ABSTRACT

MAGNETIC PROPERTIES AND BIOLOGICAL RELEVANCE OF SCORPIONATE-BASED TRANSITION METAL COMPLEXES

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There are two major components to this research dissertation. The first component describes the synthesis and characterization of high-spin, first-row transition metal complexes supported by facially-coordinating “scorpionate” ligands. These studies have sought to uncover fundamental relationships between molecular structure and magnetic properties, with the ultimate aim of assisting in the design of single molecule magnets (SIMs). To this end, comprehensive series of four and five-coordinated M(II)-X complexes (M = Co, Fe, and Cu; and X = F, Cl, Br, and I) were prepared using hydrotris(pyrazol-1-yl)borate ligands ($Tp^{R,R'}$; where R and R’ indicate substituents at the 3- and 5-position of the pyrazolyl rings). The resulting complexes were structurally characterized by X-ray crystallography. Electronic structure investigations employed advanced spectroscopic and theoretical techniques, including magnetometry, ultraviolet-visible near-infrared (UV-vis NIR) absorption spectroscopy, high-frequency and -field electron paramagnetic resonance (HFEPR) spectroscopy, far-infrared magnetic spectroscopy (FIRMS), Mössbauer spectroscopy, and *ab initio* calculations. Collectively, these collaborative studies elucidated key factors that control magnetic anisotropy, which serves as the basis of SIM behavior. The implications of these findings for the development of new magnetic molecules are thoroughly discussed.

The second aspect of this research centers on the synthesis of biomimetic M(II) complexes (where M = Fe, Co, and Ni) to better understand the mechanism of oxidative ring cleavage by non-heme iron dioxygenases. Specifically, our efforts are directed towards preparing structural and functional models of *o*-aminophenol dioxygenases (APDOs), gentisate dioxygenase (GDO), salicylate dioxygenase (SDO), and 2,5-dihydroxypyridine dioxygenase (NicX) enzymes. The enzymes use redox-active substrates, implying that these substrates act as "noninnocent" ligands. Biomimetic model complexes have been synthesized using substituted Tp ligands to mimic the 2-His-1-carboxylate facial triad that is found in the active sites of many nonheme dioxygenase enzymes. Thus far, we have synthesized functional APDO models that react with O_2 to yield the oxidized ring-cleaved product. Multiple spectroscopic methods, including UV-vis absorption, resonance Raman, EPR, and Fe-57 Mössbauer, are used to characterize intermediates observed at low temperatures during the O_2 reaction. We also outline our attempts to generate synthetic models for GDO, SDO, and NicX enzymes.