**HFEP INVESTIGATION OF REGULAR AND N-CONFUSED Porphyrin Complexes with Molybdenum**

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**Introduction**

In both biological and artificial systems, porphyrins are key ligands for metal ions, modulating the chemistry of the metal to selectively catalyze reactions and bind small molecules. This chemistry is modulated by the porphine macrocycle and we are examining the effects of pyrrole ring inversion in N-confused porphyrin, an isomer of normal porphyrin. We have generated two isomorphous molybdenum compounds: Mo(TPP)(pip)$_2$ and Mo(NCTPP)(pip)$_2$ (TPP = 5,10,15,20-tetraphenylporphyrin, NCTPP = 2-aza-21-carba 5,10,15,20-tetraphenylporphyrin or N-confused porphyrin, pip = piperidine). Although they exhibit identical structural parameters, the two compounds differ in their electronic structure, as can be seen in their UV-visible spectra and magnetic susceptibility. It was our aim to combine the existing information with that obtained from EPR, in particular its high-frequency and -field version (HFEP).

**Experimental**

The HFEP experiments were performed at the EMR facility using the 17-Tesla superconducting magnet.

**Results and Discussion**

Figure 1. Molecular structure of Mo(NCTPP)(pip)$_2$ (left) with 50% thermal ellipsoids. Selected bond lengths (Å): Mo-N(1) 2.071(2), Mo-C(8) 2.0814(19), Mo-N(3) 2.248(2);

Figure 2. EPR spectrum of polycrystalline Mo(NCTPP)(pip)$_2$ at 369 GHz and 10 K (black trace) and its preliminary simulation (red). The simulation required a presence of two spin species, each $S = 1/2$, characterized by the following axial g tensors: (a) $g_\perp = 2.003$, $g_\parallel = 1.945$, and (b) $g_\perp = 1.965$, $g_\parallel = 1.99$.

The general features of the Mo(NCTPP)(pip)$_2$ complex EPR spectra agree with those obtained from susceptibility measurements, in particular the ground $S = 1/2$ spin state. The exact nature of the two species responsible for different g-tensors is not yet clear. It is clear at this point, however, that the properties of Mo(II) (4d$^4$) are very different from nominally isoelectronic Mn(III) of Cr(II) ions (both 3d$^3$). The reasons for this observation require further investigation, both experimental and theoretical, as do the complexes of the 4d element block in general.

**References**