Spectroscopic Characterization of a Trinuclear, Oxo-Bridged Iron Cluster

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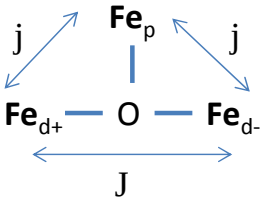
Introduction

Oxo-bridged iron polynuclear complexes are widespread in nature and are essential to the process of iron biomineralization. In particular, the bacterial iron storage proteins, ferritins, employ an active site that encloses a trinuclear iron cluster to oxidize cytotoxic ferrous ions (ferroxidation) and store the oxidized iron inside the inner hollow cavity of the protein. Here, we investigated an oxo-bridged iron cluster, $[(^3\mu O)Fe^{III}_3]$ (**1**), that exhibits a metal site topology analogous to that of the ferroxidase center of bacterial ferritins, see Scheme 1.



Scheme 1

Experimental

Field/temperature-dependent ^{57}Fe Mössbauer and high-field EPR spectra were recorded using the constant acceleration Mössbauer spectrometer and the transmission EPR spectrometers of the EMR facility at the NHFML.

Results and Discussion

Analysis of the high-field EPR spectra revealed that **1** exhibits a sextet, S_t = 5/2 ground state characterized by a small, negative, nearly axial zero-field splitting. Furthermore, magnetic susceptibility data and magneto-structural correlations indicate that |J| >> |j| and thus the electronic ground state originates from a strong, antiferromagnetic interaction of two iron(III) spins, Fe_{d+} and Fe_{d-}, which are in turn weakly coupled to the spin of the third, Fe_p, site. Interestingly, these exchange interactions lead to a $|S_t = 5/2, S_{d\pm} = 0\rangle$ ground state for which we anticipate the magnetic properties to be essentially determined by the weakly coupled site Fe_p, whereas the two strongly interacting sites, Fe_{d+} and Fe_{d-}, are expected to appear nonmagnetic and have little contribution to the properties of the ground state. In order to assess the contributions of the individual spins to the total ground state of the trinuclear cluster we used ^{57}Fe Mössbauer spectroscopy to probe the magnetic hyperfine interactions of the iron sites. Analysis of a series of Mössbauer spectra recorded at 4.2 K (Figure 1) revealed the presence of an iron site that exhibits a large negative internal field typical of ferric ions (red line) and two sites that exhibit small, but not null, negative (blue line) and positive (green line) internal fields. Since, for an isolated $|S_t = 5/2, S_{d\pm} = 0\rangle$ ground state, the internal fields acting on the iron sites of a strongly coupled pair are expected to be strictly zero, the observation of non-vanishing fields for these two sites of **1** indicates a sizable mixing of the ground state with excited states.

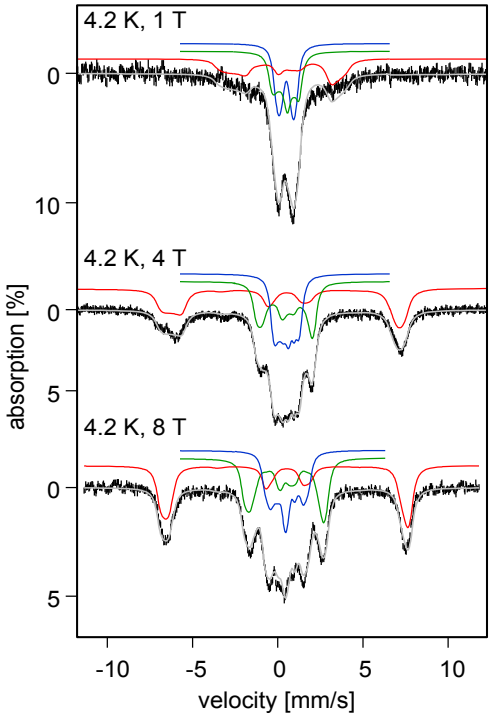


Figure 1. Field-dependent Mössbauer spectra recorded at 4.2 K for a polycrystalline sample of **1**. The solid gray traces overlaying the experimental data are simulations based on a standard S = 5/2 spin-Hamiltonian. The theoretical gray curves result from the superposition of three distinct sub-spectra that have equal intensities and account for the individual iron sites, as drawn above the experimental data in red (Fe_p), blue (Fe_{d-}) and green (Fe_{d+}).

Conclusions

The combined analysis of the high-field EPR and Mössbauer spectra allowed us to assess the fine details of the electronic structure of **1**.

Acknowledgements

The Mössbauer instrument was funded by the UCGP-5064 grant to A. Ozarowski. This work was also supported by the National Science Council of Taiwan No. NSC-100-2113-M-030-005.