HIGH-FREQUENCY AND -FIELD EPR OF HIGH-SPIN C_{3v} NICKEL(II) HALIDES

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High-spin (HS) nickel(II) is a prominent feature in the chemistry of this metal ion, and the $S = 1$ spin state is a general characteristic of Ni(II) in pseudo-tetrahedral four-coordinate geometries like Tp*NiX (Figure 1).[1] EPR measurements at high frequencies and fields coupled with quantum mechanical and empirical modeling have yielded general bonding parameters for Ni(II) in these systems.[2] These parameters can be used to describe the effects of coordination symmetry and donor atoms on the electronic and magnetic properties of HS Ni(II). This strategy applied to C_{3v} nickel halides in the present work will complement previously reported results for T_d and C_{2v} nickel halides.[3]

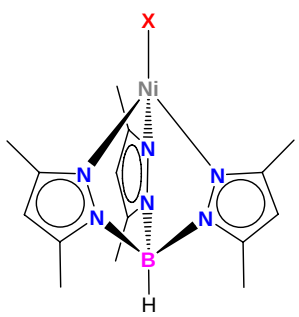

Figure 1. Molecular structure of Tp*NiX complexes.

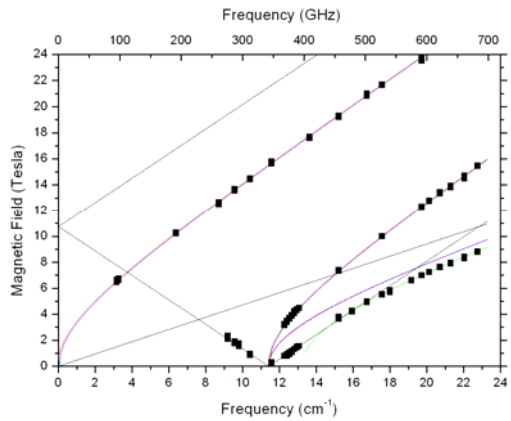

Figure 2. Experimental (squares) and simulated (lines) resonance field vs. energy (frequency) dependence of EPR resonances in polycrystalline Tp*NiBr at 4.2 K.

HFEPR spectra for formally C_{3v} Tp*NiBr, Tp*NiI, $(Tp^*)_2Ni$ and preliminary spectra for Tp*Ni-cysteine complexes were recorded. Similar to results obtained for the chloride derivative,[3] variable frequency spectra for Tp*NiBr and Tp*NiI, yielded turning points assignable to allowed $\Delta M_s \pm 1$ and nominally forbidden $\Delta M_s \pm 2$ transitions, and g tensors characteristic of HS Ni(II). For Tp*NiBr $g_x = g_y = 2.232(5)$, $g_z = 2.28(3)$ with $D = 11.43(3)$ cm^{-1} and $E = 0.02(2)$ cm^{-1} obtained from field vs. energy dependent fits (Figure 2). For Tp*NiI $g_x = g_y = g_z = 2.18(1)$ with $D = 22.806(3)$ and $E = 0.039(5)$ cm^{-1}. The large D value observed for the iodine form is among the largest recorded by EPR for an $S = 1$ spin system. Experimental D and E values for the halides were independently reproduced by angular overlap modeling (AOM) of solution-phase UV-visible electronic spectra. The increasingly larger zero-field splitting tensors moving down the halide series, while maintaining effectively axial symmetry throughout, is consistent with similar C_{3v} molecular structures for all of the Tp*NiX complexes, an increasingly greater covalent nickel-halide interaction and extensive nickel-halogen spin orbital coupling. Independent AOM methods, corroborated by HFEPR measurements, should allow covalent nickel-ligand interactions to be parsed into σ and π contributions from Tp* and from the various halides. The preliminary HFEPR measurements for the Tp*NiCys complex also demonstrate the utility of this spectroscopic tool even to very low symmetry (maximum C_s) Ni(II) systems.

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References

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[3] Desrochers, P.J., *et al.,* NHMFL Annual Report, (2004).