HFEPR Studies on Ferryl Complexes Relevant to Heme and Non-Heme Iron Enzymes

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Introduction

Non-heme iron enzymes are widely found in biology and perform a broad range of functions, particularly activation of dioxygen and subsequent oxidative chemistry.[1] Considerable effort has been devoted to their spectroscopic characterization, by a variety of techniques including MCD and Mössbauer spectroscopies, as well as conventional EPR. In parallel, synthetic efforts have led to the isolation and characterization of model complexes for high-valent intermediates in non-heme enzymes.[2]

The currently accepted model for the action of non-heme iron enzymes is via a ferryl ($[Fe^{IV}O]^{2+}$) intermediate.[1,2] The electronic spin ground state of ferryl species can be either high-spin $S = 2$, or intermediate spin $S = 1$. Most model complexes have thus far exhibited $S = 1$ ground states;[3] however, $S = 2$ has surprisingly been observed for the reactive ferryl intermediate in non-heme iron enzymes.[1] The basis for this electronic difference between enzyme and model compounds is of great interest as it may be correlated with reactivity. As a step towards understanding this difference, we have applied HFEPR to study a frozen solution of $[Fe^{IV}(O)(TMG_3tren)](OTf)_2$ (**1**), where TMG_3tren is 1,1,1-tris{2-[*N*2-(1,1,3,3-tetramethylguanidino)]ethyl}amine), OTf = $CF_3SO_3^-$. TMG_3tren is a bulky ligand that provides trigonal coordination of the metal ion and stabilizes its high oxidation state. Complex **1** is the first structurally characterized synthetic iron(IV)oxo complex to exhibit an $S = 2$ ground state.[4]

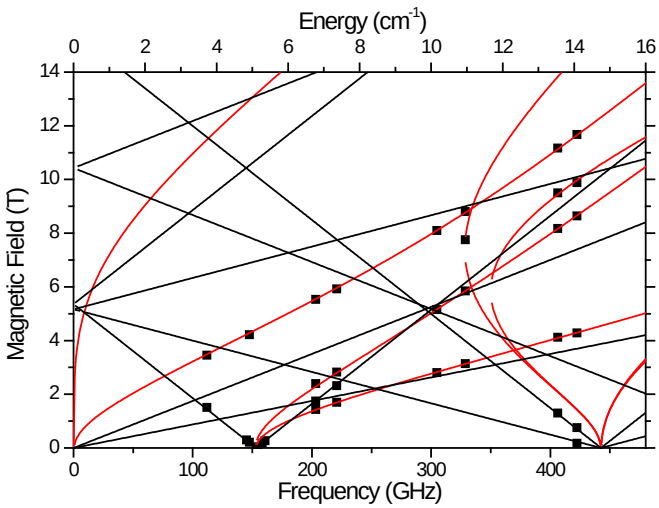

Figure 1. A field vs. frequency map of turning points in the frozen CH_2Cl_2 solution of $[Fe(O)(TMG_3tren)]^{2+}$. Squares are experimental points while the lines were drawn using spin Hamiltonian parameters as in the text.

Experimental

The EMR Facility with the superconducting 15/17-T magnet was used to study a frozen solution of **1** in dichloromethane.

Results and Discussion

The sample yielded good-quality resonances at low temperature (5 K). The field vs. frequency dependence of those resonances is shown in **Figure 1**. The patterns are characteristic for a quintet ($S = 2$) spin state with an axial zero-field splitting tensor. A computer fit of spin Hamiltonian parameters yields the following values: $|D| = 4.95$ cm^{-1}, $|E| = 0$, $B_4^0 = -13 \times 10^{-4}$ cm^{-1}, $B_4^2 = -9 \times 10^{-4}$ cm^{-1}, $B_4^4 = +3 \times 10^{-4}$ cm^{-1}, $g_\perp = 2.004$, $g_\parallel = 2.04$. Note that the fit quality was vastly improved by including the 4th-rank zero-field splitting parameters (B_4^m).

Conclusions

This study is the first application of HFEPR to the ferryl ($[Fe^{IV}O]^{2+}$) ion in (frozen) solution, which is of great relevance to biological oxidation processes by both non-heme iron and heme enzymes.

Acknowledgements

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References

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