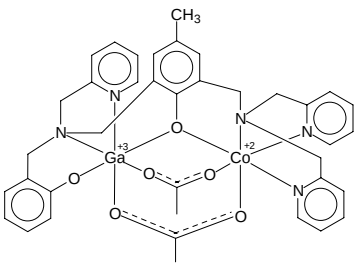
HFEPR Studies on Dinuclear Complexes Relevant to Purple Acid Phosphatase (PAP) Enzymes

J. Telser (Roosevelt U., Chemistry); A. Ozarowski, D. Smirnov, J. Krzystek (NHMFL); F. R. Xavier, A. Casellato, A. Neves (Universidade Federal de Santa Catarina, Florianópolis-SC, Brazil, Chemistry)

Introduction

Phosphate ester hydrolysis is a fundamental reaction in biochemistry and is catalyzed by enzymes known as purple acid phosphatases (PAP), which are found in many organisms, including humans.[1] The active site of PAP comprises two transition metal ions, of which Fe is the most common, however many other 2+ and 3+ metal ions show activity, including Co(II). We have begun a project to characterize by conventional and high-field and -frequency EPR (HFEPR) a series of PAP model complexes prepared with a variety of metal ions. These complexes are based on the novel, asymmetrically binucleating ligand, 2-bis[{(2-pyridylmethyl) aminomethyl}-6-{(2-hydroxybenzyl)(2-pyridylmethyl)}-aminomethyl]-4-methylphenol (H_2BPBPMP).[1] Here, the complex as shown at left, wherein the two metal ions are Ga(III) ($3d^{10}$, $S = 0$) and Co(II) ($3d^7$, $S = 3/2$) is studied.



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 [GaCo(BPBPMP)(μ-OAc)$_2$]ClO$_4$ (abbreviated as **[GaCo]**).

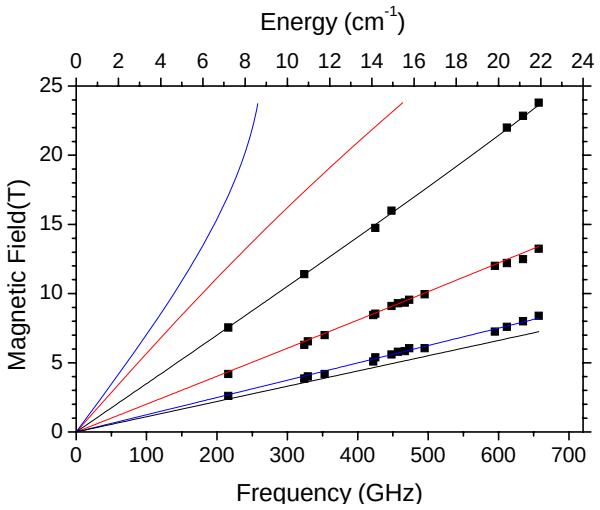


Figure 1. Field vs. frequency dependence of HFEPR turning points (squares) for polycrystallline **[GaCo]**. Lines were calculated using: $S = 3/2$, $D = 45$ cm^{-1}, $E = 7.5$ cm^{-1}, $g_x = 2.4$, $g_y = 2.35$, $g_z = 2.22$. Black line: field along z; red line: along x; blue line: along y.

Results and Discussion

The HFEPR spectrum of **[GaCo]** displays a rhombic powder pattern that can be modeled by a zero-field splitting (zfs) parameter ratio $|E/D| \sim 1/6$, likely with $D > 0$. The field versus frequency dependence of the pattern's turning points is shown in Fig. 1. The complete absence of any inter-Kramers ($|\pm1/2\rangle \leftrightarrow |\pm3/2\rangle$) transition in the currently available frequency-field parameter space indicates that $D > 15$ cm^{-1}, and further, the lack of curvature in the slope of the turning points belonging to the intra-Kramers transition ($|\pm1/2\rangle \leftrightarrow |\pm1/2\rangle$; see Fig. 1) suggests that $D > 40$ cm^{-1}. The large zfs is typical of 6-coordinate Co(II), but has been very seldom quantified to the extent possible here.

Conclusions

This study provides valuable data on the electronic parameters of the M(II) site in this PAP model compound, specifically for Co(II). These parameters are being used in analysis of magnetic susceptibility data for the magnetically coupled complex **[FeCo]**. The data also show the need for still higher frequencies and fields so that the electronic parameters of 6-coordinate Co(II) complexes can be fully characterized.

Acknowledgements

We thank the NHMFL, Roosevelt University, and CNPq (Brazil) for support.

References

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