

Field- and Frequency-Domain Magnetic Resonance of Model Complexes for Non-Heme Iron Oxidase Enzymes

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Introduction

Oxoiron(IV) ($[\text{Fe}^{\text{IV}}=\text{O}]^{2+}$) units are often implicated as intermediates in the catalytic cycles of non-heme iron oxygenases.[1-3] Many oxoiron(IV)-containing small molecule model complexes have been synthesized and their reactivity towards biomimetic chemistry, such as C-H bond activation reactions, examined. The most reactive synthetic analogs of these intermediates are supported by tetradentate tripodal ligands with quinoline or N-methylbenzimidazole donors, but their instability often precludes structural characterization. A representative structure is shown in **Fig.1**. In this case, two *cis* ligands are pyridyl donors and the other two are quinolyl (N2Py2Q), so the molecule has only approximate C_s symmetry, rather than roughly four-fold symmetry (ideally C_{4v}). This complex (**1**) exhibits an $S = 1$ ground state, although Fe(IV) ($3d^4$) can also have an $S = 2$ ground state, as proposed in non-heme Fe oxidases [1-3.] The relation between these two spin states can have consequences on the reactivity of the overall oxoiron(IV) system [4].

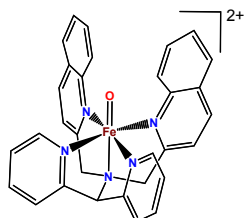


Fig.1 Structure of cation (anion ClO_4^-) of **1** (ligand N2Py2Q).

Experimental

Complex **1** (**Fig.1**), along with its N-methylbenzimidazole analog (ligand = N2Py2B, complex **2**), have been synthesized as perchlorate salts and structurally characterized by x-ray diffraction and by vibrational and Mössbauer effect spectroscopies. These moderately stable solids, as microcrystalline powders, were then investigated at NHMFL by HFEPR using the SC spectrometer of the EMR Facility and the FIRMS setup of the DC Field Facility. Low temperatures were employed.

Results and Discussion

The $S = 2$ spin Hamiltonian parameters were readily extracted for complexes **1** and **2** by the combination of HFEPR and FIRMS (**Fig.2**) and the values are summarized in **Table I**. These results can be correlated with those for the more symmetric “parent” complex, i.e., N4Py ligand, that with four pyridyl donors and roughly four-fold symmetry.[5] Despite their lower symmetry, which includes a “tilt” of the Fe=O bond relative to the equatorial ligand plane, **1** and **2** are still axial systems. However, their D values are larger than for the less reactive N4Py complex, which is consistent with a two-state reactivity (i.e., $S = 1$ and 2) theory for such systems.[4]

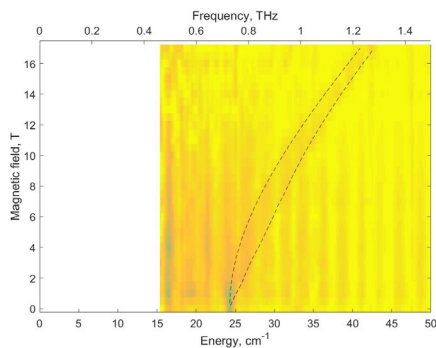


Fig.2 Simulations of the two most prominent turning points in the powder spectrum of **1** (dashed lines) superimposed on a FIRMS map of resonances. Adjusting g_{\perp} provided the value of 2.08(5) in **Table I**; that for **2** is assumed to be the same value.

Conclusions

The combination of field-domain (HFEPR) and frequency-domain (FIRMS) techniques provides detailed information on the electronic structure of novel oxoiron(IV) complexes that can be correlated with geometrical structure and biomimetic chemical reactivity.

Acknowledgements

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Table I Spin Hamiltonian parameters for **1** and **2**.

Complex (Ligand)	D (cm^{-1})	E (cm^{-1})	g_{\perp}	g_{\parallel}
1 (N2Py2Q)	24.3(1)	0.00(5)	2.08(5)	2.000(5)
2 (N2Py2B)	23.3(1)	0.00(5)	(2.08)	2.006(3)

References

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