High-field/frequency EPR Studies of Symmetry-induced Magneto-structural Correlations in Ni(II) Coordination Complexes

S. Rodríguez-Jiménez, R. Díaz-Torres (U. of Barcelona, Chemistry); C.C. Beedle (NHMFL); S. Hill (NHMFL, FSU Physics); N. Aliaga-Alcalde (U. Autònoma de Barcelona).

Introduction

High-field/frequency powder EPR studies were carried out on a series of six-coordinate zero- and one-dimensional Ni(II) complexes of the formula: $Ni(9\text{-}Accm)_2(L)_x$, where L is a mono- or bi-dentate pyridyl-based ligand that occupies *trans*- (pyridine and 3-methylpyridine) or *cis*- (phenanthroline and 4,4'-dimethylbipyridine) coordination environments. The studies reveal that the symmetry of a complex, *i.e. cis* or *trans* coordination environments, and lattice dimensionality, correlate to the magnitude of axial and transverse zero-field splitting parameters.

Experimental

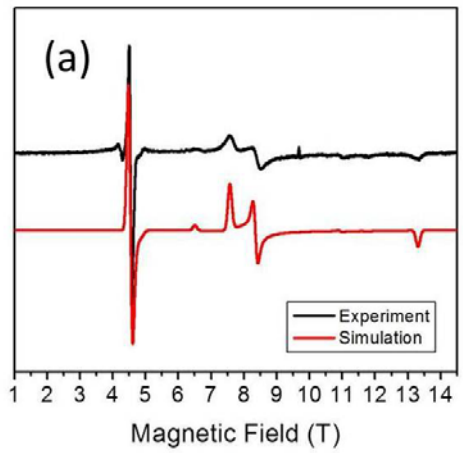
Powder EPR data were collected at 50-450 GHz in a 17T superconducting magnet. A phase-locked Virginia Diodes solid-state source was employed, followed by a chain of multipliers and amplifiers.

Results and Discussion

Figure 1a shows a powder EPR spectrum, for the *trans*-pyridine complex, collected at 302.4 GHz and 5K, and a simulated spectrum generated employing the parameters given in the top left corner of fig.1b. **Figure 1b** shows the frequency dependent experimental data (open circles), and simulations, solid black, red and blue lines for the z, x and y components, respectively. The data were simulated employing the Hamiltonian of Eq. (1), with S = 1, and the parameters given in fig.1b:

$$\hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{S} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) \qquad (1)$$

The solid green line represents simulations for the double-quantum half-field transition (HFT) ($\Delta m=2$). We note that all of the Ni^{II} complexes in this series exhibit easy-plane type anisotropy (D > 0), and that simulations for the remaining complexes (not shown) reveal that the magnitude of D and E in the higher symmetry *trans* complexes are measurably smaller than the lower symmetry *cis* complexes.



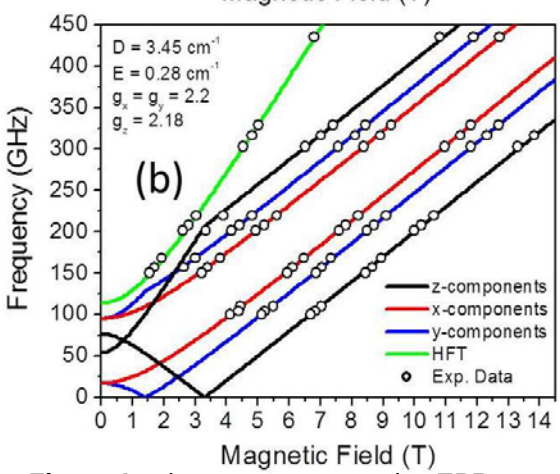


Figure 1a shows a representative EPR spectrum and simulated spectrum collected at 302.4 GHz. **Figure 1b** shows the frequency versus field data (open circles) and simulations (solid lines).

Conclusions

EPR studies have been carried out on a series of mononuclear Ni(II) complexes that exhibit varying coordination environments, and that the magnitudes of 2nd order zero-field splitting terms are governed by the symmetry of the system. We are currently studying analogous complexes that form one-dimensional chains in an effort to understand magneto-structural correlation effects in these interesting systems [1].

Acknowledgements

The National High Magnetic Field Laboratory is supported by NSF Cooperative Agreement no. DMR0654118 and by the State of Florida. SH acknowledges the support of the NSF (CHE0924374)

References

[1] Rodríguez-Jiménez, S., *et al.*, in preparation.