ELECTRONIC STRUCTURE OF FOUR-COORDINATE C_{3V} NICKEL(II) SCORPIONATE COMPLEXES: INVESTIGATION BY HIGH-FREQUENCY AND -FIELD ELECTRON PARAMAGNETIC RESONANCE AND ELECTRONIC ABSORPTION SPECTROSCOPIES

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Introduction

High-Frequency and -Field Electron Paramagnetic Resonance (HFEPR) allows magnetic resonance measurements for high spin nickel(II) (S = 1) systems that are considered EPR silent at conventional X- and Q-band frequencies (9.5 and 35 GHz, respectively). HFEPR provides a more complete description of the electronic environment in Tp*NiX, pseudo-tetrahedral nickel(II) centers. This can enhance the understanding of similar sites in nickel proteins and nickel-substituted zinc enzymes.

Experimental

HFEPR spectra were recorded for powders, Tp*NiX (X = Br, I), at liquid helium temperatures the EMR Facility using a 17 T superconducting magnet with some experiments performed at the DC facility using the 25 T "Keck" resistive magnet.

Results and Discussion

Spin Hamiltonian parameters were extracted from fits of resonance field vs frequency dependence measurements, Table 1.[1] These results were summarized in a manuscript recently published in *Inorganic Chemistry*.[2] Simulation of single frequency spectra for $Tp^{tBu}NiY$ (Y = Cl and NCS) yielded positive values for D, and by association the same was assumed for Tp*NiCl. Simulations of spectra recorded for Tp*NiBr established a larger but *negative* sign for D. Transitions for Tp*NiI were limited to the $B_{||z}$ branches due to field-induced torquing. At high frequencies (600 GHz) a single zero-field transition was observed and assigned to B_{3z}, whereas at lower frequencies (200 – 350 Hz) only the B_{1z} transition was observable. This is consistent with the |+1> and |-1> pair of levels lying lower in energy than the |0> level for Tp*NiI, and corresponds to a negative value of D. Angular overlap modeling (AOM) of solution-phase electronic absorption spectra for Tp*NiX independently reproduced the experimental values of D derived from solid-phase HFEPR.[2]

Conclusions

HFEPR on a series of Tp*NiX complexes demonstrated the increasing halogen contribution to the zero-field splitting (D) observed in these systems. The monotonous variation in D down the series (X = Cl, Br, and I) can in part be traced to the increasing atomic halogen contribution (Tp*Ni• X•) to the electronic structure of these complexes. Collectively, AOM and HFEPR provided described the relative contributions of Tp* and X to bonding with nickel(II).

Table 1: $Tp^{R}NiX$ Spin Hamiltonian parameters from HFEPR.

$Tp^{R}NiX$	D (cm^{-1})	E (cm^{-1})[a]	g_x, g_y, g_z
$Tp^{tBu}NiNCS$	+5.4	+1.1	2.15, 2.15, 2.3
$Tp^{tBu}NiCl$	+5.5	+1.3	2.20 isotropic
Tp*NiCl	+3.93(2)	+0.348(9)	2.280(2), 2.265(6), 2.254(6)
Tp*NiBr	–11.43(3)	–0.02(2)	2.232(5), 2.232[b], 2.28(3)
Tp*NiI	–23.01(4)	–0.74(4)	2.16[b], 2.16[b], 2.16(1)

[a] Assumed to have the same sign as D.
[b] Assumed, no experimental points available.

Acknowledgements

This work was funded in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 39644-B3).

References

[1] Desrochers, P.J., *et al.* NHMFL Annual Reports (2004 & 2005).
[2] Desrochers, P.J.; Telser, J.; Zvyagin, S.A.;Ozarowski, A.; Krzystek, J.; Vicic, D.A. *Inorg. Chem.*, **45**, 8930-8941 (2006).