

University of Louisville
Department of Chemistry

Sanjit Karki Literature Seminar

When: February 16, 2023

Time: **12:00 p.m.**

Location: CBL-16

Valence Tautomerism in Cobalt Dioxolene Complexes

Abstract:

The study of bistable materials, spin crossover complexes, or valence tautomeric complexes has tremendously increased over the decades. As the optical and magnetic properties of the molecules change with the intramolecular electron transfer (valence tautomerism) and high-spin/low-spin electronic state transition (spin crossover), these molecules have potential applications in data storage, display devices, and molecular electronics.¹ Valence tautomerism (VT), mainly exhibited by cobalt dioxolene system, arises when intramolecular electron transfer occurs between a metal center and a redox-active ligand upon external stimulation including changes in temperature or pressure or the application of an electric field or visible light resulting in the transition of the electronic spin state.^{2,3} Thermally induced VT is entropically driven, which arises from the higher spin state degeneracy of the high-spin form and the higher density of the vibrational states of the high-spin form due to its longer metal to ligand distances.⁴ Moreover, VT can be induced by light irradiation, which is proposed to occur through a light-induced excited spin state trapping (LIESST) effect.⁵ Many studies have shown that the spin transition process on dinuclear VT complexes can be achieved by a concerted or stepwise mechanism. Here the steps refer to the existence of intermediates during the process and can be seen as a plateau in the variable temperature magnetic susceptibility profile. Since the VT is an intramolecular redox process governed by the frontier orbital energy difference between metal and ligand, the successful synthesis of the potential VT complex can be attained by the appropriate choice of ligand and ancillary ligand system.⁶ Recent studies on VT complexes are mainly focused on understanding the factors that cause the origin of the VT in the light of metal-ligand frontier energy difference, vibronic coupling parameter in the bridged ligand system, and the role of the ancillary ligand for the stabilization of the valence tautomeric complexes⁷.

References:

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