

Experimental and Theoretical Investigation of Effects of Nitrogen Co-ligand in Valence Tautomeric Cobalt Bis(*o*-dioxolene) Complexes

H. Winnie Liang^{*†‡}, Chunjing Jia[‡], Tsu-Chien Weng[‡], Dimosthenis Sokaras[‡], Cortlandt G. Pierpont[#], Tyrel M. McQueen[§], Thomas P. Devereaux[^], Kelly J. Gaffney^{*‡}

[†] Department of Chemistry, Stanford University, Stanford, California 94305, United States

[‡] PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

[‡] Stanford Institute for Materials and Energy Sciences, SLAC National Laboratory and Stanford University, Menlo Park, California 94025, United States

[‡] Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

[#] Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, United States

[§] Department of Chemistry, Department of Physics and Astronomy, Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States

[^] Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, United States

Given the potential applications of transition metal complexes displaying valence tautomeric interconversion (VT)—a chemical process characterized by an intramolecular electron transfer between a redox-active metal center and a redox-active ligand coupled to a spin crossover at the metal center—in spintronic devices, data storage and molecular switches, this research field has attracted interest from inorganic chemists, materials scientists and chemical engineers alike. While these valence tautomers share the basic chemical structure of a metal center coordinated to two *o*-dioxolenes and a nitrogen co-ligand, studies on the effects of nitrogen co-ligand and its roles in valence tautomerism have been few and far between. In some valence tautomers, they are found to influence the temperature-dependence of the magnetic properties. In others, they are reported to affect the transition temperatures at which the interconversion occurs. Lastly, their effects can also be manifested in changes to the molecular charge distribution and photoswitching properties. In this work, we have synthesized and compared the transition temperatures of a series of VT complexes that are coordinated to nitrogen co-ligands of various degrees of electron donating/withdrawing property. With the help of DFT calculations, we noticed a strong correlation between the transition temperatures and the LUMO energies of their corresponding nitrogen co-ligands. Meanwhile, the high-temperature valence tautomeric states of Co(phen)(3,5-DBSQ)₂ and Co(tmeda)(3,5-DBSQ)₂ have been examined by the 1*s*-3*p* Resonant Inelastic X-ray Scattering (RIXS) at the Co *K* absorption pre-edge region. By spreading the excitation energies and energy transfers out in two dimensions, we can examine and investigate the spectral features buried underneath the Co *K* pre-edge region. In combination with charge-transfer multiplet calculations, with charge transfer effects included in the final state, we are able to simulate the RIXS spectra and properly assign the peak intensities that were previously attributed to a multi-configurational ground state of the Co(phen) complex. Based on our results, these intensities reflect the π back-bonding interaction between the cobalt center and phenanthroline ligand, explaining why they can only be observed in valence tautomers with aromatic nitrogen co-ligands.