HFEPR Studies of High-Oxidation State Iron Complexes with Axial Nitrogen Donor Ligands

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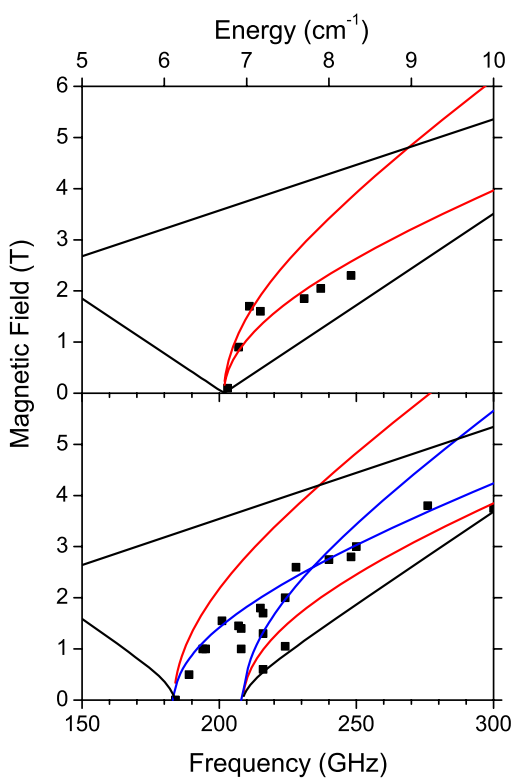
Introduction

Iron in high oxidation states (Fe(IV), Fe(V)) is the putative active species in many iron-containing enzymes,[1] possibly including nitrogenase. The high oxidation state is the result of highly charged axial ligands, such as oxo (O^{2-}), nitrido (N^{3-}), and imido (NR^{2-}), in combination with a suitable supporting ligand. Such a ligand is phenyltris(1-mesityl-imidazol-2-ylidene)borate, abbreviated here as $PhB(MesIm)_3^-$.[2] This "scorpionate" analog, which has three carbon rather than three nitrogen donors, forms a variety of unusual transition metal ion complexes. Reaction with $FeCl_2(thf)_{1.5}$ affords $(PhB(MesIm)_3)Fe^{II}Cl$, which is of interest in its own right. Reaction with N_3^- affords $(PhB(MesIm)_3)Fe^{IV}N$ after photolysis, which has $S = 0$ ground state.[2] Reaction with N_3R^-, followed by one electron oxidation leads to $[(PhB(MesIm)_3)Fe^{IV}NR]OTf$, where R = 1-adamantyl (Ad),[3] *tert*-butyl (^{t}Bu), both of which have spin triplet ground states, as in Fe(IV) oxo complexes.[1]

Experimental

Both Mm and Sub-mm Wave and EMR Facilities were used in this work. The former employs a range of tunable backward wave oscillators as sources, and a 25-T resistive magnet; the latter uses solid state sources and a 17-T superconducting magnet. Polycrystalline samples of $[PhB(MesIm)_3)Fe^{IV}N(Ad)]^+$ and $[PhB(MesIm)_3)Fe^{IV}N(^tBu)]^+$ were used.



Results and Discussion

Both complexes exhibit HFEPR resonances that can be analyzed to yield preliminary spin Hamiltonian parameters, as shown in Fig. 1. This study will be continued in conjunction with optical spectroscopy and ligand-field and density functional theory.

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Conclusions

Although preliminary, HFEPR shows potential in obtaining valuable information on high-oxidation state Fe complexes with novel ligands.

Acknowledgements

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References

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Figure 1. 2D field vs. frequency (energy) maps of EPR resonances in polycrystalline $[(PhB(^tBuIm)_3)Fe^{IV}NR]^+$, R= ^{t}Bu (top), R = Ad (bottom) at 4.2 K in the vicinity of $|D|$, $|D - E|$ or $|D + E|$ zero-field transitions. Full squares are experimental turning points while curves were simulated using following spin Hamiltonian parameters: $S = 1$, $|D| = 6.75$ cm^{-1}, $g_{iso} = 2.0$ (top); $S = 1$, $|D| = 6.5$ cm^{-1}, $|E| = 0.42$ cm^{-1}, $g_{iso} = 2.0$ (bottom). Red curves are turning points with $B \parallel x$, blue curves – $B \parallel y$, and black curves – $B \parallel z$.