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

K. Ray, J. England, L. Que, Jr. (U. of Minnesota, Chemistry); A. Ozarowski, D. Smirnov, J. Krzystek (NHMFL); J. Telser (Roosevelt U.; Chemistry)

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. Considerable effort has been devoted to their spectroscopic characterization, by a variety of techniques including MCD and Mössbauer spectrosopies, as well as conventional EPR. In parallel, synthetic efforts have led to the isolation and characterization of model complexes for non-heme enzymes.

The currently accepted model for the action of non-heme iron enzymes is via a ferryl ([Fe$^{IV}$O]$^{2+}$) intermediate. The electronic spin ground state of ferryl species can be either $S = 2$, or intermediate spin $S = 1$. Model complexes have thus far exhibited $S = 1$ ground states; however, surprisingly a $S = 2$ ground state has been observed for the reactive ferryl intermediate in a non-heme iron enzyme. The basis for this difference between enzyme and model compounds is of great interest. As a step towards understanding this difference, we have applied High Frequency EPR to study two stable ferryl complexes in the solid state: [FeO(tmc)(CH$_3$CN)](CF$_3$SO$_3$)$_2$ (1) and [FeO(N4py)(CH$_3$CN)](CF$_3$SO$_3$)$_2$ (2), where tmc is tetramethylcyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and N4py is bis(2-pyridylmethyl)bis(2-pyridyl)methylamine.

Experimental

The NHMFL Mm- and Sub-mm Wave Facility with the resistive (“Keck”) 25-T magnet, and the EMR Facility with the superconducting 17-T magnet were used to study polycrystalline samples of 1 and 2.

Results and Discussion

An HFPEPR spectrum of 1 is shown in Fig. 1. The field vs. frequency dependence of the observed resonances confirm the triplet ($S = 1$) ground spin state characterized by a zfs parameter $|D|$ of $\approx 27$ cm$^{-1}$ and small rhombicity ($E \approx 0$). A computer fit of this entire dataset provided complete spin Hamiltonian parameters as given in Fig. 1 caption. Similar results were obtained for 2, although the zfs was significantly smaller ($D = \pm 22.0$ cm$^{-1}$).

Conclusions

This study is the first application of HFPEPR to the ferryl ([Fe$^{IV}$O]$^{2+}$) ion, which is of great relevance to biological oxidation processes by iron-containing enzymes. From a technological and methodological point of view, the study is significant in that a new high value for zero-field splitting of the triplet spin state (nearly 30 cm$^{-1}$) has been directly measured by HFPEPR.

Acknowledgements

We thank the NHMFL-IHRP Program, Roosevelt University, and NIH (GM-33162 to LQ) for support.

References