HIGH FIELD AND FREQUENCY EPR STUDIES OF A MODEL FOR PHOSPHATASE ENZYME ACTIVE SITES: $[FeZn(BPBPMP)(\mu\text{-}OAc)_2]ClO_4$

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Introduction

Phosphate ester hydrolysis is a fundamental reaction in biochemistry. Enzymes known as purple acid phosphatases (PAP) have been isolated from a variety of sources, including humans.[1] The active site of PAP comprises two transition metal ions, of which Fe is the most critical for enzyme function. Recently, Neves and co-workers have synthesized a binucleating ligand, 2-bis[{(2-pyridylmethyl)-aminomethyl}-6-{(2-hydroxybenzyl)(2-pyridylmethyl)}-aminomethyl]-4-methylphenol ($H_2BPBPMP$).[1] We have begun a project to investigate by HFEPR the electronic structure of these dinuclear models for PAP, beginning by understanding the electronic structure of the single ion sites, in particular that of the functionally required Fe^{III}.

Experimental

The complex, $[FeZn(BPBPMP)(\mu\text{-}OAc)_2]ClO_4$, **1**, was synthesized as given previously for the Fe^{III}-Cu^{II} analogue.[1] A microcrystalline powder was studied by HFEPR at the EMR facility using a 17-T superconducting magnet.

Results and Discussion

The Fe^{III} ($3d^5$) ion in complex **1** is six-coordinated and in high-spin (S = 5/2) configuration, while the Zn^{II} ion ($3d^{10}$) is diamagnetic, allowing elucidation of the single ion electronic structure of Fe^{III} in a complex that is active as a phosphatase. Conventional EPR of such a system is totally uninformative. However, HFEPR allows direct determination of the axial zero-field splitting parameter for Fe^{III}, as demonstrated by preliminary data shown in Fig. 1. Future studies will be performed on frozen solution samples to elucidate the electronic structure of the Fe^{III} site as a function of phosphatase action.

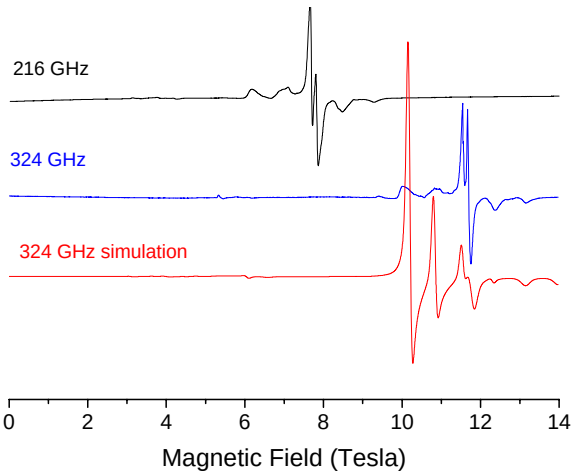

Figure 1. HFEPR spectra recorded for microcrystalline complex **1** at 216 GHz (black trace) and 324 GHz (blue trace) at 10 K. Preliminary powder pattern simulation (red trace) for S = 5/2 with D = +0.70 cm^{-1}, E = 0, g_{iso} = 1.99.

Conclusions

HFEPR gives direct determination of electronic parameters for the functionally vital Fe^{III} ion in a model compound for PAP.

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References

[1] Lanznaster, M., *et al*., J. of Biol. Inorg.Chem., **10**, 319-332 (2005).