drying.[11] As can be seen from Figure 1, the complex has a face-shared octahedral structure with an Fe••Fe distance of 2.830(1) Å and Fe−O bond distances similar to those observed for **1**.

The magnetic susceptibilities of **1** and **2** were examined with the use of a SQUID susceptometer in the temperature range 5−300 K. Compound **1** exhibits antiferromagnetic exchange coupling between the iron atoms. A least-squares fit of the molar susceptibility vs temperature data was made by using the standard Hamiltonian $H = -2JS_1\cdot S_2$, and the two parameters J and g were refined to give $J = -4.50(4)$ cm^{-1} and $g = 2.062(8)$. The fit is shown in supplementary Figure S1. The value for J is within the range reported for several other $Fe^{III}_2(\mu\text{-}OR)_2$ compounds.[12] In compound **2**, however, the two iron atoms are *ferromagnetically* coupled, all of the spins on two iron atoms aligning parallel with the applied magnetic field at very low temperature. The best fit parameters were $J = +1.87(8)$ cm^{-1} and $g = 1.937(1)$; this fit together with the experimental data are shown in supplementary Figure S2. Ferromagnetic coupling is rare for a face-shared d^5−d^5 system. To our knowledge, the only other crystallographically characterized, face-shared diiron(III) compound which exhibits such behavior is $Cs_3Fe_2F_9$.[13]

In the presence of excess citric acid, the anions of **1** and **2** are in equilibrium in aqueous solution, as judged by the fact that the two different compounds selectively crystallize depending upon which cation is added to obtain solid material. Previous workers isolated a yellow-green compound formulated as the hydrated double salt $Na_2Fe_2(OH)_2(H_2O)_2(cit)_2\cdot 6H_2O\cdot 0.4(Na_2(cit)\cdot 2H_2O)$, which may correspond to the sodium salt of the anion in **1**.[14] A dimeric ferric citrate species has also been identified by potentiometric titrations.[15] It will be interesting to determine whether solutions of **1** or **2** are taken up by living cells.

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Supplementary Material Available: For complexes **1** and **2**, textual details of the syntheses and structure determinations, tables giving crystallographic details, intramolecular distances, intramolecular angles, positional parameters, and *B*(eq) values, and plots of the best fits to the magnetic data (29 pages). Ordering information is given on any current masthead page.

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(10) Anal. Calcd for $C_{22}H_{28}Fe_2N_2O_{18}$: C, 36.69; H, 3.92; N, 3.89. Found: C, 36.17; H, 3.99; N, 4.44.

(11) Anal. Calcd for $C_{60}H_{66}Fe_2N_6O_{27}$: C, 50.93; H, 4.70; N, 5.94. Found: C, 50.74; H, 4.44; N, 6.00.

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