

Why the “Unmakeable” Can Be Made and the “Undoable” Can Be Done – Understanding Purportedly Inaccessible Transition Metal Species Through X-ray Spectroscopies and Electronic Structure Calculations

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Late first row transition metals, such as cobalt, nickel and copper, are essential metal co-factors found in metalloenzymes that perform a wide variety of important biochemical transformations. In addition, small molecule complexes derived from these transition metal centers perform a wide-variety of synthetically and industrially desirable transformations. A significant number of reactions that late first row transition metal complexes are capable of facilitating are unexpected given their predicted reactivities. In fact, the observation that some of these compounds can even be made is unexpected when one considers conventional bonding models that are typically applied to transition metal complexes. In this talk it will be shown that the reactivity and unexpected behavior observed in such late first-row transition metal complexes is in large part a consequence of the divergence of their bonding properties relative to early first-row transition metal complexes, which were used to derive traditional transition metal bonding models.

This talk will focus on two different classes of biologically and synthetically relevant compounds: the metalloenzyme nickel superoxide dismutase (NiSOD) and late first row transition metal oxo species (Ni and Co) that superficially break the so-called oxo-wall. NiSOD is a cysteinylated metalloenzyme that catalyzes the disproportionation of O_2^- into H_2O_2 and O_2 . It is unusual in that the metalloenzyme active-site does not undergo oxidative damage upon exposure to the highly reactive oxidants during catalysis like other metal-thiolate have a propensity to do. Concerning late first row transition metal oxo compounds, it is predicted that such compounds should not exist because of the high nucleophilicity and basicity of the M-O moiety predicted in late first row transition metal compounds. However, such species can be stabilized and display *electrophilic behavior*, not nucleophilic. To understand why these species not only exist, but also display the properties and reactivity they do, we have subjected a number of compounds relevant to the above systems to X-ray absorption (metal K- and L-edge XAS and ligand K-edge XAS) and X-ray emission (Ni and Co 1s2p RIXS and valence to core XES) spectroscopy to experimentally define the electronic structure of these species. Such results are rationalized using hybrid-DFT and *ab initio* (MRCI/CAS-SCF) computational methods. It will be shown that the reason such compounds can be made and stabilized is because commonly employed bonding models are inadequate at describing the bonding of such late first row transition metal compounds. These metals occupy an “intermediate position” on the periodic table where the dative bonding models employed in describing transition metal complexes breakdown; for these metals covalency effects observed predominantly in the main-group metals become more prominent and thus significantly modify the electronic structure from what one would predict based on a naive application of ligand-field theory.

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