HIGH FIELD AND FREQUENCY EPR OF A MAGNETICALLY COUPLED MODEL FOR DINUCLEAR HYDROLASE ENZYME ACTIVE SITES: $[FeCo(BPBPMP)(\mu\text{-}OAc)_2]ClO_4$

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Introduction

Phosphatase enzymes are found in almost all living systems, catalyzing the fundamental reaction of phosphate ester ($(RO)_3P(O)$) hydrolysis. These enzymes include a subclass known as purple acid phosphatases (PAP), which have been isolated from both plants and animals, including humans.[1] In contrast to other phosphatases, the active site of PAP comprises two transition metal ions. The nature of the interaction between these two ions is important in understanding PAP enzyme action. Recently, Neves and co-workers have synthesized an unsymmetrical, N_5O_2 donor binucleating donor ligand, $H_2BPBPMP$.[1] We have begun a project to investigate by HFEPR the electronic structure of these dinuclear models for PAP.

Experimental

The complex, $[FeCo(BPBPMP)(\mu\text{-}OAc)_2]ClO_4$, **1**, was synthesized as described previously for the Fe^{III}-Cu^{II} analogue.[1] A microcrystalline powder was studied by HFEPR using the Mm and Sub-mm Wave Spectroscopy Facility.

Results and Discussion

The Fe^{III} ($3d^5$) and Co^{II} ($3d^7$) ions in complex **1** are six-coordinate and expected to exhibit high-spin electronic ground states, respectively, $S_1 = 5/2$ and $S_2 = 3/2$. However, the nature of the magnetic interaction between the two has been unknown. Conventional (X-band) EPR studies of the $Fe^{III}Cu^{II}$ analogue suggested weak ferromagnetic coupling between these two ions.[1] HFEPR of **1** ($Fe^{III}Co^{II}$) clearly indicates *antiferromagnetic* coupling to give $S_{tot} = S_1 - S_2 = 1$, as shown in Fig. 1.

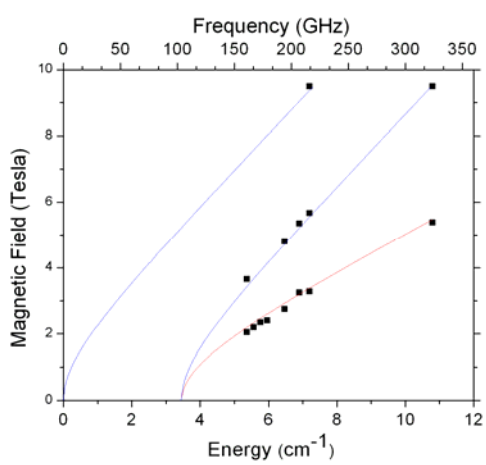

Figure 1. Field vs. frequency dependence of EPR resonances observed in complex **1** (squares) with preliminary simulations (lines) calculated for a triplet ground state ($S_{tot} = 1$) with $D = +3.45$ cm^{-1} (3.7 T), $E = 0$, $g_{iso} = 2.00$. Blue lines: allowed ($\Delta M_S = \pm 1$), red line: nominally forbidden ($\Delta M_S = \pm 2$) transitions. No other spin state can successfully fit the data.

Conclusions

HFEPR clearly indicates an antiferromagnetic interaction between the two high-spin transition metal ions (Fe^{III} and Co^{II}) in a model compound for purple acid phosphatases.

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References

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